19

Structure and Reactions Based Problems

Problems based on reactions and structures of organic compounds:

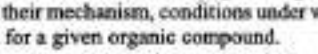
In order to solve the problems based upon reaction and assign the structure of organic compounds, one must be familiar with characteristic reactions, mechanism of reaction of the functional groups present in organic compound. It has, therefore, been advised to students to go through a deep insight of reactions, their mechanism, conditions under which reaction will proceed for a given organic compound.

However, a few reactions, on which generally the problems are based, are given below :

1. Unsaturation in molecule :

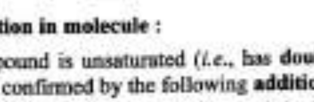
A compound is unsaturated (*i.e.*, has **double** or **triple**) bonds if it is confirmed by the following **addition reactions.**

(a) Discharges or decolourizes Br_2 in CCl_4 or Br_2 water :



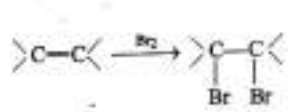
$$>C=C< \xrightarrow{Br_2} >\underset{\underset{Br}{|}}{C}-\underset{\underset{Br}{|}}{C}<$$

(b) Shows addition of H_2 :



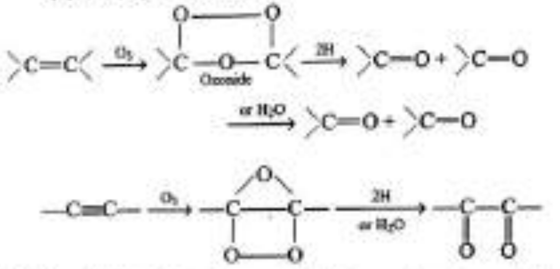
$$>C=C< \xrightarrow{H_2} >\underset{\underset{H}{|}}{C}-\underset{\underset{H}{|}}{C}<$$

(c) Decolourizes Baeyer's reagent, *i.e.*, 1% cold alk. $KMnO_4$:



$$>C=C< \xrightarrow[H_2O + O]{alk.\ KMnO_4} \underset{Colourless}{>\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{C}<}$$

(d) Undergoes ozonolysis :



NOTE : (i) Ozonolysis of symmetrical alkene produces two mole of same carbonyl compounds.

(ii) Ozonolysis of cycloalkenes gives one product having two carbonyl groups.

(iii) Ozonolysis of alkynes gives one product having two carbonylic groups.

(iv) The products formed during ozonolysis also **help** in deciding the nature and position of unsaturation in molecule.

(v) If organic compound is terminal alkyne, it

(a) gives H_2 with Na.

$$-C\equiv CH \xrightarrow[\text{in } NH_3]{Na} -C\equiv CNa + \frac{1}{2}H_2$$

(b) reduces amm. $AgNO_3$ to give white ppt.

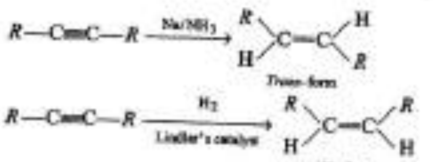
$$-C\equiv CH + \underset{\text{Amm. } AgNO_3}{\underset{\text{or}}{Ag_2O}} \longrightarrow \underset{\text{white ppt.}}{\underset{\text{Silver alkylide}}{-C\equiv C\cdot Ag}} + H_2O$$

(c) gives red ppt. with ammonical Cu_2Cl_2.

$$2[-C\equiv CH] + Cu_2O \longrightarrow \underset{\text{Red ppt.}}{2[-C\equiv C\cdot Cu]} + H_2O$$

(e) Hydrogenation of alkynes :

Non-terminal alkynes are hydrogenated to give *trans*-isomers if Na/NH_3 is used whereas *cis*-isomer is formed if Lindlar's catalyst is used.



(f) Halogenation of alkenes :

Addition of Br_2 on *cis*-2-butene forms a racemic mixture of 2,3-dibromobutane whereas *trans*-2-butene forms *meso* derivative of 2,3-dibromobutane. Both follow anti addition.

2. Halides :

(i) Monohalides on treating with KOH(*aq.*) give alcohol.

$$R—X \xrightarrow{\text{KOH }(aq.)} ROH$$

(ii) Monohalides on treating with alc. KOH give alkene. (Also, read Saytzeff rule for elimination).

$$R\cdot CH_2\cdot CH_2X \xrightarrow{(\text{alc.})\text{ KOH}} R\cdot CH{=}CH_2$$

(iii) Dihalides on treating with KOH(*aq.*), give—

(a) Diol—It is dihalide with halogens on different carbon atoms.

$$CH_2X—CH_2X \xrightarrow{\text{KOH }(aq.)} CH_2OH\cdot CH_2OH$$

(b) Aldehyde—It is gem dihalide with terminal position to halogens.

$$CH_3\cdot CH_2\cdot CHX_2 \xrightarrow{\text{KOH }(aq.)} CH_3\cdot CH_2\cdot CHO$$

(c) Ketone—It is gem dihalide with non-terminal position to halogens.

$$CH_3\cdot CX_2\cdot CH_3 \xrightarrow{\text{KOH }(aq.)} CH_3\cdot CO\cdot CH_3$$

(iv) Trihalides on treating with KOH(*aq.*) give acid, then all the three halogens are on terminal carbon atoms.

$$CH_3CX_3 \xrightarrow{\text{KOH }(aq.)} CH_3COOH$$

(v) Carbylamine reaction of haloform.

$$CHCl_3 + RNH_2 + \underset{\text{Alcoholic}}{3KOH} \longrightarrow \underset{\text{Unpleasant odour}}{RNC} + 3KCl + 3H_2O$$

This is a distinction test in between $CHCl_3$ and CCl_4; primary amines with other amines.

3. Alcohols :

(i) Give effervescences of H_2 gas with Na or K.

$$R—OH + Na \longrightarrow RONa + \frac{1}{2}H_2$$

(ii) Give red colour with ceric ammonium nitrate.

(iii) Form esters with acids, acid chlorides and acid anhydrides.

$$\underset{\text{Alcohol}}{R—OH} + \underset{\text{Acid}}{HOOCR'} \longrightarrow \underset{\text{Ester}}{R'COOR} + H_2O$$

(iv) Distinction in primary, secondary and tertiary alcohols.

(a) Primary alcohols on oxidation give aldehydes and then acid. (Both contain the same number of carbon atoms as the parent alcohol.

$$R—CH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$$

(b) Secondary alcohols on oxidation give ketone with same number of carbon atoms and then acids on prolong oxidation containing lesser number of carbon atom than the parent alcohol.

$$R\cdot CHOH\cdot R' \xrightarrow{[O]} R\cdot COR'$$

(c) Tertiary alcohols on vigorous oxidation form ketones and then acids. (Each with lesser number of carbon atoms then the parent alcohol.)

$$(CH_3)_3\cdot COH \longrightarrow CH_3\cdot CO\cdot CH_3$$

(d) **Lucas reagent test :** Primary alcohol react with Lucas reagent [$ZnCl_2$ (anhy.) + HCl(conc.)] only on heating. Secondary alcohols give white turbidity only after 5–10 minutes of reaction. Tertiary alcohols give white turbidity immediately.

(v) Alcohols on dehydration at relatively :

(a) lower temperature give ether.

$$2R—OH \xrightarrow[\text{agent}]{\text{Dehydrating}} ROR$$

(b) higher temperature give alkene. The order of ease of dehydration of alcohol is tertiary alcohol > secondary alcohol > primary alcohol

$$CH_3\cdot CH_2OH \xrightarrow[\text{agent}]{\text{Dehydrating}} CH_2{=}CH_2$$

4. Ethers :

(i) Inert and neutral in nature.

(ii) An ether with conc. HI—

(a) In cold gives an alcohol and alkyl iodide.

$$R—O—R + HI \longrightarrow RI + ROH$$

In case of mixed ethers, the iodide attaches to the smaller alkyl group.

$$CH_3\cdot OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

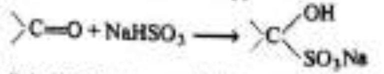
(b) In hot it gives two mole of alkyl iodide.

$$ROR + 2HI \longrightarrow 2RI + H_2O$$

$$R—O—R' \xrightarrow{2HI} RI + R'I + H_2O$$

5. Aldehydes and ketones or carbonyl compounds :

(i) A carbonyl compound shows addition reaction with sodium bisulphite forming white ppt.



$$>C{=}O + NaHSO_3 \longrightarrow >C\begin{matrix} OH \\ SO_3Na \end{matrix}$$

NOTE: Only methyl ketones and all aldehydes show this test.

(ii) Carbonyl compounds form oximes and hydrazones.

$$>C{=}O + H_2NOH \longrightarrow \underset{\text{Oxime}}{>C{=}NOH}$$

$$>C{=}O + H_2N \cdot NHC_6H_5 \longrightarrow \underset{\text{Phenyl hydrazone}}{>C{=}N \cdot NHC_6H_5}$$

(iii) A carbonyl compounds is aldehyde if it;

(a) Reduces Fehling solution (except benzaldehyde).

$R{-}CHO + 2CuO \longrightarrow RCOOH + Cu_2O$ (red ppt.)

(b) Reduces Tollens reagent.

$R{-}CHO + Ag_2O \longrightarrow RCOOH + 2Ag$ (silver mirror)

(c) Reduces Schiffs reagent and gives pink colour.

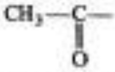
(d) Gives red ppt. with Benedict's reagent.

(e) On reduction gives primary alcohol.

$$R{-}CHO \xrightarrow{2H} RCH_2OH$$

(iv) A carbonyl compound, if does not show above tests for aldehyde, is ketone.

(v) Some other characteristic tests are :

(a) **Iodoform test** : Organic compounds having  $CH_3{-}\underset{\underset{O}{\|}}{C}{-}$ unit attached to carbon or hydrogen give yellow ppt. (iodoform) with $I_2 + NaOH$

$$CH_3 \cdot CO \cdot CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

only acetaldehyde and all methyl ketones respond this test.

(b) **With 2,4-dinitrophenylhydrazine** : Both aldehydes and ketones give orange yellow solid with 2,4-dinitrophenylhydrazine.

6. Acids :

(i) An acid turns blue litmus red.

(ii) An acid gives effervescences with $NaHCO_3$.

$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$

(iii) An acid forms ester with alcohols in presence of concentrated H_2SO_4.

$$RCOOH + R'OH \xrightarrow{\text{Conc. } H_2SO_4} RCOOR' + H_2O$$

(iv) An acid on decarboxylation (on heating with soda lime) loses CO_2 and forms hydrocarbon.

$$RCOOH \xrightarrow{NaOH + CaO} R{-}H + CO_2\uparrow$$

(v) Dry distillation of Ca salt of an acid gives aldehydes and ketones.

$$2(HCOO)_2Ca \longrightarrow 2HCHO + 2CaCO_3$$

$$2(CH_3COO)_2Ca \longrightarrow 2CH_3COCH_3 + 2CaCO_3$$

$$(HCOO)_2Ca + (CH_3COO)_2Ca \longrightarrow 2CH_3CHO + 2CaCO_3$$

NOTE: (a) Aldehydes are formed only when at least one of the component is $Ca(HCOO)_2$.

(b) In case of dry distillation of mixed Ca salts of acids all possible products are formed.

$$(HCOO)_2Ca + (CH_3COO)_2Ca \longrightarrow CH_3CHO + HCHO + CH_3COCH_3$$

(vi) Acids form amides on heating with NH_3 which on further heating with P_2O_5 give cyanides.

$$RCOOH + NH_3 \longrightarrow \underset{\text{Amm. salt}}{RCOONH_4} \xrightarrow{\Delta} \underset{\text{Amide}}{RCONH_2} \xrightarrow{P_2O_5} RCN$$

7. Acid derivatives :

(a) Esters :

(i) all the esters possess fruity smell.

(ii) Esters on hydrolysis give acid and alcohol.

$$RCOOR' \xrightarrow{HOH} RCOOH + R'OH$$

(iii) Esters on reduction produce two molecules of alcohol.

$$RCOOR' \xrightarrow{\text{Red}} RCH_2OH + R'OH$$

(iv) Phenolphthalein test.

(v) Feigl test.

(b) Acid chlorides :

(i) On hydrolysis give HCl and carboxylic acid.

$$RCOCl \xrightarrow{HOH} RCOOH + HCl$$

(ii) On reduction give alcohols.

$$RCOCl \xrightarrow{\text{Reduction}} RCH_2OH$$

(c) Acid amides :

(i) On boiling with alkali give ammonia.

$RCONH_2 + NaOH \longrightarrow RCOONa + NH_3\uparrow$

(ii) On heating with HNO_2 give acids and N_2 gas.

$RCONH_2 + HONO \longrightarrow RCOOH + N_2 + H_2O$

(iii) On heating with P_2O_5, yield nitriles.

$$RCONH_2 \xrightarrow[-H_2O]{P_2O_5,\ \Delta} RCN$$

(iv) Amides, on heating with Br_2 and KOH(*aq*.), undergo Hofmann's bromamide reaction to give primary amines.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(d) Acid anhydrides :

(i) On hydrolysis give acid.

$$(RCO)_2O \xrightarrow{HOH} 2RCOOH$$

(ii) On reacting with alcohols give acid and ester.

$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$

8. Amines :

(i) Primary amines undergo carbylamine reaction. (See trihalides)

(ii) Action of HNO_2 on amines are given below.

(a) Primary amine :

$$R \cdot CH_2NH_2 \xrightarrow{HNO_2} RCH_2OH + N_2 + H_2O$$

(b) Secondary amine :

$$R_2NH \xrightarrow{HNO_2} \underset{\text{Yellow oil, nitroso compound}}{R_2N{-}N{=}O}$$

(c) Tertiary amine :

$$(R)_3N \xrightarrow{HNO_2} R_3N \cdot HNO_2 \xrightarrow{\Delta} R_2N \cdot NO + ROH$$

(iii) Action of **$C_4H_5SO_2Cl$** (Hinsberg test).

(a) Primary amines : Give sulphonamide, soluble in alkali.

$$C_6H_5SO_2Cl + RNH_2 \longrightarrow RNHSO_2C_6H_5 \xrightarrow{NaOH} RNNaSO_2C_6H_5$$

(b) Secondary amines : Give sulphonamide, insoluble in alkali.

$$C_6H_5SO_2Cl + R_2NH \longrightarrow R_2NSO_2C_6H_5$$

(c) Tertiary amines : Do not react.

(iv) Some other characteristics of aromatic amines having $—NH_2$ gp. in nucleus.

(a) Undergo diazotization with $NaNO_2 + HCl$ or $NaNO_2 + H_2SO_4$ at 0°C.

(b) Undergo coupling reaction.

(c) Easily oxidised even by air.

9. Cyanides and Isocyanides :

(i) On reduction give primary amines and secondary amines respectively.

$$\underset{\text{Cyanides}}{RCN} \xrightarrow{\text{Reduction}} RCH_2NH_2$$

$$\underset{\text{Isocyanide}}{RNC} \xrightarrow{\text{Reduction}} RNHCH_3$$

(ii) On hydrolysis give acid and primary amine respectively.

$$RCN \xrightarrow{HOH} RCOOH$$

$$RNC \xrightarrow{HOH} RNH_2 + HCOOH$$

10. Nitro compounds :

(i) Give yellow colour with NaOH solution.

(ii) On reduction in acid medium (Sn + HCl), give primary amines.

$$R{—}NO_2 \xrightarrow{Sn/HCl} RNH_2$$

11. Aromatic compounds :

(a) An aromatic compound is one which obey Huckel rule, *i.e.*, aromaticity is due to extensive delocalisations of π-electrons (*i.e.*, $(4n+2)\,\pi$-electron where n is any integer or 0, 1, 2 ....) in planar ring system.

(b) A host group already present in benzene nucleus directs the incoming (guest) substituent to occupy ortho, meta or para position.

(c) Some groups are *o*- and *p*-directing, *e.g.*, $—NH_2$—OH—OR, $—NHCOCH_3$, —SH, $—CH_3$, —X, $—NH_3^+$, —NC, etc., whereas some are *m*-directing, *e.g.*, —CN, $—SO_3H$, $—NO_2$, —CHO, —COOH, $—CCl_3$, etc.

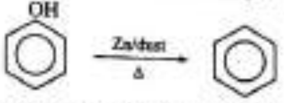
12. Phenols :

(i) Soluble in alkali.

(ii) Turn blue litmus to red.

(iii) Give no effervescences with $NaHCO_3$, although acidic in nature.

(iv) On distillation with Zn dust give benzene.



(v) Show characteristic colour with $FeCl_3(aq.)$.

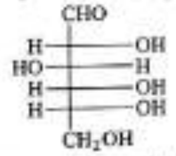
13. Carbohydrates :

(i) Molish's test : A drop or two of alcoholic solution of α-naphthol is added to 2 mL of aqueous solution of compound. 1 mL of conc. H_2SO_4 is added carefully along the sides of test tube. The formation of a violet ring at the junction of two liquids confirm the presence of carbohydrate.

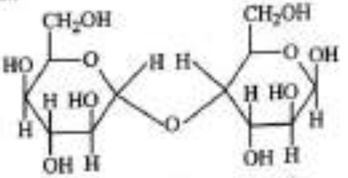
(ii) Osazone formation : Glucose and fructose on heating with excess of phenylhydrazine in acetic acid gives a yellow crystalline compound osazone having m.pt. 205°C.

• NUMERICAL PROBLEMS •

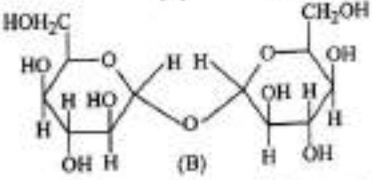
1. Select the chiral objects from the following list.
   Nail, screw, scissor, knife, spool of thread, empty spool or thread less spool, glove, shoe, a pair of shoe, sock, pullover sweter, rubber ball, pyramid of cheeps, helix, double helix, tennis racket, hand, foot, ear, rifle, letters (*M*, *O*, *A*), letters (*P*, *J*, *F*).
2. Write down the structure of stereoisomers of the following:
   (a) 2,3-Dihydroxybutane.
   (b) 3-Phenyl-2-propenoic acid.
3. Write down the no. of asymmetric carbon in each optically active compound and report the no. of isomers.
   (a) $CH_3 \cdot (CHOH)_2\,COOH$
   (b) $COOH \cdot (CHOH)_2\,COOH$
4. Write down the structures of stereoisomers formed when *cis*-2-butene is reacted with Br_2. **(IIT 1995)**
5. A racemic mixture of (±) 2-phenyl propanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of two esters formed. **(IIT 2003)**
6. Draw Newmann projection of relatively less stable staggered form of *n*-butane. The reason of low stability of this form is due to (a) torsional strain (b) van der Waals' repulsion, (c) both of them. **(IIT 2004)**
7. The Fischer projection of *D*-(+) glucose is given as:



   Write the Fischer projection of (a) L-(−) glucose and (b) the products formed after its reaction with Tollen's reagent. **(IIT 2004)**
8. Which of the following disaccharide will not reduce Tollens reagent? **(IIT 2005)**

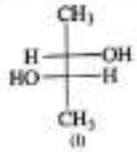


(A) and

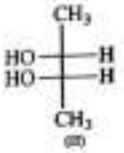


(B)

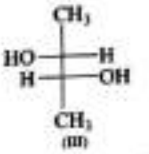
9. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III. **(IIT 2000)**



(I)

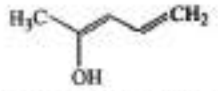


(II)



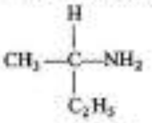
(III)

10. How many asymmetric carbon atoms are created during the complete reduction of benzil (PhCOCOPh) with $LiAlH_4$? Also, write the number of possible stereoisomers in the product. **(IIT May 1997)**
11. Optically active 2-iodobutane on treatement with NaI in acetone gives a product which does not show optical activity. Explain why? **(IIT 1995)**
12. Write resonance structure of the given compound. **(IIT 2003)**



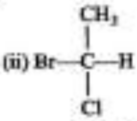
13. Write the stereoisomers formed when trans-2-butene reacts with (i) Bromine (ii) Baeyer's reagent.
14. Write the stereoisomers formed when *cis*-2-butene reacts with (i) Bromine (ii) Baeyer's reagent.
15. (a) Predict the nature of *R* or *S* configuration for the following compounds.

(i)



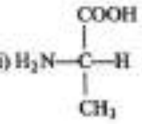
$CH_3-\overset{H}{\underset{C_2H_5}{C}}-NH_2$

(ii)



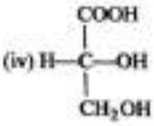
$Br-\overset{CH_3}{\underset{Cl}{C}}-H$

(iii)



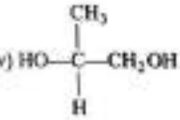
$H_2N-\overset{COOH}{\underset{CH_3}{C}}-H$

(iv)



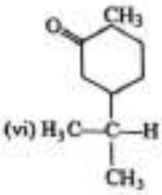
$H-\overset{COOH}{\underset{CH_2OH}{C}}-OH$

(v)



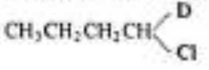
$HO-\overset{CH_3}{\underset{H}{C}}-CH_2OH$

(vi)



   (b) Draw the *R* or *S* configuration for the following predicting precedence order of groups.
   (i) 3-bromohexane (ii) 1,3-dichloro pentane (iii) 3-chloro, 3-methyl pentane (iv) 1,2-dibromo-2-methyl butane (v) 3-chloro, 2,2,5-tri methyl heptane (vi) lactic acid

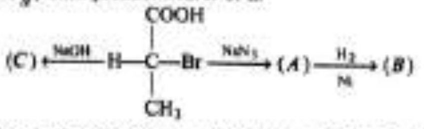
(vii)



$CH_3CH_2CH_2CH\genfrac{}{}{0pt}{}{D}{Cl}$

16. Optically active sec-butyl alcohol retains its activity indefinitely in contact with aqueous base, but it rapidly converted into optically inactive (racemic) sec-butyl alcohol by dil. H_2SO_4. Explain.

17. Complete the equation and assuming all but one of the steps are S_N2 each product with *D* or *L*.



$$(C) \xleftarrow{NaOH} H-\overset{COOH}{\underset{CH_3}{C}}-Br \xrightarrow{NaN_3} (A) \xrightarrow[Ni]{H_2} (B)$$

18. (*W*) and (*X*) are optically active isomers of C_5H_9Cl. (*W*) on treatment with one mole of H_2 is converted to an optically inactive compound (*Y*), but (*X*) gives an optically active compound (*Z*) under the same conditions. Give structure of (*Y*) and configuration of (*W*), (*X*) an (*Z*) in Fischer projections. **(Roorkee 2000)**

19. 0.90 g of an organic compound $C_4H_{10}O_3$ (*A*) when treated with sodium, 224 mL of hydrogen were evolved at NTP. Compound (*A*) could be separated into fractions (*B*) and (*C*) by crystallization of which, fraction (*B*) could only be resolved into optical isomers (*D*) and (*E*). Write down the structure formulae of (*A*) to (*E*) with proper reasoning.

20. Write down the structures of close homologues of heptane having in their molecule one quaternary C-atom and the other having two tertiary carbon atoms.

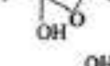
21. A hydrocarbon (*A*) was found to have vapour density 36. It forms only single monochloro substitution product. Suggest (*A*).

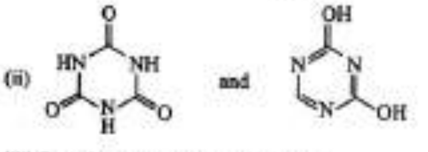
22. Which alkane having a molar mass of 86, will form only two monobromo alkanes?

23. How will you distinguish 1-chloro-2-butene and 2-chloro-2-butene?

24. C_6H_{12} is an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound C_6H_{14}. What are these?

25. Point out the isomerism shown by each pair ;

(i) CH_3COCH_2OH and 

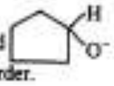
(ii) 

(iii) Propylamine and isopropylamine.

(iv) Methyl propylamine and diethylamine.

26. Pentan-2-one forms two oximes whereas pentan-3-one forms two oximes. Explain.

27. List the following alkoxide nucleophiles in order of decreasing S_N2 reactivity :

Me_3CO^-, MeO^-, $MeCH_2O^-$, Me_2CHO^- and 

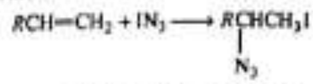
How does S_N2 mechanism account for this order.

28. Discuss the nature of products formed and the mechanism for the addition of HCl on 3-methyl-1-butene.

29. Predict the major product of dehydrohalogenation of 4-bromo-1-hexene.

30. Account for the fact that addition of $CBrCl_3$ in the presence of peroxide takes place faster to 2-ethyl-1-hexene than to 1-octene.

31. Suggest the intermediate and mechanism for the reaction :



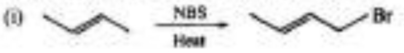
$$RCH{=}CH_2 + IN_3 \longrightarrow R\underset{N_3}{CH}CH_2I$$

32. On treatment with HCl, 1,3-butadiene yields a mixture of 3-chloro-1-butene and 1-chloro-2-butene. How do you account for the formation of these two products?

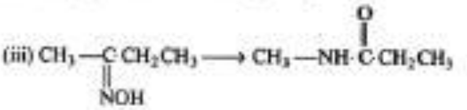
33. Write down the two products (major and minor) obtained on dehydration of neopentyl alcohol.

34. Which acts as an acid in aqueous solution of HBr and in dry HBr? Which is the stronger one? Which can better transfer a hydrogen ion to an alkene?

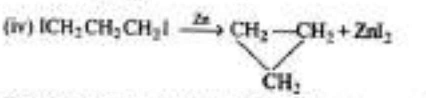
35. Write down the type of chemical changes :

(i) 

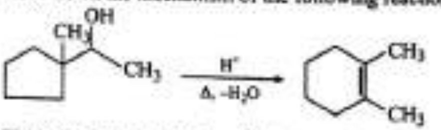
(ii) $CHCl_3 + OH^- \longrightarrow \colon CCl_3 + H_2O + Cl^-$

(iii) 

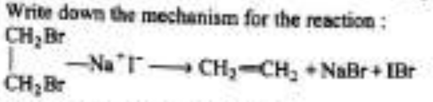
$$CH_3-\underset{NOH}{\underset{\|}{C}}CH_2CH_3 \longrightarrow CH_3-NH\cdot\overset{O}{\overset{\|}{C}}CH_2CH_3$$

(iv) 

36. Write down the mechanism of the following reaction :



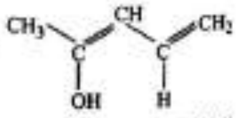
37. Write down the mechanism for the reaction :



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} -Na^+I^- \longrightarrow CH_2{=}CH_2 + NaBr + IBr$$

38. Complete the following reaction :

$$BrCH_2C{\equiv}CCH_2Br \xrightarrow[\Delta]{Zn} ? \xrightarrow[H_2O/Zn]{O_3} ?$$

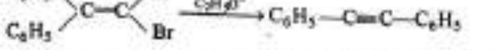
39. Write resonance structure for 

(IIT 2003)

40. 3,3-dimethyl butan-2-ol loses a molecule of water in the presence of conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism. **(IIT 1996)**

41. Ethyl acetoacetate has two form keto and enol but phenol (enol) do not show keto form.

42. Write down the mechanism of the reaction



43. Write down the mechanism for the reduction of alkyne in ethanol by Na.

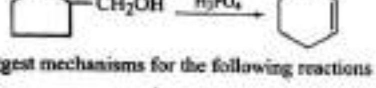
44. Write the mechanism of the reaction,

$$ClCH_2 \cdot CHCl_2 \xrightarrow{OH^-} CH_2{=}CCl_2$$

45. Write down the mechanism of oxidation of isopropyl alcohol by $K_2Cr_2O_7/H_2SO_4$.

46. Write the mechanism for the acid dehydration of cyclobutyl carbinol.

47. Write the mechanism for



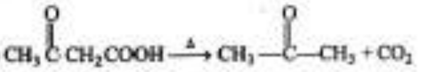
48. Suggest mechanisms for the following reactions :

(a) $RH + SO_2 + Cl_2 \xrightarrow{h\nu} RSO_2Cl + HCl$

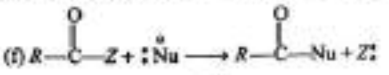
(b) $RCONH_2 \xrightarrow{NaOH + Br_2} RNH_2$

(c) $n\text{-}C_4H_9OH \xrightarrow{HBr} nC_4H_9Br$

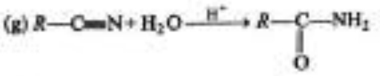
(d) $(CH_3)_3C \cdot OH \xrightarrow{HBr} (CH_3)_3C \cdot Br$

(e)


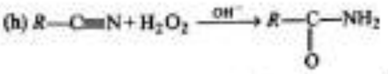
$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOH \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$$

(f)


$$R-\overset{O}{\overset{\|}{C}}-Z + :\overset{\ominus}{Nu} \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu + Z:$$

(g)


$$R-C{\equiv}N + H_2O \xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-NH_2$$

(h)


$$R-C{\equiv}N + H_2O_2 \xrightarrow{OH^-} R-\underset{\underset{O}{\|}}{C}-NH_2$$

49. Write down the mechanism for the cleavage of 2,2-dimethyl oxirane by acid (H^+). **(IIT 1997)**

50. Write down the mechanism for the addition of $NaHSO_3$ on carbonyl gp.

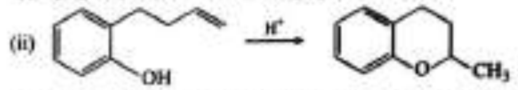
51. There are two $-NH_2$ gps. in semicarbazide that might react with a carbonyl gp. Why the $-NH_2$ gp. adjacent to $-\overset{O}{\overset{\|}{C}}-$ in $NH_2 \cdot NH \cdot \overset{O}{\overset{\|}{C}} \cdot NH_2$ does not react with carbonyl compound?

52. Peroxy acetic acid (CH_3CO_3H) is a weaker acid than acetic acid, Why ?

53. 3,3-Dimethyl-butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. **(IIT 1996)**

54. (a) Write the intermediate steps for each of the following reaction. **(IIT 1998)**

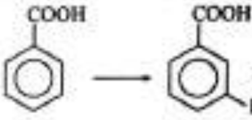
(i) $C_6H_5CH(OH)C{\equiv}CH \longrightarrow C_6H_5CH{=}CHCHO$

(ii)


(b) Show the steps to carry out the following transformations.

(i) Ethylbenzene ⟶ benzene **(IIT 1998)**

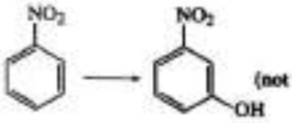
(ii) Ethylbenzene ⟶ 2-phenylpropionic acid **(IIT 1998)**

(iii)

(not more than 3 steps)

(IIT 2003)

(iv)

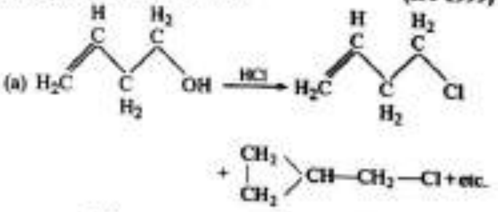
⟶ Aspirin **(IIT 2003)**

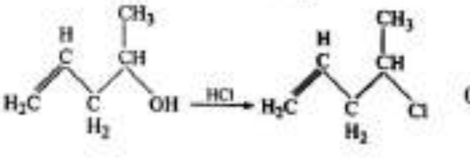
(v)

(not more than 4 steps)

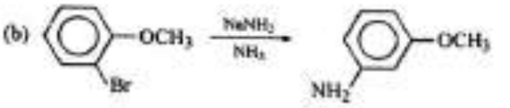
(IIT 2004)

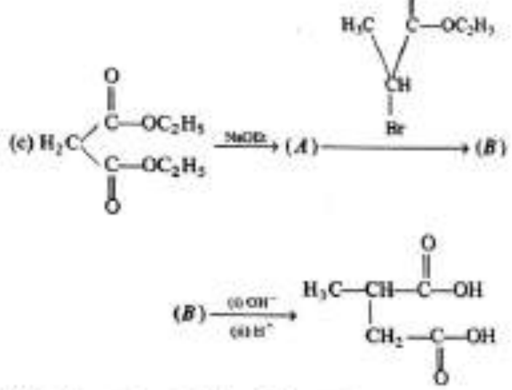
(vi) Aniline ⟶ Benzylamine not more than three steps **(IIT 2000)**

55. Explain briefly the formation of the products giving the structures of the intermediates. **(IIT 1999)**

(a)



(only)

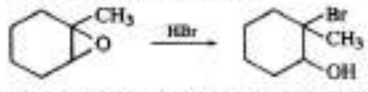
(b)


(c)


56. Write down the mechanism of the reaction :

$$C_6H_5CH_2CH{=}CH_2 \xrightarrow[\Delta]{KOH} C_6H_5CH{=}CHCH_3$$

57. Write mechanism for the reaction :



58. Isobutylene, a gas an dissolution in 63% H_2SO_4 yields a deliquescent white solid (*A*). On heating solid (*A*) with water liquid (*B*) is obtained. What are (*A*) and (*B*).

59. Sulphanilic acid is insoluble in water and acid but soluble in alkali, why?

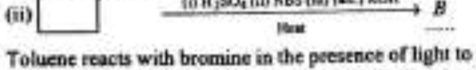
60. Which one is the stronger acid : 3-butenoic acid or 3-butynoic acid and why?

61. Discuss action of heat on α-, β- and γ-hydroxy carboxylic acids.

62. $CHCl_3$ is more acidic than CHF_3. Explain.

63. Complete the following giving the structures of the major organic products :

(i) $2F_2C{=}CCl_2 \xrightarrow{Heat} \underset{\cdots}{A}$

(ii)


64. Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives *p*-bromotoluene. Give explanation for the above observations.

65. Give reasons for the following :

(i) Tert-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$. **(IIT 2000)**

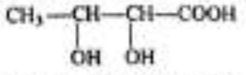
(ii) $CH_2{=}CH^-$ is more basic than $HC{\equiv}C^-$. **(IIT 2000)**

(iii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. **(IIT 2000)**

(iv) Which one is more soluble in diethyl ether, anhydrous $AlCl_3$ or hydrous $AlCl_3$? **(IIT 2003)**

66. Read the statements given below and write 'true' against correct statement(s). If any of the statements is wrong, rectify the mistake/mistakes and give a correct statement in its place. **(Roorkee 2001)**

(a) Tollens reagent converts $CH_3{-}CH{=}CH{-}CHO$ to



$$CH_3{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}COOH$$

(b) Total number of optical isomers of 3,4-dichlorohexane is 3.

(c) When heated with dilute H_2SO_4, $C_6H_5SO_3H$ undergoes further sulphonation to give $C_6H_4(SO_3H)_2$.

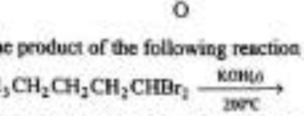
(d) Addition of HI to 3,3-dimethyl-1-butene not only gives 1-iodo-3,3-dimethylbutane, but also 2-iodo-2,3-dimethyl butane.

67. 7-bromo-1,3,5-cycloheptatriene remains in ionic form but 5-bromo-1,3-cyclopentadiene does not ionise even in presence of Ag^+ ion. Explain. **(IIT 2004)**

68. Write the structures of but-2-ene and 2-methylpropene and show addition of HBr on both of them in presence and absence of peroxide.

69. 2,3-dimethyl but-2-ene does not decolorise Br_2/CCl_4 but decolorises Br_2/H_2O. Explain.

70. Give the product of the following displacement reaction :

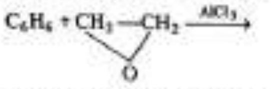


$$(S){-}Br{-}\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}{-}\underset{O}{\underset{\|}{C}}OEt \xrightarrow{CN^-}$$

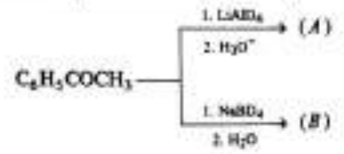
71. Give the product of the following reaction :

$$CH_3CH_2CH_2CH_2CHBr_2 \xrightarrow[200°C]{KOH(s)}$$

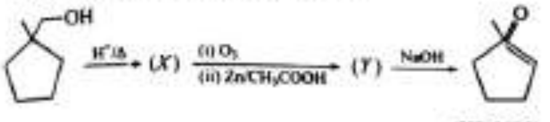
72. Give the product of the following reaction :



73. Give the products of the following reactions :



74. Identify X and Y in the given reaction.



(IIT 2005)

75. Give the structure of the major organic products formed 3-ethyl-2-pentene under each of the following reaction conditions.

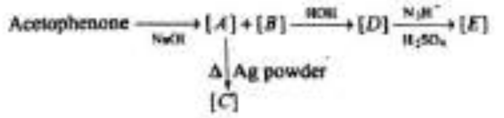
(a) HBr in the presence of peroxide

(b) Br_2/H_2O

(c) $Hg(OAc)_2/H_2O; NaBH_4$. **(IIT 1996)**

76. Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes. **(IIT July 1997)**

77. Complete the following :

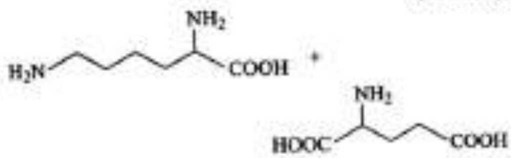


$$\text{Acetophenone} \xrightarrow[\text{NaOI}]{} [A] + [B] \xrightarrow{\text{HOH}} [D] \xrightarrow[H_2SO_4]{N_3H} [E]$$

$[A] \xrightarrow{\Delta,\ \text{Ag powder}} [C]$

78. Following two amino acids liosine and glutamine form dipeptide linkage. What are two possible dipeptides?

(IIT 2003)

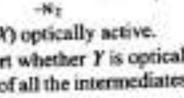


79. Identify X and Y in the following change :

$C_5H_{13}N \xrightarrow[-N_2]{NaNO_2 + HCl} Y$ (Tertiary alcohol) + other products (X) optically active.

Also, report whether Y is optically active or not. Report the structures of all the intermediates. **(IIT 2005)**

80. (a) Dehydration of,



gives a compound which exists in two isomeric forms. Give the structures of both the isomers.

(b) Explain in not more than 2,3 lines.

(i) Aniline does not undergo Friedel-Crafts reaction.

(ii) Mineral acid is added in excess in diazotization of arylamines.

(c) Complete the reaction,

$(CH_3)_2C{=}CH_2 + \text{isobutane} \xrightarrow[273\,K]{HF}$ **(Roorkee 1999)**

81. Give structures of (W), (X), (Y) and (Z) in the following reactions. **(Roorkee 2000)**

$$H_2C{=}CH{-}CH_2OH \xrightarrow[(CH_2Cl_2)]{CrO_3 \cdot 2C_5H_5N} (W)$$

$$\xrightarrow{CH_3OH,\ H^+} (X)\ C_5H_{10}O_2$$

$$(X)\ C_5H_{10}O_2 \xrightarrow[\text{(cold, dilute)}]{KMnO_4,\ OH^-} (Y)\ C_5H_{12}O_4$$

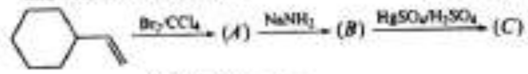
$$\xrightarrow[H_2O]{H_3O^+} (Z)\ C_3H_6O_3.$$

82. Write the products in the following reactions :

(i) $CH_3CH{=}CH_2 + Br \cdot CCl_3 \xrightarrow{\text{Peroxide}}$

(ii) $CH_3CH{=}C(CH_3)_2 + HCl \xrightarrow{\text{Peroxide}}$ **(Roorkee 1998)**

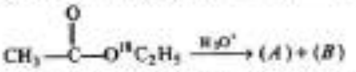
83. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures : **(IIT 2001)**



$(C) \xrightarrow{NH_2NHCONH_2} (D)$

$(C) \xrightarrow{NaOD/D_2O(\text{excess})} (E)$

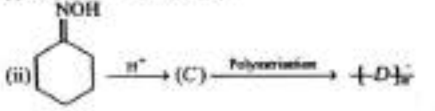
84. Write the structures of the products (A) and (B). **(IIT 2000)**



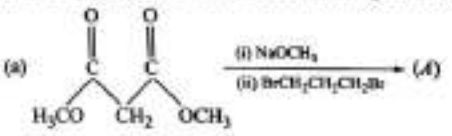
$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{18}C_2H_5 \xrightarrow{H_3O^+} (A) + (B)$$

85. Give the structures of the products in each of the following reactions : **(IIT 2000)**

(i) Sucrose $\longrightarrow (A) + (B)$



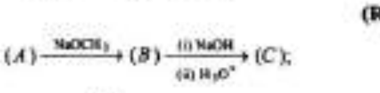
86. What are (A) to (L) in the scheme of reactions given below ?

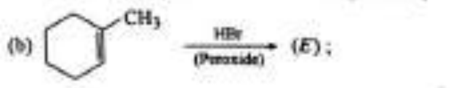


(Roorkee 2000)

$(A) \xrightarrow{NaOCH_3} (B) \xrightarrow[(ii)\ H_3O^+]{(i)\ NaOH} (C);$

$(C) \xrightarrow{-CO_2} (D)$ (cyclo alkane carboxylic acid)



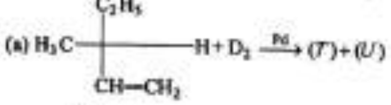


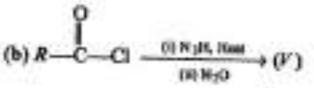
$(G) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ (BH_3)_2} (H)$

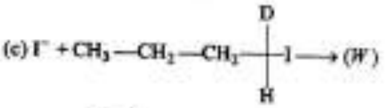
(d) $(J) \xleftarrow[H_2O]{HCrO_4} (I) \xrightarrow[\text{(Pyridine)}]{CrO_3} CH_3CHO$

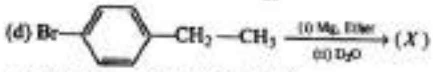
(e) Acetone (2 mol.) $\xrightarrow{OH^-} (K) \xrightarrow[\text{Heat}]{NaHSO_4} (L)$.

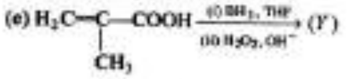
87. Give structures/configurations of the products (*T*) to (*Z*) of the following reactions : **(Roorkee 2001)**

(a) 
$H_3C-\overset{C_2H_5}{\underset{CH=CH_2}{C}}-H + D_2 \xrightarrow{Pd} (T) + (U)$

(b) 
$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{(ii) } H_2O]{\text{(i) } N_3H, \text{ Heat}} (V)$

(c) 
$I^- + CH_3-CH_2-CH_2-\overset{D}{\underset{H}{C}}-I \longrightarrow (W)$

(d) 

(e) 
$H_2C=\underset{CH_3}{C}-COOH \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3,\ THF} (Y)$

(f) $2HC\equiv C-H \xrightarrow[O_2]{Cu^{2+}} (Z)$

88. Identify (*A*) to (*K*) as reactant, reagent, product and name of the reaction in the following : **(Roorkee 1999)**

(i) $3(CH_3)_2C=O \xrightarrow{(A)} (B)$ Aldol condensation

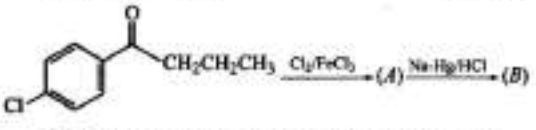
(ii) $CH_3COCl + H_2 \xrightarrow{(C)} (D)$ Rosenmund's reaction

(iii) $(E) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3 (F)$

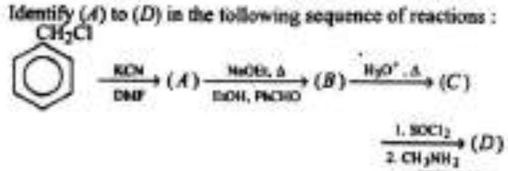
(iv) $C_6H_5OH \xrightarrow{(G)} (H_1) + (H_2)$ Elb's oxidation

(v) $C_6H_5N_2Cl \xrightarrow[HCl]{(J)} (K)$ Gattermann reaction

89. Write structures of the products (*A*), (*B*), (*C*), (*D*) and (*E*) in the following scheme : **(IIT 2002)**



90. Identify (*A*) to (*D*) in the following sequence of reactions :



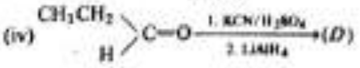
(IIT 2004)

91. Predict the major products in the following reactions :

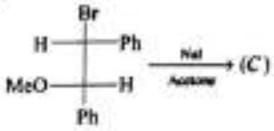
(i) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

(ii) $C_6H_5CH_2COOCH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ \text{(excess)}}$

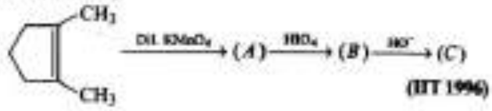
(iii) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.\ Br_2,\ \text{Heat, Light}}$ **(IIT 1994)**

(iv) 
$\begin{matrix} CH_3CH_2 \\ H \end{matrix}\!\!>\!C=O \xrightarrow[2.\ LiAlH_4]{1.\ KCN/H_2SO_4} (D)$ **(IIT 1996)**

(v) Predict the structure of the product in the following reaction. **(IIT 1996)**

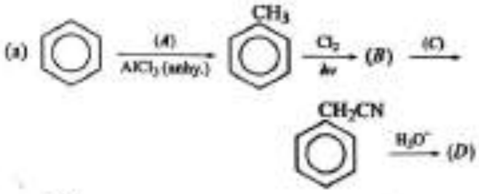


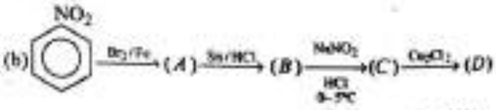
(vi) Suggest appropriate structure of the missing compounds.
(The number of carbon atoms remains the same throughout the reactions.)



(IIT 1996)

92. Complete the following :

(a) 

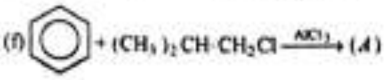
(b) 

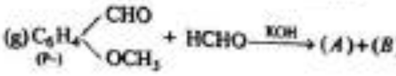
(IIT 1992)

(c) $CH_3CH_2CH_2OH \xrightarrow{P + Br_2} (A) \xrightarrow{KOH\ alc.} (B) \xrightarrow{HBr} (C) \xrightarrow[\Delta]{NH_3(g)} (D)$

(d) $C_6H_5COOC_6H_5 \xrightarrow{\text{Mononitration}} (A)$ **(IIT 1993)**

(e) $C_6H_5CONH_2 \xrightarrow{P_2O_5} (A) \xrightarrow[H_2O,\ \Delta]{H^+} (B)$ **(IIT 1992)**

(f) 
$+ (CH_3)_2CH \cdot CH_2Cl \xrightarrow{AlCl_3} (A)$



(g) $C_6H_4(CHO)(OCH_3)$ (P-) + HCHO $\xrightarrow{KOH}$ (A)+(B) **(IIT 1992)**

(h) $CH_3—CH_2—COOH \xrightarrow[\text{Bromine}]{\text{P and}} (A)$

$(A) \xrightarrow[\text{2. H}^+]{\text{1. Alcoholic KOH (excess)}} (B)$ **(IIT 1995)**

(i) 2,4-Dinitroaniline $\xrightarrow[\text{anisole}]{\text{NaNO}_2\text{ and HCl at 5°C}} (C)$ **(IIT 1995)**

(j) $C_6H_5—CHO + CH_3—COOC_2H_5$

$\xrightarrow[\text{C}_2\text{H}_5\text{OH and heat}]{\text{NaOC}_2\text{H}_5\text{ in absolute}} (D)$ **(IIT 1995)**

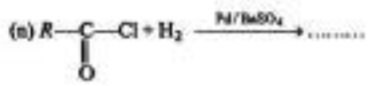
(k) o-$HOOC—C_6H_4—CH_2—C_6H_5 \xrightarrow{SOCl_2} (G)$

$(G) \xrightarrow[\text{AlCl}_3]{\text{Anhydrous}} (H); (H) \xrightarrow[\text{HCl}]{\text{Zn-Hg}} (I)$ **(IIT 1995)**

(l) $(A) \xrightarrow{PCl_5} (B) \xrightarrow{LiAlH_4} (C) \xrightarrow[H_2SO_4]{HBr} (D) \xrightarrow[\text{Ether}]{Na}$

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$

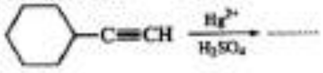
(m) $R—C(=NOH)—R' \xrightarrow{\text{Acidic reagent}}$ ………



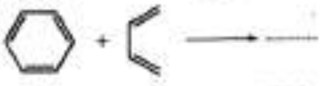
(n) $R—C(=O)—Cl + H_2 \xrightarrow{Pd/BaSO_4}$ ………

(o) $BrCH_2 \cdot CH_2Br \xrightarrow{?} C_2H_2$

(p)



(q)



(r) $C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alcoholic KOH, heat}} (A) + (B)$

(IIT 1998)

(s) $CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O,\ \text{Heat}} (A) + (B)$ **(IIT 1998)**

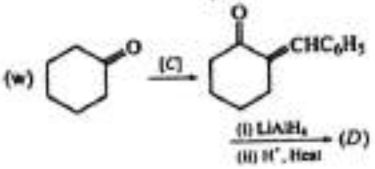
(t) $(CH_3)_2CHOCH_3 \xrightarrow{\text{HI (excess), Heat}} (A) + (B)$ **(IIT 1998)**

(u) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe} (A) + (B)$ **(IIT 1998)**

(v) $C_6H_5CH{=}CH_2 \xrightarrow{Br_2} (A) \xrightarrow[\text{(ii) CH}_3\text{I}]{\text{(i) NaNH}_2\text{ (3.0 equiv.)}} (B)$

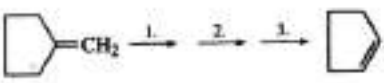
(IIT 1998)

(w)



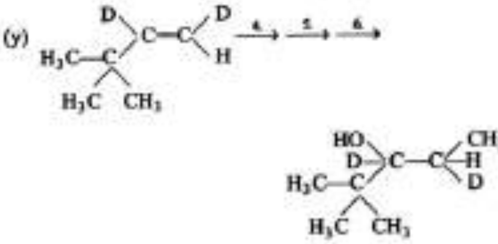
(IIT 1998)

(x)

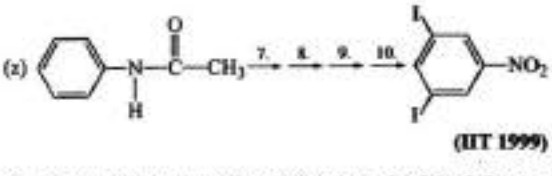


(IIT 1999)

(y)

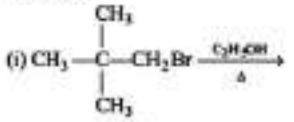


(z)



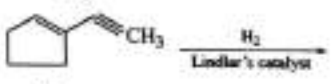
(IIT 1999)

93. What would be the major product in each of the following reactions? **(IIT 2000)**

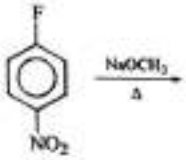


(i) $CH_3—C(CH_3)_2—CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$

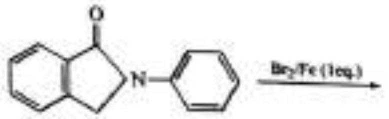
(ii)



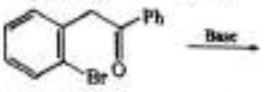
(iii)



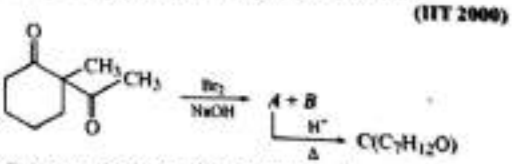
(iv)



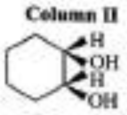
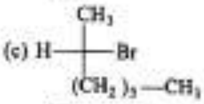
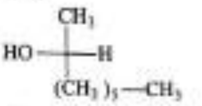
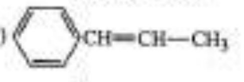
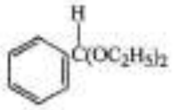
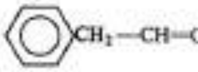
(v)



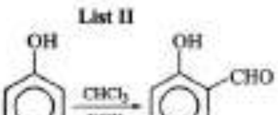
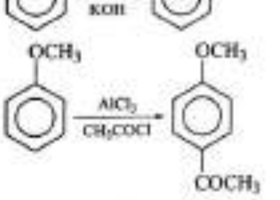
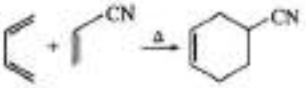
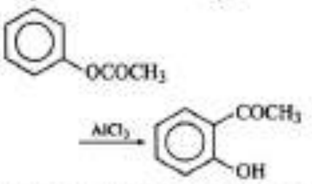
94. Idenfity (A), (B) and (C) and give their structures. **(IIT 2000)**



95. Structure of some reactants and products are given in columns I and II respectively. First match the appropriate reactant-product pair from columns I and II and then suggest another suitable reagent for each pair. **(Roorkee 2001)**

Column I	Column II
(a) R—CH=CH$_2$	(i) 
(b) 	(ii) 
(c)  $$\begin{array}{c} CH_3 \\ H-\!\!\!-\!\!\!+\!\!\!-\!\!\!-Br \\ (CH_2)_3-CH_3 \end{array}$$	(iii)  $$\begin{array}{c} CH_3 \\ HO-\!\!\!-\!\!\!+\!\!\!-\!\!\!-H \\ (CH_3)_3-CH_3 \end{array}$$
(d) 	(iv) 
(e) 	(v) 
(f) 	(vi) R—CHCl—CH$_2$—CCl$_3$

96. Match the name reactions in **list I** with the transformations provided in **list II.**

List I	List II
(1) Friedel-Crafts reaction	(A) 
(2) Hofmann's rearrangement	(B) 
(3) Diels-Alder reaction	(C) $R\text{CONH}_2 \xrightarrow[Br_2]{NaOH} R\text{NH}_2$
(4) Fries rearrangement	(D) 
(5) Reimer-Tiemann reaction	(E) 

97. Draw the various structures of molecular C_4H_6 on the basis of following characteristics :

(a) If C_4H_6 reacts with ammoniacal $AgNO_3$.

(b) If C_4H_6 does not react with ammoniacal $AgNO_3$ but reacts with hot alkaline $KMnO_4$ to give CH_3COOH.

(c) If C_4H_6 decolourises Br_2 water and by catalytic hydrogenation (using 1 mole) and subsequent reaction with alkaline $KMnO_4$ gives CH_3COOH.

(d) If C_4H_6 on ozonolysis gives succinic acid.

98. An alkane (A), C_5H_{12} on chlorination at 300°C gives a mixture of four different monochlorinated derivatives, (B), (C), (D) and (E). Two of these derivatives give the same stable alkene (F) on dehydrohalogenation. On oxidation with hot alkaline $KMnO_4$, followed by acidification, (F) gives two products (G) and (H). Give structures of (A) to (H) with proper reasoning. **(Roorkee 1995)**

99. There are six different alkenes (A), (B), (C), (D), (E) and (F). Each on addition of one mole of hydrogen gives (G) which is the lowest molar mass hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes give acetone as a product on ozonolysis. Give structures of (A) to (F). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment with a warm conc. solution of alkaline $KMnO_4$. Show various configurations of (G) in Fischer projections. **(Roorkee 1992)**

100. Draw the various structures of compound (A) having molecular formula $C_5H_{10}O$ on the basis of following characteristics :

(a) If (A) undergoes Cannizzaro's reaction.

(b) If (A) gives iodoform test and forms isobutyric acid salt and iodoform.

(c) If (A) reacts with Na and decolorises Br_2 water and shows geometrical isomerism.

(d) If (A) reduces Tollens reagent and has chiral carbon atom.

(e) If (A) does not reduces Tollens reagent but gives iodoform test and forms white crystalline solid with $NaHSO_3$.

(f) If (A) gives red-orange solid with 2-4 dinitro phenyl hydrazine but does not give white crystalline solid with $NaHSO_3$.

101. How many g of Br_2 will react with 5 g of :

(a) Pent-1-ene (b) Pent-1-yne (c) Pentane?

102. (a) A halide $C_5H_{11}X$ on treating with alc. KOH gives pentene-1. What is halide?

(b) A halide $C_5H_{11}X$, on treating with (alc.) KOH gives only pentene-2. What is halide?

103. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures.

$$CH_3CH_2C\equiv CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} (X) \xrightarrow{H_2/Pd\text{-}BaSO_4} (Y) \xrightarrow{\text{Alkaline } KMnO_4} (Z)$$

Is the compound (Z) optically active? **(IIT 2002)**

104. An unsaturated hydrocarbon (*A*), C_9H_{16} which reacts with one mole of Br_2, on ozonolysis gives compound (*B*) and two carbon containing aldehyde (*C*), of which one of the compound undergoes reaction with cold and conc. NaOH to give products (*D*) and (*E*) in equimolar proportion, both containing same number of carbon atoms. Identify (*A*), (*B*), (*C*) and gives reactions.

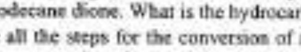
105. An unknown optically active hydrocarbon (*X*) (M.F. C_8H_{12}) gives an optically inactive compound (*Y*) (M.F. C_8H_{18}) after hydrogenation. The compound (*X*) gives no precipitate with $[Ag(NH_3)_2]^+$ and gives optically inactive compound (*Z*) (M.F. C_8H_{14}) with H_2 and Na/liq. NH_3. Determine the structures of (*X*), (*Y*) and (*Z*).

106. A hydrocarbon (*X*) was found to have a molar mass of 80-85 g mol^{-1}. A 10.02 mg sample took up 8.40 mL of H_2 gas measured at 0°C and 760 mm pressure. Ozonolysis of (*X*) yields only HCHO and CHOCHO. What was hydrocarbon?

107. A hydrocarbon of formula $C_{10}H_{18}$ absorbs only one mole of H_2 upon hydrogenation. On ozonolysis it yields 1,6-cyclodecane dione. What is the hydrocarbon?

108. Out line all the steps for the conversion of *trans*-1-phenyl propene to *cis*-1-phenyl propene.

109. Complete the following :



110. An organic compound (*A*), C_4H_9Cl on reacting with aqueous KOH gives (*B*) and on reaction with alcoholic KOH gives (*C*) which is also formed on passing the vapours of (*B*) over heated copper. The compound (*C*) readily decolorises bromine water. Ozonolysis of (*C*) gives two compounds (*D*) and (*E*). Compound (*D*) reacts with NH_2OH to give (*F*) and the compound (*E*) reacts with NaOH to give an alcohol (*G*) and sodium salt (*H*) of an acid. (*D*) can also be prepared from propyne on treatment with water in presence of Hg^{2+} and H_2SO_4. Identify (*A*) to (*H*) with proper reasoning. **(Roorkee 1996)**

111. An organic compound (*A*), $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound (*B*). The compound (*B*) on ozonolysis gives compound (*C*), which in presence of a base gives 1-acetyl cyclopentene (*D*). The compound (*B*) on reaction with HBr gives compound (*E*). Write the structures of (*A*), (*B*), (*C*) and (*E*). Show how (*D*) is formed from (*C*). **(IIT 2000)**

112. $A\,(C_6H_{12}) \xrightarrow{HCl} \underset{(C_6H_{13}Cl)}{B + C}$

$B \xrightarrow{(alc.) KOH} D$ (isomer of A)

$D \xrightarrow{Ozonolysis} E$ (Negative test with Fehling solution but + ve iodoform test)

$A \xrightarrow{Ozonolysis} F + G$ (Both give positive test with Fehling solution but – ve iodoform test)

$F + G \xrightarrow{Conc.\ NaOH}$ HCOONa + a primary alcohol.

113. In the study of chlorination of propane four products (*A*, *B*, *C* and *D*) of the formula $C_3H_6Cl_2$ were isolated. Each was further chlorinated to provide trichloro products $C_3H_5Cl_3$. It was found that (*A*) provided one trichloro product, (*B*) gave two while (*C*) and (*D*) each gave three products. What are (*A*), (*B*), (*C*) and (*D*)?

114. A hydrocarbon (*A*) of molar mass 54 reacts with an excess of Br_2 in CCl_4 to give a compound (*B*) whose molar mass is 593% more than that of (*A*). However, on catalytic hydrogenation with excess of hydrogen, (*A*) forms (*C*) whose molar mass is only 7.4% more than that of (*A*). (*A*) reacts with CH_3CH_2Br in the presence of $NaNH_2$ to give another hydrocarbon (*D*) which on ozonolysis yields diketone (*E*). (*E*) on oxidation gives propanoic acid. Give structures of (*A*) to (*E*) with reason.

(Roorkee 1997)

115. An organic compound C_4H_6 on ozonolysis gives HCHO, CO_2 and CH_3CHO. What is this?

116. An organic compound *E* (C_5H_8) on hydrogenation gives compound *F* (C_5H_{12}). Compound *E* on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound *E*. **(IIT 1995)**

117. After complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH_2O and one mole of CH_3COCHO. Identify the monomer and draw the all *cis*-forms of natural polymer. **(IIT 2005)**

118. One mole of the compound (*A*) (molecular formula C_8H_{12}), incapable of showing stereoisomerism, reacts with only one mole of H_2 on hydrogenation over Pd. (*A*) undergoes ozonolysis to give a symmetrical diketone (*B*) ($C_8H_{12}O_2$). What are the structure of (*A*) and (*B*)? **(IIT May 1997)**

119. A hydrocarbon (*A*) of the formula C_7H_{12} on ozonolysis gives a compound (*B*) which undergoes aldol condensation giving 1-acetyl cyclopentane. Identify (*A*) and (*B*).

(IIT May 1997)

120. Hydrocarbon (*A*), C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/liquid ammonia forms three different reduction products (*B*), (*C*) and (*D*) respectively. (*A*) does not form any salt with ammoniacal $AgNO_3$ solution, but forms a salt (*E*) on heating with $NaNH_2$ in an inert solvent. Compound (*E*) reacts with CH_3I to give (*F*). Compound (*D*) on oxidative ozonolysis gives *n*-butanoic acid along with other product. Give structures of (*A*) to (*F*) with proper reasoning. **(Roorkee 1998)**

121. An organic compound (*A*), C_5H_4Br which readily decolorises bromine water and $KMnO_4$ solution, gives (*B*), $C_5H_{11}Br$ on treatment with Sn/HCl. The reaction of (*A*) with $NaNH_2$ produces (*C*) with evolution of ammonia. (*C*) neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar's catalyst to give (*D*) and on reaction with $Na/NH_3(liq.)$ produces (*E*). Both the compounds (*D*) and (*E*) are isomeric. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1996)**

122. 1,4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound (*X*) which upon reaction with excess of Mg in dry ether forms (*Y*). Compound (*Y*) on treatment with ethyl acetate followed by dilute acid yields (*Z*). Identify the structures of compounds (*X*), (*Y*) and (*Z*). **(IIT 1995)**

123. Dehydrobromination of compounds (*A*) and (*B*) yield the same alkene (*C*). Alkene (*C*) can regenerate (*A*) and (*B*) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of (*A*) and (*B*) give isomeric products, (*D*) and (*E*) respectively. 1,1-diphenyl ethane is obtained on reaction of (*C*) with benzene in presence of H^+. Give structures of (*A*) to (*E*) with reasons. **(Roorkee 1997)**

124. An alkene (*A*) on passing through Br_2/CCl_4 gives a compound (*B*), which on dehydrobromination in the presence of $NaNH_2$ gives a hydrocarbon (*C*). Compound (*C*) yields (*D*) when warmed with dilute H_2SO_4 in the presence of $HgSO_4$. (*D*) gives a yellow precipitate of (*E*) on treatment with I_2 and NaOH and also forms sodium salt of 3,4-dimethylpentanoic acid. Give structures of (*A*) to (*E*) with reasons. **(Roorkee 2001)**

125. 36.4 g of 1,1,2,2-tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal $AgNO_3$. What is the mass of precipitate obtained? Give equations for the reactions involved.

126. Write the structure and give IUPAC name of the alkene which gives only pentan-2-one on ozonolysis.

(Roorkee 1985)

127. An alkyne with 5 carbon atoms per molecule when passed through dilute sulphuric acid containing mercuric sulphate gives a compound which forms an oxime, but has no effect on Fehling's solution. The compound on oxidation give dimethyl acetic acid. It reacts with sodamide to form a hydrocarbon. What is the structure of the alkyne?

128. Write the structure formulae and IUPAC names for the different alkanes formed when a mixture of 1-bromopropane and 2-bromopropane is reacted with sodium in presence of ether. What is the name of the reaction?

129. Which of the following has larger dipole moment? Explain?

1-Butyne or 1-Butene **(Roorkee 1999)**

130. An organic compound (*A*) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (*A*) with PCl_5 gives (*B*) which reacts with KCN to form (*C*). The reduction of (*C*) with warm Na/C_2H_5OH produces (*D*) which on heating gives (*E*) with evolution of ammonia. Pyridine is obtained on treatment of (*E*) with nitrobenzene. Give structure of (*A*) to (*E*) with proper reasoning. **(Roorkee 1996)**

131. Alkenes (*A*) and (*B*) yield the same alcohol (*C*) on hydration. On vigorous oxidation with $KMnO_4$ (*A*) gives a carbonyl compound (*D*) and an acid (*E*), each containing four carbon atoms. On the other hand (*B*) gives an acid (*F*) and a carbonyl compound (*G*). In (*G*) no two identical groups are attached to the same carbon atom. Give structure of (*A*) to (*G*) with proper reasoning. **(Roorkee 1995)**

132. Compound (*A*) contains only carbon and hydrogen. It decolorises bromine in CCl_4 solution and reacts slowly with concentrate H_2SO_4. Compound (*A*) reacts with HBr to form (*B*). (*B*) reacts with NaOH to form (*C*). On oxidation (*C*) gives hexanone-3. Write the structures of (*A*), (*B*) and (*C*) and give reactions. **(Roorkee 1986)**

133. It required 0.7 g of a hydrocarbon (*A*) to react completely with Br_2 (2.0 g). On treatment of (*A*) with HBr it yielded monobromo alkane (*B*). The same compound (*B*) was obtained when (*A*) was treated with HBr in presence of peroxide. Write down the structure formulae of (*A*) and (*B*) and explain the reactions involved. **(Roorkee 1987)**

134. A liquid (*A*) is reacted with hot aqueous sodium carbonate solution. A mixture of two salts (*B*) and (*C*) are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid (*A*) again. Identify (*A*), (*B*) and (*C*) and write the equations involved.

(IIT May 1997)

135. Compound (*A*) C_6H_{12} gives a positive test with bromine in carbon tetrachloride. Reaction of (*A*) with alkaline $KMnO_4$ yields only (*B*) which is the potassium salt of an acid. Write structure formulae and IUPAC names of (*A*) and (*B*).

(IIT July 1997)

136. The silver salt of an unknown alkyne contains 67.08% of Ag. Assuming no other functional gp. present, what is the structure of alkyne?

137. A chloro compound (*A*) showed the following properties :

1. Decolorised bromine in CCl_4.
2. Absorbed hydrogen catalytically.
3. Gave a precipitate with ammonical cuprous chloride.
4. When vapourised 1.49 g of (*A*) gave 448 mL of vapours at STP. Identify (*A*) and write down the equations of reactions.

(Roorkee 1991)

138. An unsaturated hydrocarbon (*A*), C_6H_{10} readily gives (*B*) on treatment with $NaNH_2$ in liquid NH_3. When (*B*) is allowed to react with 1-chloropropane, a compound (*C*) is obtained. On partial hydrogenation in the presence of Lindlar's catalyst, (*C*) gives (*D*), C_9H_{18}. On ozonolysis (*D*) gives 2,2-dimethylpropanal and 1-butanal. Give structures of (*A*), (*B*), (*C*) and (*D*) with proper reasoning. **(Roorkee 1992)**

139. An organic compound (*A*), C_6H_{10} on reduction first gives (*B*), C_6H_{12} and finally (*C*) C_6H_{14}. (*A*) on ozonolysis followed by hydrolysis gives two aldehydes (*D*) C_2H_4O and (*E*) $C_2H_2O_2$. Oxidation of (*B*) with acidified $KMnO_4$ gives acid (*F*), $C_4H_8O_2$. Determine the structures of (*A*) to (*F*) with proper reasoning. **(Roorkee 1993)**

140. A 10 g mixture of isobutane and isobutene requires 20 g of Br_2 (in CCl_4) for complete addition. If 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127°C, which exclusive product and how much of it would be formed? (Atomic mass of bromine = 80). **(Roorkee 1998)**

141. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions :

(a) On hydrogenation, Bombykol gives a compound A, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester.

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound (A) and Bombykol. How many geometrical isomers are possible for Bombykol?

(IIT 2002)

142. An alkyl halide, (X) of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z) (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of (X), (Y) and (Z). **(IIT 1996)**

143. One mole of each bromoderivative (A) and NH_3 react to give one mole of an organic compound (B). (B) reacts with CH_3I to give (C). Both (B) and (C) react with HNO_2 to give compounds (D) and (E), respectively. (D) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methylpropane. Give structures of (A) to (E) with proper reasoning. **(Roorkee 1994)**

144. An organic compound (A) of molecular formula C_5H_8 when treated with sodium in liquid ammonia followed by reaction with n-propyl iodide yields (B), C_8H_{14}. (A) gives a ketone (C), $C_5H_{10}O$, when treated with dilute H_2SO_4 and $HgSO_4$. (B) on oxidation with alkaline $KMnO_4$ gives two isomeric acids (D) and (E), $C_4H_8O_2$. Give structures of compounds (A) to (E) with proper reasoning. **(Roorkee 1994)**

145. When gas (A) is passed through dry KOH at low temperature, a deep red coloured compound, (B) and a gas (C) are obtained. The gas (A) on reaction with but-2-ene, followed by treatment with Zn/H_2O yields acetaldehyde. Identify (A), (B) and (C).

146. When t-butanol and n-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? **(IIT 1994)**

147. 0.037 g of an alcohol, ROH, was added to CH_3MgI and the gas evolved measured 11.2 cm^3 at STP. What is the molar mass of ROH? On dehydration, ROH gives an alkene which on ozonolysis gives acetone as one of the products. ROH on oxidation easily gives an acid containing the same number of carbon atoms. Give structures of ROH and the acid with proper reasoning. **(Roorkee 1994)**

148. Hydrocarbon (X), C_7H_{12} on reaction with boron hydride followed by treatment with CH_3COOH yields (A). On reductive ozonolysis (A) yields a mixture of two aldehydes, (B) and (C). Of these, only (B) can undergo Cannizzaro's reaction. (A) exists in two geometrical isomers, (A–1) and (A–2), of which (A–2) is more stable. Give structures of (X), (A), (B), (C), (A–1) and (A–2) with proper reasoning. **(Roorkee 2000)**

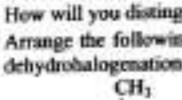
149. A hydrocarbon (A), of the formula C_8H_{16}, on ozonolysis gives compound (B), ($C_4H_8O_2$) only. The compound (B) can also be obtained from the alkyl bromide, (C), (C_3H_7Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify (A), (B) and (C) and also give equations for the reactions. **(IIT 1996)**

150. An O.C. (A) reacts with H_2 to give (B) and (C) successively. On ozonolysis of (A), two aldehydes (D) C_2H_4O and (E) $C_2H_2O_2$ are formed. On ozonolysis of (B) only propanal is formed. What are (A) to (E)?

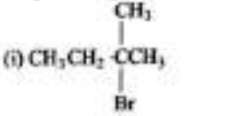
151. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B)? **(IIT 2001)**

152. How will you distinguish divinyl ether and diethyl ether?

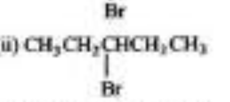
153. Arrange the following in order of increasing tendency for dehydrohalogenation with proper reasoning :

(i) 

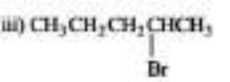
$\mathrm{CH_3CH_2}\text{-}\underset{\mathrm{Br}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_3}$

(ii) 

$\mathrm{CH_3CH_2}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{HCH_2CH_3}$

(iii) 

$\mathrm{CH_3CH_2CH_2}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{HCH_3}$

(iv) 

$\mathrm{CH_3CH_2CH_2CH_2}\underset{\mathrm{Br}}{\mathrm{C}}\mathrm{H_2}$

(v) CH_3CH_2Br

154. (a) An organic compound C_5H_8 on ozonolysis gives pentane-1,5-dial. Identify and convert 'C_5H_8' into cyclopentane-1,2-diol.

(b) A small amount of NaI catalyses the hydrolysis of RCl.

155. A hydrocarbon (A) (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. (A) adds HBr in accordance with Markownikoff's rule to form a compound (B) which on reaction with silver hydroxide forms an alcohol (C), $C_5H_{12}O$. Alcohol (C) on oxidation gives a ketone (D). Deduce (A) to (D) and give the reactions involved.

156. 0.369 g of a bromo-derivative of a hydrocarbon (A) when vaporized occupied 67.2 mL at NTP. (A) on reaction with aqueous NaOH gives (B). (B) when passed over alumina at 250°C gives a neutral compound (C) while at 350°C it gives a hydrocarbon (D). (D) when heated with HBr gives an isomer of (A). When (D) is treated with conc. H_2SO_4 and the product is diluted with water and distilled, (E) is obtained. Identify (A) to (E) and explain the reactions.

157. Compound (*x*) (C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of MeMgBr, 0.42 g of (*x*) gives 224 mL CH_4 at STP. Treatment of (*x*) with H_2 in presence of Pt catalyst followed by boiling with excess HI gives *n*-pentane. Suggest structure for (*x*) and write equations involved. **(IIT 1992)**

158. 0.535 g ethanol and acetaldehyde mixture when heated with Fehling solution gave 1.2 g of a red precipitate. What is the percentage of acetaldehyde in the mixture?
(Atomic mass of Cu = 63.8)

159. An organic compound (*A*) reacts with ethanol to give (*B*) and (*C*). On acid hydrolysis (*C*) yields (*B*) and (*D*). Oxidation of (*D*) gives (*B*). (*B*) is an acid and forms a salt with $Ca(OH)_2$ which on dry distillation gives (*E*), C_3H_6O. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 2000)**

160. Compound (*A*) gives positive Lucas test in 5 minutes. When 6.0 g of (*A*) is treated with sodium metal, 1120 mL of hydrogen is evolved at STP. Assuming (*A*) to contain one atom of oxygen per molecule, write structure formula of (*A*). Compound (*A*) when treated with PBr_3 gives (*B*) which when treated with benzene in presence of anhydrous aluminium chloride gives (*C*). What are (*B*) and (*C*)? **(Roorkee 1990)**

161. When 0.0088 g of compound (*A*) was dissolved in 0.50 g of camphor, the melting point of camphor was lowered by 8°C. Analysis of (*A*) gave 68.18% C and 13.16% H. Compound (*A*) showed the following reactions :

(i) It reacted with acetyl chloride and evolved hydrogen with sodium.

(ii) When reacted with HCl + $ZnCl_2$, a dense oily layer separated out immediately.

Compound (*A*) was passed over Al_2O_3 at 350°C to give compound (*B*). (*B*) on ozonolysis followed by hydrolysis gave two neutral compounds (*C*) and (*D*), which gave positive test wtih carbonyl reagents but only (*C*) gave a positive test with Fehling solution and resinous substance with NaOH. Identify (*A*), (*B*), (*C*) and (*D*) with proper reasoning. K_f for camphor = 40 K mol^{-1} kg. **(Roorkee 1991)**

162. Compound (*X*) with molecular formula $C_9H_{10}O$ forms a semicarbazone and gives negative Tollens and iodoform tests. Upon reduction it gives *n*-propyl benzene. Deduce the structure of *X*.

163. An optically active alcohol (*A*) ($C_6H_{10}O$) absorbs two mole of hydrogen per mole of (*A*) upon catalytic hydrogenation and gives a product (*B*). The compound (*B*) is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of (*A*) and (*B*). **(IIT 1996)**

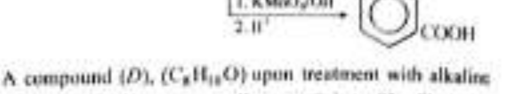
164. Give the aldol products and the corresponding alkenes (aq. NaOH or KOH used, 100°C) from :

(i) 2,5-hexanedione

(ii) 2,4-pentanedione

165. An aromatic ketone (*X*) has the M.F. ($C_{10}H_{12}O_2$) on vigorous oxidation, it gives (*Y*), a dibasic acid ($C_8H_6O_4$) which easily gives an anhydride on heating. The ketone (*X*) gives (*Z*) ($C_9H_{10}O_3$), a monobasic acid on heating with bromine and NaOH. (*Z*) on decarboxylation with soda lime gives 3-methyl anisole. Determine (*X*), (*Y*) and (*Z*).

166. Complete the following :



167. A compound (*D*), ($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (*E*), ($C_7H_6O_2$). Write the structures of (*D*), (*E*) and explain the formation of (*E*). **(IIT 1996)**

168. $A \xrightarrow[250°C]{Al_2O_3} (B) \xrightarrow[(ii)\ AgOH]{(i)\ HBr} (C) \xrightarrow[150°C]{Al_2O_3} (B) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} (A)$

In the above reactions scheme (*A*) and (*C*) are isomers. (*B*) has a formula of C_5H_{10} which can also be obtained from the product of the reactions of CH_3CH_2MgBr and $(CH_3)_2CO$. Give structures of (*A*), (*B*) and (*C*). **(Roorkee 2000)**

169. A compound (*A*) $C_4H_{10}O_4$ yields on acetylation (*B*) of formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in compound ? Also write structures of (*A*) and (*B*).

170. Compounds (*A*) and (*B*) on reaction in ether medium and subsequent acidification and oxidation give 2,5-dimethyl-3-hexanone. What are (*A*) and (*B*)? **(Roorkee 1998)**

171. The compound $C_4H_8Cl_2$ (*A*) on hydrolysis gives a compound C_4H_8O, (*B*). The compound (*B*) reacts with hydroxylamine and gives a negative test with Tollens reagent. What are (*A*) and (*B*)? Support your answer with proper reasoning and give the equations of reactions. **(Roorkee 1985)**

172. An acid (*A*) contains carbon = 40.7%; hydrogen = 5.1% and its silver salt contains 65.1% silver. The ethylester of (*A*) has V.D. of 87 (H_2 = 1). What structure (*A*) may have? How would you distinguish between isomers?

173. Compound (*A*) $C_4H_8O_2$ has the following properties. What is this?

(i) It reacts with sodium bicarbonate to liberate CO_2.

(ii) On fusion with alkali gives propane.

(iii) With $Ca(OH)_2$ it gives $C_8H_{14}O_4Ca$ which on heating decomposes to di-isopropyl ketone.

174. A Grignard reagent (*A*) and a haloalkene (*B*) react together to give (*C*). Compound (*C*) on heating with KOH yields a mixture of two geometrical isomers, (*D*) and (*E*), of which (*D*) predominates. (*C*) and (*E*) have the same molecular formula and (*C*) gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide. Give structures of (*A*), (*B*) and (*C*) and configurations of (*D*) and (*E*) with reasons. **(Roorkee 2001)**

175. An acidic compound (*A*), $C_4H_8O_3$ loses its optical activity on strong heating yielding (*B*), $C_4H_6O_2$ which reacts readily with $KMnO_4$. (*B*) forms a derivative (*C*) with $SOCl_2$, which on reaction with $(CH_3)_2NH$ gives (*D*). The compound (*A*) on oxidation with dilute chromic acid gives an unstable compound (*E*) which decarboxylates readily to give (*F*), C_3H_6O. The compound (*F*) gives a hydrocarbon (*G*) on treatment with amalgamated Zn and HCl. Give structures of (*A*) to (*G*) with proper reasoning.

(Roorkee 1995)

176. An organic compound (*A*) C_5H_8O adds Br_2 to give $C_5H_8Br_2O$. It does not react with Tollens reagent but enters into reaction with phenyl hydrazine. Ozonolysis of (*A*) gives acetaldehyde and $C_3H_4O_2$ which readily loses CO to form acetaldehyde.

177. A compound has two isomers (*A*) and (*B*) of formula $C_5H_{10}O$. Isomer (*A*) on treating with NaOH(*aq*.) gives 2,2-dimethylpropan-1-ol and 2,2-dimethylpropanoic acid salt. The isomer (*B*) on treating with NaOH(*aq*.) gives 3-hydroxy, 2-propylheptanal. What are (*A*) and (*B*)?

178. An organic acid (*A*), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (*B*). Compound (*B*) contains an asymmetric carbon atom and yields (*C*) on dehydrobromination. Compound (*C*) does not show geometric isomerism and on decarboxylation gives an alkene (*D*) which on ozonolysis gives (*E*) and (*F*). Compound (*E*) gives a positive Schiff's test but (*F*) does not. Give structures of (*A*) to (*F*) with reasons.

(Roorkee 1997)

179. An organic compound (*A*) $C_4H_7Cl_3$ yields (*B*) with KOH(*aq*.). (*B*) on treating with NH_3 gives (*C*) which on heating gives (*D*). On heating (*D*) with P_2O_5, 2-methylpropannitrile is formed. What are (*A*), (*B*), (*C*) and (*D*)?

180. Two isomers (*A*) and (*B*) have formula $C_3H_6O_2$. (*B*) gives effervescenses with $NaHCO_3$ while (*A*) does not do so. (*B*) gives out H_2 when treated with metallic Zn but (*A*) has no reaction with it. (*A*) on treatment with excess of NaOH yields two compounds (*C*) and (*D*). Compound (*C*) when treated with dil. H_2SO_4 gives (*E*) which reduces Tollens reagent. (*D*), however, can form iodoform with I_2 and alkali. Identify (*A*) to (*E*).

181. An organic compound (*A*), $C_6H_{12}O_3$ on treatment with concentrated H_2SO_4 gives CO_2, H_2O and (*B*). Compound (*B*) can be prepared by passing vapours of pentanol-1 over heated copper at 570 K. Compound (*A*) on heating gives (*C*), $C_{12}H_{20}O_4$.

Give structures of (*A*) to (*C*) with proper reasoning.

(Roorkee 1998)

182. An ester has molar mass 102 g mol^{-1}. On aqueous hydrolysis it produces a monobasic acid and an alcohol. If 0.185 g of the acid produced completely neutralizes 25 mL of 0.1 *N* NaOH, find out the structure formulae of the produced alcohol, acid and the ester with proper reasoning.

(Roorkee 1990)

183. A liquid (*X*) having molecular formula $C_6H_{12}O_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (*Y*) and an alcohol (*Z*). Oxidation of (*Z*) with chromic acid gives (*Y*). What are (*X*), (*Y*) and (*Z*)?

184. An organic compound (*A*) on treatment with ethyl alcohol gives a carboxylic acid (*B*) and compound (*C*). Hydrolysis of (*C*) under acidic conditions gives (*B*) and (*D*). Oxidation of (*D*) with $KMnO_4$ also gives (*B*). (*B*) on heating with $Ca(OH)_2$ gives (*E*) (Molecular formula C_3H_6O). (*E*) does not give Tollens test and does not reduce Fehling solution but forms 2,4-dinitrophenylhydrazone. Identify (*A*) to (*E*).

(IIT 1992)

185. Two mole of an ester (*A*) are condensed in presence of sodium ethoxide to give a β-keto ester (*B*) and ethanol. On heating in an acidic solution (*B*) gives ethanol and a β-keto acid (*C*). On decarboxylation (*C*) gives 3-pentanone. Identify (*A*), (*B*) and (*C*) with proper reasoning and give reactions. **(Roorkee 1992)**

186. Compound (*A*) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compound (*B*) and (*C*). The compound (*B*) on oxidation gave (*D*) which on treatment with alkali (aqueous) and subsequent heating furnished (*E*). The later on catalytic hydrogenation gave (*C*). The compound (*D*) was oxidized further to give (*F*) which was found to be monobasic acid (m.wt. 60.0). Deduce structures of (*A*) to (*E*). **(IIT 1990)**

187. Compound (*A*) $C_5H_8O_2$ liberated CO_2 on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yielded compound (*B*), $C_5H_{10}O_2$ on hydrogenation. Compound (*B*) can be separated into enantiomorphs. Write structures of (*A*) and (*B*).

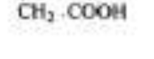
188. The sodium salt of a carboxylic acid, (*A*) was produced by passing a gas (*B*) into aqueous solution of caustic alkali at an elevated temperature and pressure. (*A*) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid (*C*). A sample of 0.4 g of (*C*) on combustion gave 0.08 g of H_2O and 0.39 g of CO_2. The silver salt of the acid, weighing 1.0 g, on ignition yielded 0.71 g of Ag as residue. Identify (*A*), (*B*) and (*C*).

(IIT 1990)

189. An organic compound (*A*), $C_5H_8O_3$ on heating with soda lime gives (*B*), which reacts with HCl to give (*C*). The compound (*C*) reacts with thionyl chloride to produce (*D*) which on reaction with KCN gives compound (*E*). Alkaline hydrolysis of (*E*) gives a salt (*F*) which on heating with soda lime produces *n*-butane. Careful oxidation of (*A*) with dichromate gives acetic acid and malonic acid. Give structures of (*A*) to (*F*) with proper reasoning.

(Roorkee 1999)

190. Aspartame, an artificial sweetener, is a peptide and has the following structure :



$$H_2N\underset{\underset{CH_2\cdot COOH}{|}}{CH}\cdot CONH\cdot\overset{\overset{CH_2C_6H_5}{|}}{CH}\cdot COOCH_3$$

(i) Identify the four functional groups.
(ii) Write the zwitterionic structure.
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
(iv) Which of the two amino acids is more hydrophobic? **(IIT 2001)**

191. From analysis and molar mass determination, the molecular formula of (*A*) is C_3H_7NO. The compound gave following reactions :

(1) On hydrolysis it gives an amine (*B*) and a cabroxylic acid (*C*).
(2) Amine (*B*) reacts with benzene sulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution.
(3) Acid (*C*) on reaction with Tollens reagent gives a silver mirror, what are (*A*), (*B*) and (*C*)? Explain the reactions.

192. A basic volatile, nitrogen compound gave a foul smelling gas when treated with $CHCl_3$ and alcoholic KOH. A 0.295 g sample of the substance dissolved in aqueous HCl and treated with $NaNO_2$ solution at 0°C liberated a colourless; odourless gas whose volume correspond to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave yellow precipitate. Identify the original substance. Assume it contains one N-atom per molecule. **(IIT 1993)**

193. An organic compound (*A*) containing C, H, N and O, on analysis gives 49.32% C, 9.59% H and 19.18% N. (*A*) on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid (*B*). The silver salt of (*B*) contains 59.67% silver. Deduce structures of (*A*) and (*B*). **(IIT 1988)**

194. Compound '*X*' containing chlorine, on treatment with NH_3 gives a solid '*Y*' which is free from chlorine. (*Y*) analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound (*Z*). (*Z*) reacts with HNO_2 to give ethanol. Suggest structures for (*X*), (*Y*) and (*Z*). **(IIT 1992)**

195. Write the structure of alanine at pH = 2 and pH = 10. **(IIT 2000)**

196. Compound (*A*), $C_5H_{11}NO$ is not soluble in cold dilute alkaline or acidic solutions. When (*A*) is refluxed in NaOH solution, a gas (*B*) is evolved and a salt (*C*) is formed. Acetyl chloride reacts with (*B*) to give (*D*), C_4H_9NO. (*B*) reacts with HNO_2 to give a yellow oil (*E*). Give structures of (*A*) to (*E*) with reason. **(Roorkee 2000)**

197. An organic compound $C_2H_7NO_2$, on slow distillation loses water and gives (*B*) which on further distillation with P_2O_5 forms (*C*). (*C*) on hydrolysis gives (*D*) which on treating with P + Cl_2 followed with hydrolysis forms glycollic acid. What are (*A*), (*B*), (*C*) and (*D*)?

198. As ester *A* ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved. **(IIT 1998)**

199. A mixture of an acid anhydride (*A*) and a monobasic acid (*B*) on heating produces another monobasic acid (*C*) of equivalent mass 74 and an anhydride (*D*). The acids and anhydrides remain in equilibrium. The anhydride (*D*) contains two identical fluoroalkyl groups. The acid (*B*) contains a trifluoromethyl group and has an equivalent mass of 128.

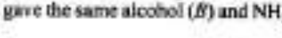
Give structures of (*A*) to (*D*) with proper reasoning (Atomic mass of fluorine = 19). **(Roorkee 1998)**

200. Two isomeric compounds (*A*) and (*B*) have $C_4H_{11}N$ molecular formula. Both on separately treating with HNO_2 lose their N_2 producing two isomeric alcohols (*C*) and (*D*) respectively of molecular formula $C_4H_{10}O$. (*C*) reacts with Lucas reagent immediately and resists oxidation. (*D*) does not react with Lucas reagent in cold but can be easily oxidized. Complete methylation of either (*A*) or (*B*) is made which on decomposition does not produce butene-1.

201. An organic compound (*A*) $C_2H_5NO_2$ gave on hydrolysis an alcohol (*B*) of molar mass 46 g mol^{-1} and an acid. On reduction it gave the same alcohol (*B*) and NH_3 gas. What is (*A*)?

202. (a) Carry out the following transformation in not more than three steps.

$$CH_3{-}CH_2{-}C{\equiv}C{-}H \longrightarrow$$



$$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$ **(IIT 1999)**

(b) Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps. **(IIT 1999)**

(c) Explain why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid. **(IIT 1999)**

203. Identify (*X*), (*Y*) and (*Z*) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (*Z*) is treated with HBr and subsequently ozonolysed. Mark the (C^*) carbon in the entire scheme.

$$BaC^*O_3 + H_2SO_4 \longrightarrow (X)\text{(gas)}\ [C^* \text{ denotes } C^{14}]$$

$$CH_2{=}CH{\cdot}Br \xrightarrow[\text{(ii) } X,\ \text{(iii) } H_3O^+]{\text{(i) Mg/Ether}} (Y) \xrightarrow{LiAlH_4} (Z)$$

(IIT 2001)

204. Complete the reaction :

(a) $CH_2{=}CHCHO \xrightarrow{LiAlH_4}$ '*A*'

(b) $\dot{C}_6H_5CH{=}CHCHO \xrightarrow{LiAlH_4}$ '*B*'

205. (a) When bromobenzene is monochlorinated, two isomeric compounds (*A*) and (*B*) are obtained. Monobromination of (*A*) gives several isomeric products of formula $C_6H_3ClBr_2$ while monobromination of (*B*) yields only two isomers (*C*) and (*D*). Compound (*C*) is identical with one of the compounds obtained from the bromination of (*A*), however, (*D*) is totally different from any of the isomeric compounds obtained from bromination of (*A*). Give structures of (*A*), (*B*) and (*D*) and also suggest structures of four isomeric monobrominated products of (*A*). Support answer with reasoning. **(Roorkee 1992)**

206. A phenolic compound (*A*), $C_7H_8O_2$ on mild oxidation gives a highly volatile oil (*B*). (*A*) forms (*C*) on reaction with dimethyl sulphate in alkali. Oxidation of (*C*) with hot $KMnO_4$ gives (*D*) which then reacts with bromine water to give (*E*) containing about 72% bromine. Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1997)**

207. A hydrocarbon (*A*) [C = 90.56%; vapour density 53] was subjected to vigorous oxidation to give a dibasic acid (*B*). 0.10 g of (*B*) required 24.1 mL of 0.05 *N* NaOH for complete neutralization. When (*B*) was heated strongly with soda lime, it gave benzene. Nitration of (*B*) gave a single mono nitro derivative. Identify (*A*) and (*B*) with proper reasoning and also give their structures. **(Roorkee 1991)**

208. There are three isomeric compounds (*A*), (*B*) and (*C*) having molecular formula $C_8H_8O_2$.
    (i) When heated with soda lime (*A*) gives C_6H_6, while (*B*) and (*C*) gives toluene.
    (ii) (*A*) is neutral compound while (*B*) and (*C*) are monobasic acid.
    (iii) (*B*) on chlorination in sunlight gave a compound containing 3 chlorine atom per molecule which is easily hydrolysed to a dibasic acid (*D*). (*D*) with soda lime gave benzene. The photo chlorination of (*C*) gave a product which contains two Cl-atoms per molecule and is strong acid. Identify (*A*), (*B*), (*C*) and (*D*).

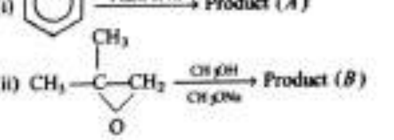
209. Catalytic dehydrogenation of methylcyclohexane, obtained from petroleum, gives a liquid which on treatment with chlorosulphonic acid at 370 K yields a mixture of two isomers (*A*) and (*B*), $C_7H_7SO_2Cl$. The major isomer (*A*) reacts with ammonia to form (*C*), which on oxidation with permanganate gives compound (*D*). On heating compound (*D*) gives a well known sweetening agent (*E*). The minor isomer (*B*) also reacts with ammonia to give a compound (*F*) which on treatment with NaClO/NaOH gives an antiseptic (*G*). Identify (*A*) to (*G*) with proper reasoning. **(Roorkee 1999)**

210. An alkene (*A*) ($C_{16}H_{16}$) on ozonolysis gives only one product (*B*) (C_8H_8O). Compound (*B*) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (*B*) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (*C*) (C_8H_{10}). Write the structure of compounds (*B*) and (*C*). Based on this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd-C) gives a racemic mixture. **(IIT 2001)**

211. (a) Prepare 3-chloroaniline from benzene (In three steps).
    (b) Identify the products in each case.

(i)

(ii)



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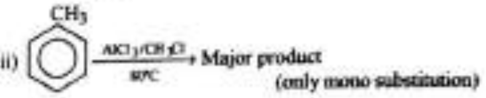

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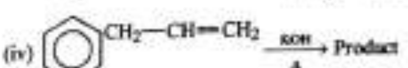
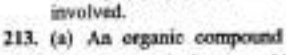


212. Compound (*A*) having empirical formula C_7H_8 is chlorinated in sunlight to give a product (*B*) which on hydrolysis gives a compound (*C*). (*C*) gives a positive test with Tollens reagent and with sodium acetate and acetic anhydride gives an acid (*D*) with an equivalent mass 148.15. Identify (*A*), (*B*), (*C*) and (*D*) and explain the reactions involved.

213. (a) An organic compound C_8H_{18} on monochlorination gives a single monochloride. Write the structure of hydrocarbon.
    (b) Write the structures of possible major monosubstituted products formed when Br^+ attacks the following molecules. Justify your answer. **(Roorkee 1999)**



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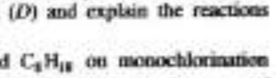

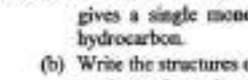

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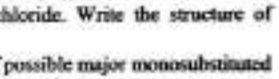


214. An aromatic compound (*A*), $C_7H_5NO_3Cl_2$ on reduction with Sn/HCl gives (*B*) which on reaction with $NaNO_2$/HCl gives (*C*). Compound (*B*) does not form a dye with β-naphthol. However, (*C*) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (*D*) of equivalent mass 191. Decarboxylation of (*D*) gives (*E*) which forms a single mononitro derivative (*F*) on nitration. Give structure of (*A*) to (*F*) with proper reasoning. **(Roorkee 1995)**

215. Compound (*A*) C_7H_8O is insoluble in aqueous sodium bicarbonate but dissolves in aqueous sodium hydroxide and gives a characteristic colour with aqueous ferric chloride. When treated with bromine, (*A*) forms a compound (*B*) $C_7H_5OBr_3$.
    (i) Give structure formulae of (*A*) and (*B*).
    (ii) What would be structure of (*A*) if it neither dissolves in aqueous sodium hydroxide nor gives a characteristic colour with $FeCl_3$? **(Roorkee 1993)**

216. An organic compound (*A*) gives positive Liebermann reaction and on treatment with $CHCl_3$/KOH followed by hydrolysis gives (*B*) and (*C*). Compound (*B*) gives colour with Schiff's reagent but not (*C*), which is steam volatile. (*C*) on treatment with $LiAlH_4$ gives (*D*), $C_7H_8O_2$ which on oxidation gives (*E*). Compound (*E*) reacts with $(CH_3CO)_2O/CH_3COOH$ to give a pain reliever (*F*). Give structures of (*A*) to (*F*) with proper reasoning.

(Roorkee 1995)

217. An organic compound (*A*) of molar mass 140.5 has 68.32% C and 6.4% H and 25.26% Cl. Hydrolysis of (*A*) with dilute acid gives compound (*B*) $C_8H_{10}O$. Compound (*B*) can be oxidized under mild conditions to compound (*C*), C_8H_8O. Compound (*C*) forms a phenyl hydrazone (*D*) with $PhNHNH_2$ and gives positive iodoform test. Deduce the structures of (*A*) to (*D*) with proper reasoning.

(Roorkee 1990)

218. An organic compound (*A*), $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound (*B*). The compound (*B*) on treatment with PCl_5, followed by reaction with $H_2/Pd(BaSO_4)$ gives compound (*C*), which on reaction with hydrazine gives a cyclised compound (*D*) ($C_{14}H_{10}N_2$). Identify (*A*), (*B*), (*C*) and (*D*). Explain the formation of (*D*) from (*C*). **(IIT 2000)**

219. An acid (*A*), $C_8H_7O_2Br$ on bromination in the presence of $FeBr_3$ gives two isomers, (*B*) and (*C*) of formula $C_8H_6O_2Br_2$. Vigorous oxidation of (*A*), (*B*) and (*C*) gives acids (*D*), (*E*) and (*F*) respectively. (*D*), $C_7H_5O_2Br$ is the strongest acid among all of its isomers, whereas (*E*) and (*F*) each has a molecular formula of $C_7H_4O_2Br_2$. Give structures of (*A*) to (*F*) with justification. **(Roorkee 2000)**

220. Two different Grignard reagents, (*X*) and (*Y*) produce $C_6H_5CH_2C(CH_3)_2OH$ on reaction with (*P*) and (*Q*) respectively. Give structures of (*X*), (*Y*), (*P*) and (*Q*).

(Roorkee 2000)

221. A mixture of two aromatic compounds (*A*) and (*B*) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing (*A*), when heated with alcoholic solution of KOH produce (*C*) C_7H_5N associated with unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds (*D*) and (*E*) of molecular formula $C_7H_6O_2$. Identify (*A*) to (*E*). **(IIT 1990)**

222. (*A*), (*B*), (*C*), (*D*), (*E*), (*F*) and (*G*) are amines, each of which forms a hydrochloride containing 32.42% chlorine. (*A*), (*B*), (*C*) and (*D*) evolve N_2 on reaction with HNO_2, but (*E*), (*F*) and (*G*) do not. Give structures of (*A*) to (*G*) with reasons.

(Roorkee 2001)

223. An O.C. (*A*) $C_7H_7NO_2$ on reduction gives a solid (*B*). (*B*) on diazotization gives (*C*) which on treating with Cu_2Cl_2/HCl gives (*D*). (*D*) on oxidation by alkaline $KMnO_4$ gives (*E*) which on reduction by Ni-Al/NaOH gives benzoic acid.

224. An organic compound (*A*) $C_9H_{13}N$ dissolves in dil. HCl and releases N_2 with HNO_2 giving an optically active alcohol (*B*). (*B*) on oxidation gives dicarboxylic acid, which on heating form anhydride. What are (*A*) and (*B*)?

225. The percentage of carbon, hydrogen and nitrogen in a disubstituted aromatic compound (*A*) is 71.11, 6.67 and 10.37 respectively. Its molecule contains a single atom of nitrogen. Compound (*A*) evolves NH_3 when heated with NaOH to form salt (*B*), from which an acid (*C*) is obtained on acidification. If an electrophilic substitution is carried on (*C*), an entering electrophile can occupy either of the two identical positions available in the ring. Acid (*C*) on heating with PCl_5, gives (*D*) which reacts with (*B*) to give an organic product (*E*). Give structures of (*A*) to (*E*) with proper reasoning. **(Roorkee 1996)**

226. Compound (*A*), $C_{10}H_{12}O$ gives off hydrogen on treatment with sodium metal and also decolourises Br_2 in CCl_4 to give (*B*), $C_{10}H_{12}OBr_2$. (*A*) on treatment with I_2 in NaOH gives iodoform and an acid (*C*) after acidification. Give structures of (*A*) to (*C*) and also of all the geometrical and optical isomers of (*A*). **(Roorkee 1997)**

227. An organic compound containing C, H and O exists in two isomeric forms (*A*) and (*B*). 0.108 g of an isomer gives 0.308 g of CO_2 and 0.072 g of H_2O. (*A*) is insoluble in NaOH and $NaHCO_3$, while B is soluble in NaOH. (*A*) reacts with conc. HI to give (*C*) and (*D*). (*C*) can be separated from (*D*) by ethanolic $AgNO_3$ solution and (*D*) is soluble in NaOH. (*B*) reacts readily with bromine water to give compound (*E*) of molecular formula $C_7H_5OBr_3$. Identify (*A*) to (*E*).

(IIT 1991)

228. Two isomeric mononitro derivatives (*B*) and (*C*) are obtained by the nitration of an organic compound (*A*), C_7H_8O. Treatment of (*A*) with acetyl chloride produces (*D*) which on reaction with CrO_2Cl_2 gives (*E*) whose oxidation with neutral $KMnO_4$ followed by acidification gives (*F*). The compound (*F*) on heating gives phenol. (*A*) on treatment with alkaline $C_6H_5SO_2Cl$ produces (*G*) which on oxidation with $KMnO_4$ gives (*H*). Hydrolysis of (*H*) also gives (*F*). Give structures of (*A*) to (*H*) with proper reasoning. **(Roorkee 1996)**

229. An aromatic hydrocarbon (*A*) $C_{16}H_{16}$ shows the following reactions :

(i) It decolourises Br_2 in CCl_4.

(ii) It adds one mole of H_2.

(iii) Oxidation with hot $KMnO_4$ gives a dicarboxylic acid (*B*) $C_6H_4(COOH)_2$. (*B*) on bromination shows only one monobromo substitution product.

Deduce the structure of (*A*) and report its stereoisomers if any.

230. A mono substituted alkyl benzene (*A*) of the formula $C_{10}H_{14}$ resists vigorous oxidation to an aryl carboxylic acid. Name the compound and write down its various mono substituted isomers.

231. Compound *A* (C_8H_8O) on treatment with $NH_2OH \cdot HCl$ gives (*B*) and (*C*). (*B*) and (*C*) rearrange to give (*D*) and (*E*), respectively, on treatment with acid. (*B*), (*C*), (*D*) and (*E*) are all isomers of molecular formula (C_8H_9NO). When (*D*) is boiled with alcoholic KOH an oil (*F*) (C_6H_7N) separates out. (*F*) reacts rapidly with CH_3COCl to give back (*D*). On the other hand, (*E*) on boiling with alkali followed by acidification gives a white solid (*G*) ($C_7H_6O_2$). Identify (*A*) to (*G*). **(IIT 1999)**

232. Two isomeric forms of an organic compound (*A*), $C_{11}H_{13}OCl$ readily decolourise bromine water and give same compound (*B*) on catalytic hydrogenation. Both the isomeric forms on vigorous oxidation give (*C*) which on treatment with soda lime gives 2-chloroethoxybenzene. However, (*C*) on treatment with Ni/Al alloy in alkaline medium gives 3-ethoxy benzoic acid. Only one of the isomers of (*A*) give geometrical isomers (*D*) and (*E*). Identify (*A*) to (*E*) with proper reasoning. **(Roorkee 1997)**

233. An organic compound (*A*) of molar mass 135 on boiling with NaOH evolves a gas which gives white dense fumes on bringing a rod dipped in HCl near it. The alkaline solution thus, obtained on acidification gives the precipitate of a compound (*B*) having molar mass 136. Treatment of (*A*) with HNO_2 also yields (*B*), whereas its treatment with Br_2/KOH gives (*C*). Compound (*C*) reacts with cold HNO_2 to give (*D*), which gives red colour with ceric ammonium nitrate. On the other hand (*E*) an isomer of (*A*) on boiling with dil. HCl gives an acid (*F*), having molar mass 136. On oxidation followed by heating, (*F*) gives an anhydride (*G*) which condenses with benzene in presence of $AlCl_3$ to give anthraquinone. Give structures of (*A*) to (*G*) with proper reasoning. **(Roorkee 1999)**

234. Two isomeric compound (*A*) and (*B*) have the same formula $C_{11}H_{13}OCl$. Both are unsaturated, yield the same compound (*C*) on catalytic hydrogenation and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (*A*) exists in geometrical isomers, (*D*) and (*E*) but not (*B*). Give structures of (*A*) to (*E*) with proper reasoning.

(Roorkee 1994)

235. An organic compound (*A*), $C_9H_{12}O$ was subjected to a series of tests in the laboratory. It was found that this compound :

(i) Rotates the plane of polarized light.

(ii) Evolves hydrogen with sodium.

(iii) Reacts with I_2 and NaOH to produce a pale yellow solid compound.

(iv) Does not react with Br_2/CCl_4.

(v) Reacts with hot $KMnO_4$ to form compound (*B*), $C_7H_6O_2$ which can also be synthesized by the reaction of benzene and carbonyl chloride followed by hydrolysis.

(vi) Loses optical activity as a result of formation of compound (*C*) on being heated with HI and P.

(vii) Reacts with Lucas reagent in about 5 min.

Give structures of (*A*) to (*C*) with proper reasoning and draw Fischer projections for (*A*). Give reactions for the steps wherever possible. **(Roorkee 1999)**

236. An organic compound (*A*), C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound (*B*), which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (*B*), when treated with iodine in aqueous KOH, yields (*C*) and a yellow compound (*D*). Identify (*A*), (*B*), (*C*) and (*D*) with justification. Show how (*B*) is formed from (*A*)?

(IIT 1994)

237. The aqueous solution of a nitrogen and chlorine containing organic compound (*A*) is acidic to litmus. (*A*) on treatment with aqueous NaOH gives a compound (*B*) containing nitrogen, but not chlorine. Compound (*B*) on treatment with $C_6H_5SO_2Cl$ in the presence of NaOH gives an insoluble product (*C*), $C_{13}H_{13}NO_2S$. Give structures of (*A*) and (*B*).

(Roorkee 2000)

238. An aldehyde (*A*) ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two mole of (*B*) on ozonolysis. Compound (*B*), on oxidation with silver ion, gives oxalic acid. Identify the compounds (*A*) and (*B*).

(IIT 1998)

239. An organic compound (*A*), $C_{18}H_{20}O$ on ozonolysis gives (*B*), $C_{10}H_{12}O$ and (*C*), $C_8H_8O_2$. Compound (*B*) gives iodoform reaction and produces an oxime (*D*), $C_{10}H_{13}ON$ on treatment with NH_2OH. Compound (*D*) reacts with PCl_5 in dry ether to give (*E*) which on hydrolysis gives (*F*), $C_8H_{11}N$ and acetic acid. (*F*) on treatment with HNO_2 followed by oxidation gives phthalic acid. Compound (*C*) on mild oxidation gives (*G*) which gives effervescence with $NaHCO_3$. (*G*) on treatment with HI produces *p*-hydroxybenzoic acid and CH_3I. Give structures of (*A*) to (*G*) with proper reasoning. **(Roorkee 1998)**

240. An aromatic compound (*A*), C_8H_9Br reacts with $H_2C(COOC_2H_5)_2$ in the presence of C_2H_5ONa to give (*B*). Compound (*B*) on refluxing with dilute H_2SO_4 gives (*C*) which on vigorous oxidation gives (*D*). The compound (*D*) is a dibasic acid but on heating does not give an anhydride. It forms a mononitro derivative (*E*), in which all the substituents are at equidistant from one another. Give structures of (*A*) to (*E*) with proper reasoning.

(Roorkee 1998)

241. A colourless substance (*A*) is sparingly soluble in water and gives (*B*) on heating with mineral acids. Compound (*B*) on reaction with $CHCl_3$ and alcoholic potash produces an obnoxious smell of carbylamine due to the formation of (*C*). Compound (*A*) on reaction with chlorosulphonic acid gives (*D*) which on treatment with ammonia gives (*E*). Compound (*E*) on acid hydrolysis gives sulphanilamide, a well known drug. Give structures of (*A*) to (*E*) with proper reasoning.

(Roorkee 1998)

242. An organic acid (*A*) on heating with $AlPO_4$ at 700°C forms (*B*). Compound (*B*) also reacts with (*A*) to give (*C*). Compound (*C*) on reaction with 1,3,5-trimethyl benzene in presence of $AlCl_3$ gives a ketone (*D*) and CH_3COOH. (*D*) on treatment with Na(Hg)/HCl gives an aromatic hydrocarbon (*E*).

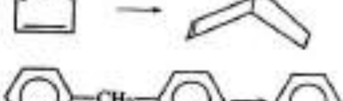
Give structures of (*A*) to (*E*) with proper reasoning.

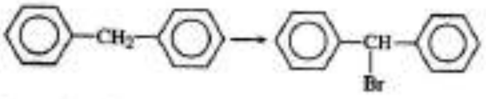
(Roorkee 1998)

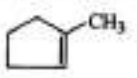
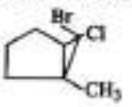
243. Five isomeric para-disubstituted aromatic compounds (*A*) to (*E*) with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds :
   (i) Both (*A*) and (*B*) form a silver mirror with Tollens reagent; also, (*B*) gives a positive test with $FeCl_3$ solution.
   (ii) (*C*) gives positive iodoform test.
   (iii) (*D*) is readily extracted in aqueous $NaHCO_3$ solution.
   (iv) (*E*) on acid hydrolysis gives 1,4-dihydroxybenzene.
   (IIT 2002)

244. Compound (*A*) of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form (*B*). On oxidation with $KMnO_4$, (*A*) gives *m*-chlorobenzoic acid. Identify (*A*) and (*B*). **(IIT 2003)**

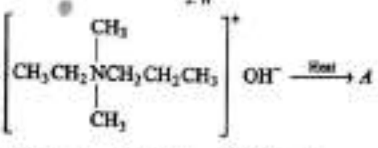
245. Bring about following one step transformations :

(i) 

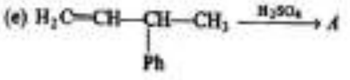
(ii) 

246. Convert the following :
   (a) 2-chlorobutanoic acid into 3-chlorobutanoic acid
   (b) $(CH_3)_3CH$ to $(CH_3)_3CD$ (in two steps)
   (c)  into 

   (d) Isobutylene to 2,2,4-trimethyl pentane
   (e) Convert $RCH{=}CH_2$ to RCH_2CH_2CHO
   (f) Acetone into ketene
   (g) Acetic acid into ketene

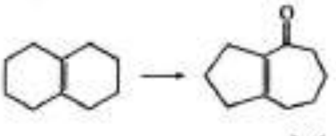
247. Give the products formed in the following reactions :
   (a) 1,1,2-cyclohexane tricarboxylic acid $\xrightarrow{\Delta}$
   (b) Phthalic acid + $NH_3 \longrightarrow D \xrightarrow{300°C} E$
   (c) $H_2C{=}CHCH_2CN \xrightarrow[2.\ H^+]{1.\ PhMgBr} A$
   (d) 

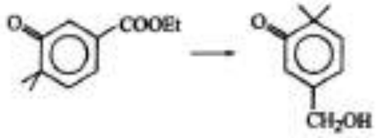
$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CH_2\overset{}{N}CH_2CH_2CH_3 \\ | \\ CH_3 \end{array}\right]^+ OH^- \xrightarrow{Heat} A$$

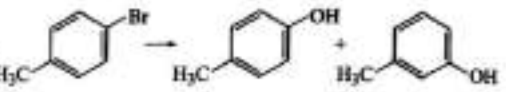
   (e) 

$$H_2C{=}CH{-}\underset{\underset{Ph}{|}}{CH}{-}CH_3 \xrightarrow{H_2SO_4} A$$

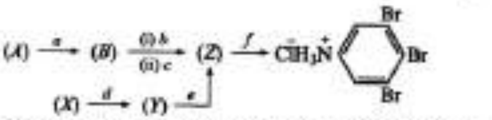
248. Suggest how following transformations will be brought in (may require more than one step) :

(a) 

(b) 

(c) 

249. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. **(IIT 2001)**

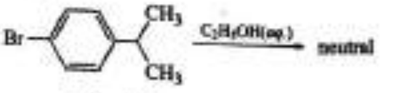
250. 

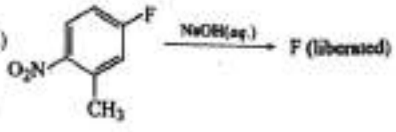
Give structures of (*A*), (*B*), (*X*), (*Y*) and (*Z*) in the above scheme of reactions, if reagents *a*, *b*, *c*, *d*, *e* and *f* are Br_2/CH_3COOH, $NaNO_2/H_2SO_4$, CuBr, HNO_3/H_2SO_4, Br_2/Fe and Sn/HCl respectively. **(Roorkee 2001)**

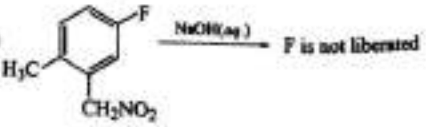
251. There is a solution of *p*-hydroxy benzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them. Also write the confirmatory tests of functional groups. **(IIT 2003)**

252. Give reasons :

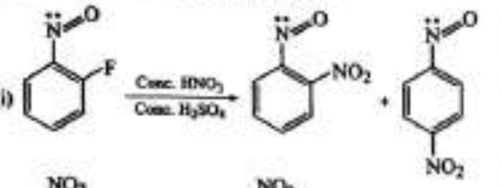
(a) (i) 

(ii) 

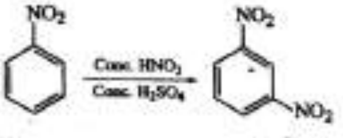
(b) (i) 

(ii) 

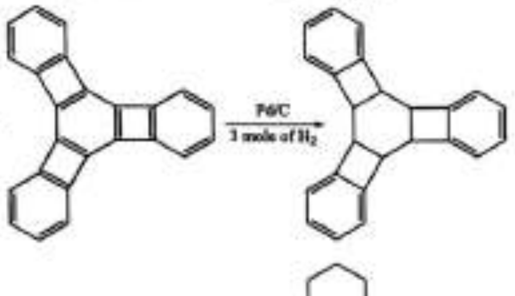
(c) (i)



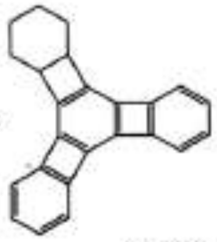
(ii)



(d)

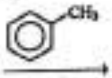


is formed but not



(IIT 2005)

253. $\left(\begin{array}{c}\text{Brown fumes and}\\ \text{pungent smell}\end{array}\right) B \xleftarrow{NaBr+MnO_2} A \xrightarrow{Conc.\ HNO_3}$



C (Intermediate) $\longrightarrow$ D (Explosive product)

Find A, B, C and D. Also write equations A to B and A to C.

(IIT 2005)

254. If $\mu_{obs} = \Sigma \mu_i x_i$, where μ_i is the dipole moment of stable conformer and x_i is the mole fraction of that conformer.

(a) Write stable conformer for $Z—CH_2—CH_2—Z$ in Newman's projection. If $\mu_{solution} = 1.0$ D and mole fraction of anti form = 0.82, find μ_{Gauche}.

(b) Write most stable meso conformer of $\begin{array}{c}CHDY\\ |\\ CHDY\end{array}$

If (i) $Y = CH_3$ about $C_2—C_3$ rotation and (ii) $Y = OH$ about $C_1—C_2$ rotation. (IIT 2005)

255. What are the relative powers of overlapping of sp, sp^2 and sp^3 with respect to s-orbitals?

256. Write various canonical forms of $CH_2=CH—CHO$ and predict their order of stability.

257. Arrange the following carbocations in order of their stability with explanations.

$(CH_3)_3C^+$, $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$

258. Why is triphenylmethyl cation is highly stable?

259. Cyanide ion is an ambident nucleophile. From which end it acts as stronger nucleophile in aqueous medium.

260. Although phenoxide ion has more number of canonical forms than carboxylate ion but carboxylic acids are stronger than phenol.

261. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethyl cyclohexanone does not. Why?

262. There are two $—NH_2$ groups in semicarbazide. However, only one NH_2 gp directly attached to $\rangle CO$ gp is not involved in the formation of semicarbazones. Why?

263. A tetrapeptide has $—COOH$ group on alanine. This produces glycine (Gly), Valine (Val), Phenyl Alanine (Phe) and Alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with $—NH_2$ group attached to a chiral center is :

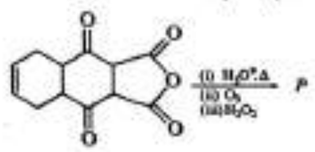
[JEE (Advanced) I 2013]

264. The total number of lone-pairs of electrons in melamine is :

[JEE (Advanced) I 2013]

265. The total number of carboxylic acid groups in the product P is:

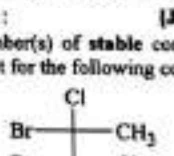
[JEE (Advanced) I 2013]



266. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in $[Co(EDTA)]^{1-}$ complex ion is :

[JEE (Advanced) I 2013]

267. The total number(s) of **stable** conformers with non-zero dipole moment for the following compound is/are :



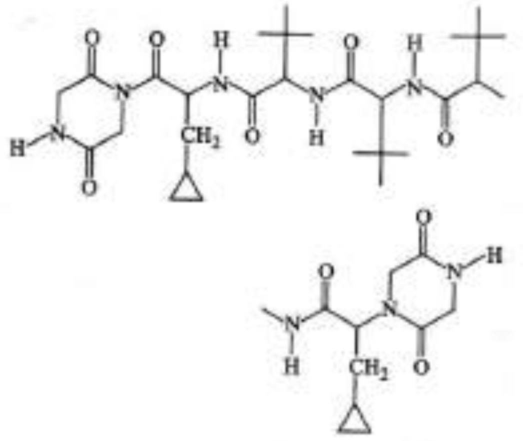
[JEE (Advanced) I 2014]

268. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$.

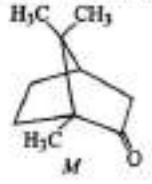
[JEE (Advanced) I 2014]

269. The total number of *distinct naturally occurring amino acids* obtained by complete acidic hydrolysis of the peptide shown ahead is :

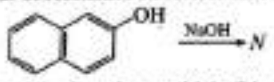
[JEE (Advanced) I 2014]



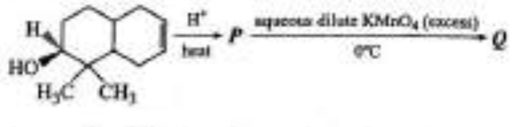
270. The total number of stereoisomers that can exist for M is :



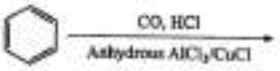
271. The number of resonance structures for N is :

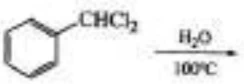


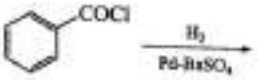
272. The number of hydroxyl group(s) in Q is :

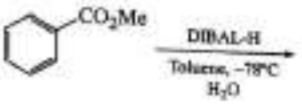


273. Among the following the number of reaction(s) that produce(s) benzaldehyde is :

(I)


(II)


(III)


(IV)


SOLUTIONS (Numerical Problems)

1. **Chiral :** An object which is non-superimposable on its mirror image is said to be chiral, *e.g.*,
Screw, scissor, spool of thread, glove, shoe, sock, helix, double helix, tennis racket, hand, foot, ear, rifle, letters (P, J, F).

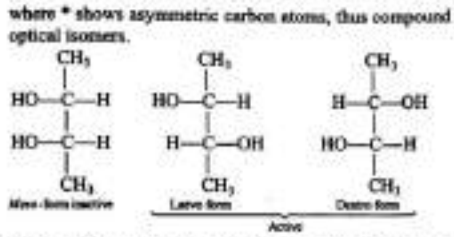
Achiral : An object which is superimposable on their mirror image, *e.g.*, empty spool of thread and rest all not included in chiral examples.

2. (a) 2,3-Dihydroxybutane

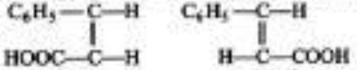
Note : This name is wrong. It should be butan-2,3-diol.

$$CH_3 \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot CH_3$$

where * shows asymmetric carbon atoms, thus compound has optical isomers.



(b) 3-Phenyl-2-propenoic acid has two geometrical isomers.



3. (a) When the molecule cannot be divided into two equal parts, *i.e.*, has no symmetry and n is the number of asymmetric carbon atoms, then

No. of optically active isomers, $a = 2^n$

Number of *meso* forms, $m = 0$

Total no. of racemic forms, $r = a/2$

Total no. of optical isomers $= a + m$

e.g., $CH_3 \cdot \overset{*}{C}HOH\,\overset{*}{C}HOH \cdot COOH$

* represents asymmetric carbon atoms, *i.e.*, $n = 2$

$\therefore$ $a = 2^2 = 4$
$m = 0$
$r = 0$

Total optical isomers $= 4 + 0 = 4$

(b) When the molecule can be divided into two equal halves (*i.e.*, has symmetry) number of asymmetric carbon atoms is even, then

Number of optically active isomers, $a = 2^{n-1}$

Number of *meso* forms, $m = 2^{(n/2)-1}$

Number of racemic forms, $r = a/2$

Total number of optical isomers $= a + m$

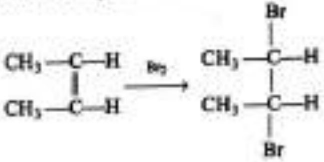
e.g., $COOH \cdot \overset{*}{C}HOH \cdot \overset{*}{C}HOH \cdot COOH$

* represents asymmetric carbon atoms, *i.e.*, $n = 2$

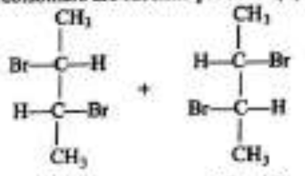
$\therefore$ $a = 2^{2-1} = 2$
$m = 2^{1-1} = 2^0 = 1$
$r = 1$

Total optical isomers $= 2 + 1 = 3$

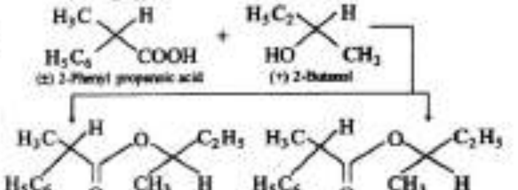
4. Addition of Br_2 is anti addition.



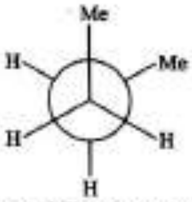
The stereoisomers are racemic products (d, l)



5.

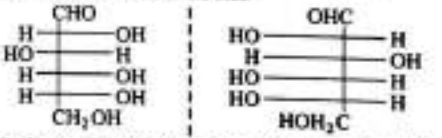


6. n-butane is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$. The staggered form of butane is :

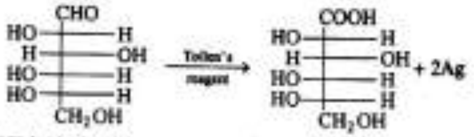


The relative lower stability of staggered form of n-butane is due to van der Waals' repulsion between the methyl groups.

7. (a) L-(–) glucose is an enantiomer, *i.e.*, mirror image of D-(+) glucose. Also, D-form has hydroxyl group next to bottom carbon atom to the left.

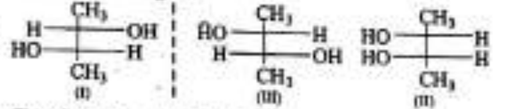


(b) L-(–) glucose is reducing agent and reduces Tollen's reagent to metallic silver, it self being oxidised to L-(–) gluconic acid.



8. In (*B*) both the rings are present in acetal form and thus, it will not hydrolyse in solution and thus, will not reduce Tollen's reagent. In (*A*) one ring is present in hemiacetal form and thus, it will hydrolyse and will give positive test with Tollen's reagent.

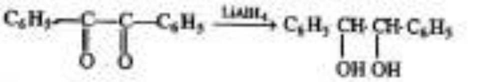
9.



(I) and (III) are enantiomers.

(I) and (II); (II) and (III) are diastereomers.

10.



$$C_6H_5-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-C_6H_5 \xrightarrow{LiAlH_4} C_6H_5\,\underset{OH}{\underset{|}{CH}}\text{-}\underset{OH}{\underset{|}{CH}}\text{-}C_6H_5$$

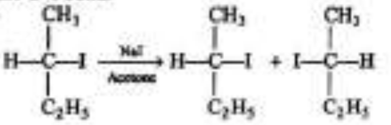
The molecule after reduction possesses two asymmetric carbon with symmetry in molecule

Thus, $a = 2^{n-1} = 2^{2-1} = 2$

$m = 2^{n/2-1} = 2^0 = 1$

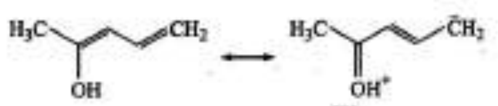
$\therefore$ No. of stereoisomers = 2 + 1 = 3.

11. The C–I bond is broken and reformed to give racemic mixture of 2-iodobutane and thus remains optically inactive. The presence of I^- provides opportunities for the remaking of the C–I bond.

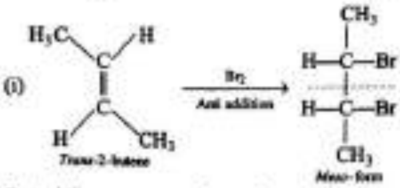


$$H-\overset{CH_3}{\underset{C_2H_5}{C}}-I \xrightarrow[\text{Acetone}]{NaI} H-\overset{CH_3}{\underset{C_2H_5}{C}}-I + I-\overset{CH_3}{\underset{C_2H_5}{C}}-H$$

12.

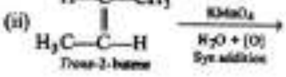


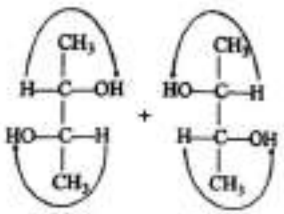
13. (i)



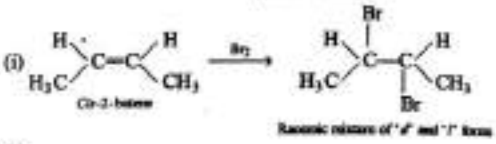
Dotted line represents plane of symmetry.

(ii)

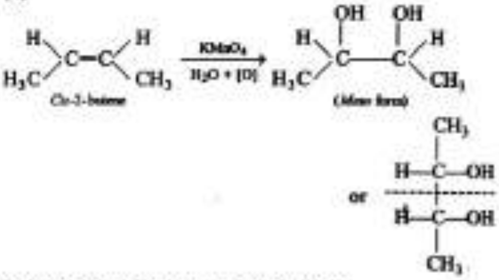




14. (i)



(ii)

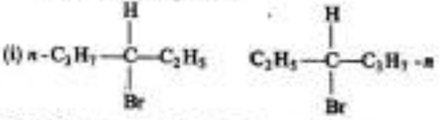


15. (a) (i) *R*, (ii) *R*, (iii) *S*, (iv) *R*, (v) *S*, (vi) *S*.

(b) *R*-(rectus or right) configuration

S-(sinister) configuration.

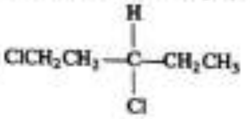
(i)



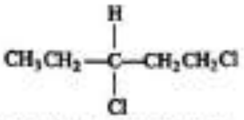
$$n\text{-}C_3H_7-\overset{H}{\underset{Br}{C}}-C_2H_5 \qquad C_2H_5-\overset{H}{\underset{Br}{C}}-C_3H_7\text{-}n$$

Precedence order : $Br > C_3H_7 > C_2H_5 > H$

(ii)



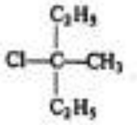
$$ClCH_2CH_2-\overset{H}{\underset{Cl}{C}}-CH_2CH_3$$



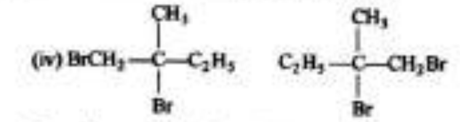
$$CH_3CH_2-\overset{H}{\underset{Cl}{C}}-CH_2CH_2Cl$$

Precedence order : $Cl > CH_2CH_2Cl > CH_2CH_3 > H$

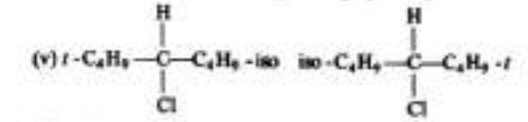
(iii) It is an achiral molecule and does not have optical isomers.



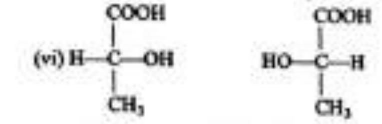
$$Cl-\overset{C_2H_5}{\underset{C_2H_5}{C}}-CH_3$$



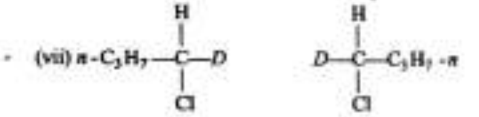
Precedence order : Br > CH_2Br > C_2H_5 > CH_3



Precedence order : Cl > t-C_4H_9 > iso-C_4H_9 > H

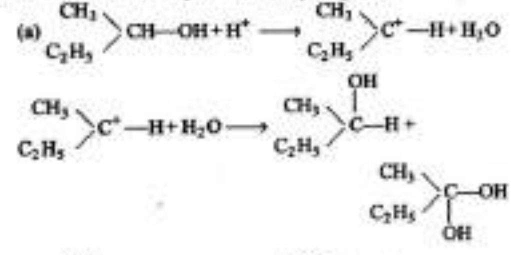


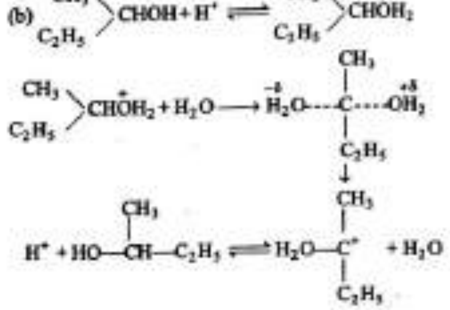
Precedence order : OH > COOH > CH_3 > H



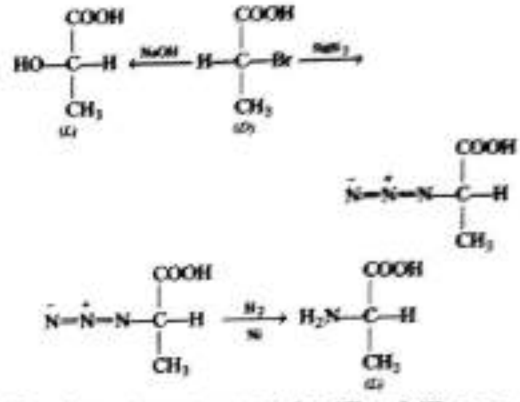
Precedence order : Cl > C_3H_7 > D > H

16. Either of the two explanations may be given.

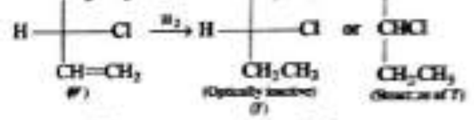


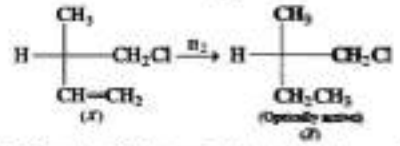


17. Catalytic hydrogenation is S_N2 . S_N2 reactions are accompanied with 100% inversion.



18. The given statements suggest that (*W*) and (*X*) are as follows:





19. (1) (*A*) reacts with Na to give H_2 and thus it contains —OH gp.

(2) Molar mass of (*A*) ($C_4H_{10}O_2$) = 90 g mol^{-1}

If one OH gp. then,

90 g (*A*) with Na gives 11200 mL H_2 (*i.e.*, half mole H_2)

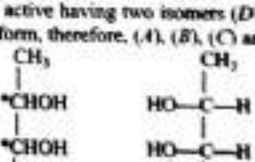
$\therefore$ 0.90 " " " $= \frac{11200 \times 0.90}{90}$ mL H_2 at NTP

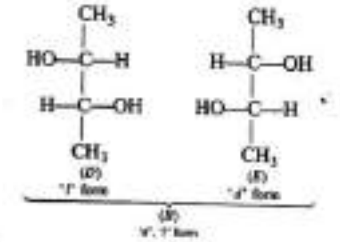
$= 112$ mL H_2 at NTP

Since, 0.90 g (*A*) gives 224 mL H_2 at NTP and thus, it contains two —OH gps.

(3) Keeping in view of above facts (*A*) is $C_4H_8\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$

(4) (*A*) Shows optical isomerism of which (*B*) form is optically active having two isomers (*D*) and (*E*); (*C*) being inactive form, therefore, (*A*), (*B*), (*C*) and (*D*) are



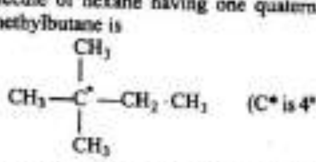


*represents two asymmetric (C) atoms.

20. Heptane is C_7H_{16}.

Homologues of heptane are C_6H_{14} and C_8H_{18}

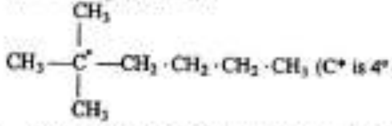
(1) Molecule of hexane having one quaternary C-atom : 2,2-Dimethylbutane is



$$CH_3-\underset{CH_3}{\overset{CH_3}{C^*}}-CH_2\cdot CH_3$$

(C* is 4° carbon atom)

Molecule of octane having one quaternary C-atom : 2,2-Dimethylhexane is

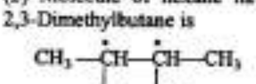


$$CH_3-\underset{CH_3}{\overset{CH_3}{C^*}}-CH_2\cdot CH_2\cdot CH_2\cdot CH_3$$

(C* is 4° carbon atom)

Note : Other structures with one quaternary may also be formed with octane.

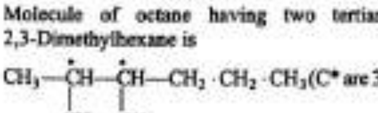
(2) Molecule of hexane having two tertiary C-atoms : 2,3-Dimethylbutane is



$$CH_3-\underset{CH_3}{\dot{C}H}-\underset{CH_3}{\dot{C}H}-CH_3$$

(C* are 3° carbon atom)

Molecule of octane having two tertiary C-atoms : 2,3-Dimethylhexane is



$$CH_3-\underset{CH_3}{\dot{C}H}-\underset{CH_3}{\dot{C}H}-CH_2\cdot CH_2\cdot CH_3$$

(C* are 3° carbon atom)

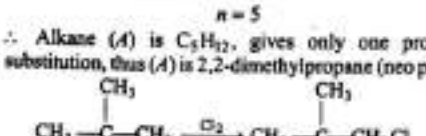
21. $$V.D. = 36$$

$\therefore$ Molar mass $= 2 \times 36 = 72\ g\ mol^{-1}$

An examination of molar mass suggests it to be alkane, *i.e.*, C_nH_{2n+2}.

$$12n + 2n + 2 = 72$$
$$n = 5$$

$\therefore$ Alkane (*A*) is C_5H_{12}, gives only one product on substitution, thus (*A*) is 2,2-dimethylpropane (neo pentane).

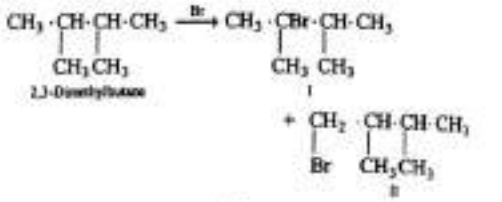


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{Cl_2} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Cl$$

22. Alkane is C_nH_{2n+2}; Molar mass = 86 g mol^{-1}

$\therefore \quad 12n + 2n + 2 = 86 \quad \therefore n = 6$

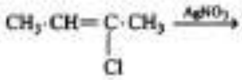
$\therefore$ Alkane is C_6H_{14} which on bromination giving two products as :



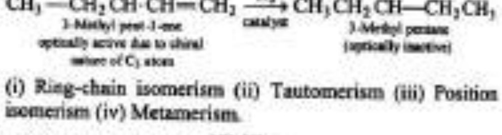
$$CH_3\cdot\underset{CH_3}{CH}\cdot\underset{CH_3}{CH}\cdot CH_3 \xrightarrow{Br} CH_3\cdot\underset{CH_3}{CBr}\cdot\underset{CH_3}{CH}\cdot CH_3 + \underset{Br}{CH_2}\cdot\underset{CH_3}{CH}\cdot\underset{CH_3}{CH}\cdot CH_3$$

23. 

$CH_3\cdot CH=CH-\underset{Cl}{CH_2} \xrightarrow{AgNO_3}$ White ppt; allylic chlorine



$CH_3\cdot CH=\underset{Cl}{C}\cdot CH_3 \xrightarrow{AgNO_3}$ No reaction ; vinylic chlorine

24. 

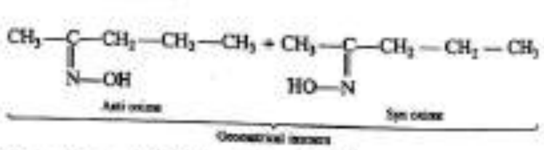
$$CH_3-CH_2\overset{CH_3}{CH}\cdot CH=CH_2 \xrightarrow[catalyst]{H_2} CH_3CH_2\overset{CH_3}{CH}-CH_2CH_3$$

3-Methyl pent-1-ene optically active due to chiral nature of C_3 atom

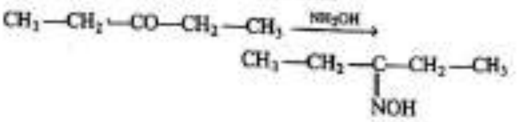
3-Methyl pentane (optically inactive)

25. (i) Ring-chain isomerism (ii) Tautomerism (iii) Position isomerism (iv) Metamerism.

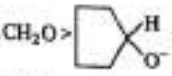
26. $\underset{\text{Pentan-2-one}}{CH_3COCH_2CH_2CH_3} \xrightarrow{NH_2OH}$



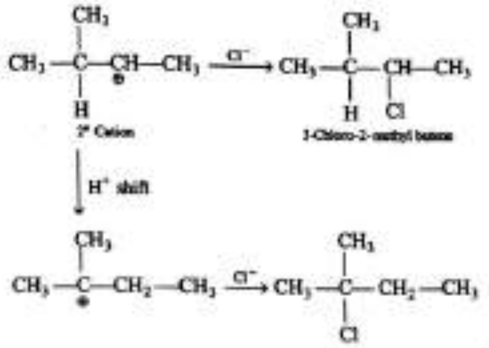
$$CH_3-\underset{\underset{N-OH}{\|}}{C}-CH_2-CH_2-CH_3 + CH_3-\underset{\underset{HO-N}{\|}}{C}-CH_2-CH_2-CH_3$$



$$CH_3-CH_2-CO-CH_2-CH_3 \xrightarrow{NH_2OH} CH_3-CH_2-\underset{NOH}{\underset{\|}{C}}-CH_2-CH_3$$

27. $MeO^- > Me_2CH_2O >$  $> Me_2CHO^- > Me_3CO^-$

As *R*'s accumulate on the carbon bonded to O^-, the nucleophile becomes bulkier and its backseat approach to the displacement site is retarded causing a decline in rate. Although (I) is an R_2CHO^- alkoxide, its *R*'s are 'tied back' away from the O^-. This arrangement permits a more facile approach than by Me_2CHO^-. The S_N2 reactivity is susceptible to steric hindrance by the nucleophile as well as by the *R*'s around the site of displacement.

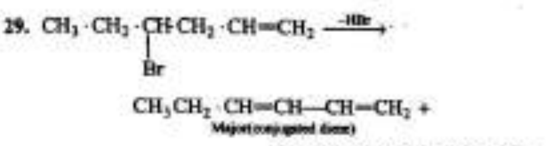
28.


$$CH_3-\overset{CH_3}{\underset{H}{C}}-\underset{\oplus}{CH}-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{H}{C}}-\underset{Cl}{CH}-CH_3$$

2° Cation 3-Chloro-2-methyl butane

H⁺ shift

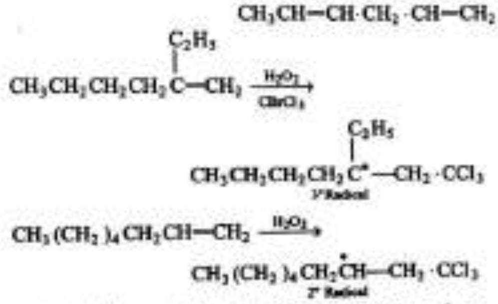
$$CH_3-\overset{CH_3}{\underset{\oplus}{C}}-CH_2-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2-CH_3$$

29.


$$CH_3\cdot CH_2\cdot \underset{Br}{CH}\cdot CH_2\cdot CH{=}CH_2 \xrightarrow{-HBr}$$

$$\underset{\text{Major(conjugated diene)}}{CH_3CH_2\cdot CH{=}CH-CH{=}CH_2} +$$

$$CH_3CH{=}CH\cdot CH_2\cdot CH{=}CH_2$$

30.


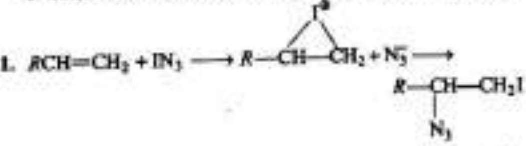
$$CH_3CH_2CH_2CH_2\overset{C_2H_5}{C}{=}CH_2 \xrightarrow[CBrCl_3]{H_2O_2}$$

$$CH_3CH_2CH_2CH_2\overset{C_2H_5}{\underset{3°\ \text{Radical}}{\dot{C}}}-CH_2\cdot CCl_3$$

$$CH_3(CH_2)_4CH_2CH{=}CH_2 \xrightarrow{H_2O_2}$$

$$CH_3(CH_2)_4CH_2\underset{2°\ \text{Radical}}{\dot{C}H}-CH_2\cdot CCl_3$$

3° Radical is more stable than 2° radical and forms faster.

31.


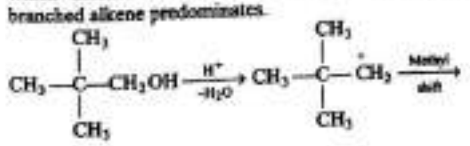
$$RCH{=}CH_2 + IN_3 \longrightarrow R-CH-CH_2 \text{ (with } I^{\oplus}\text{ bridge)} + N_3^- \longrightarrow R-\underset{N_3}{CH}-CH_2I$$

This is heterolytic addition *via* a cyclic iodonium ion and is analogous to the addition of X_2 and HOX and takes place with the same orientation.

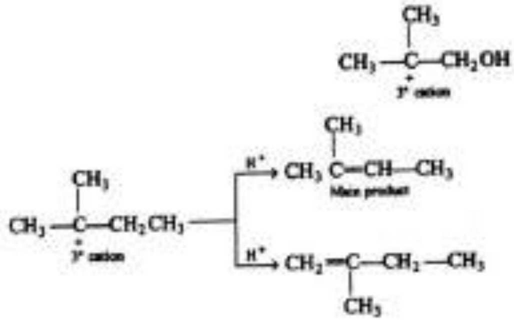
32. $CH_2{=}CH-CH{=}CH_2 \xrightarrow{HCl} \underset{1,2\text{-Addition}}{CH_3-CHCl\cdot CH{=}CH_2}$

$$\underset{1,4\text{-Addition}}{CH_3-CH{=}CH-CH_2Cl}$$

33. The first step is the formation of 1° carbocation. This rearranges by methyl shift to the more stable 3° cation, from which alkenes are formed. As usual the more highly branched alkene predominates.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH \xrightarrow[-H_2O]{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H_2 \xrightarrow[\text{shift}]{\text{Methyl}}$$



$$\underset{3°\ \text{cation}}{CH_3-\overset{CH_3}{\overset{+}{C}}-CH_2OH}$$

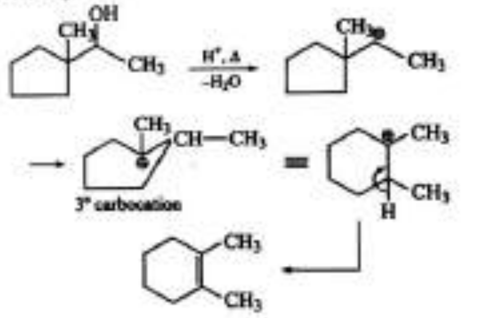
$$\underset{3°\ \text{cation}}{CH_3-\overset{CH_3}{\overset{+}{C}}-CH_2CH_3} \xrightarrow{H^+} \underset{\text{Main product}}{CH_3\overset{CH_3}{C}{=}CH-CH_3}$$

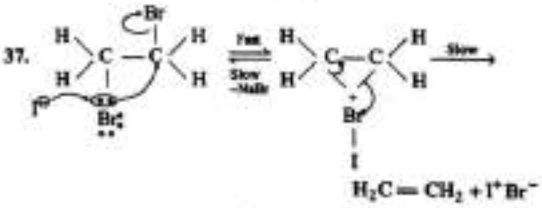
$$\xrightarrow{H^+} CH_2{=}\underset{CH_3}{C}-CH_2-CH_3$$

34. $H_3\overset{+}{O}$; HBr ; Stronger acid dry HBr; In aqueous solution, HBr reacts to yield weaker acid $H_3\overset{+}{O}$; Electrophilic addition is more easier in HBr dry.

35. (i) Allylic bromination (ii) α-elimination
(iii) Rearrangement (iv) γ-elimination.

36. Rearrangement of carbocation leads to a change in the size of the ring.



37.


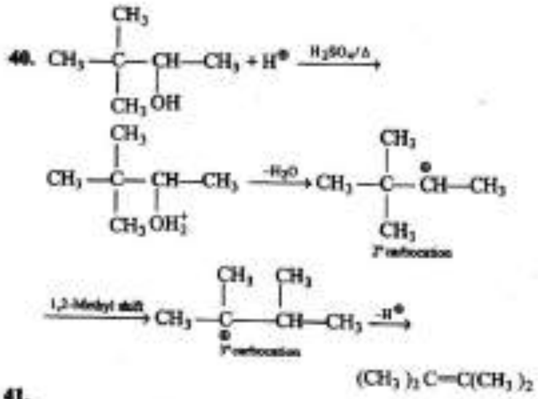
$$H_2C{=}CH_2 + I^+Br^-$$

38. $BrCH_2C{\equiv}C\cdot CH_2Br \xrightarrow[\Delta]{Zn} \underset{\text{Butatriene}}{CH_2{=}C{=}C{=}CH_2} \xrightarrow[H_2O/Zn]{O_3}$

$$2HCHO + 2CO_2$$

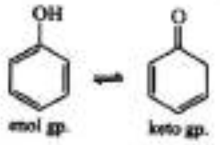
39.


40.



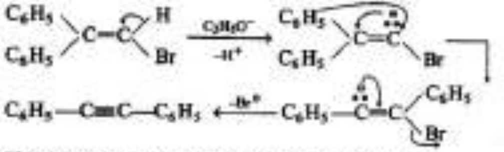
$(CH_3)_2C=C(CH_3)_2$

41.



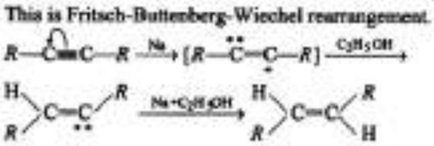
(unstable because it loses aromatic character)

42.

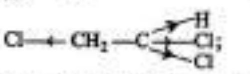


This is Fritsch-Buttenberg-Wiechel rearrangement.

43.



44.



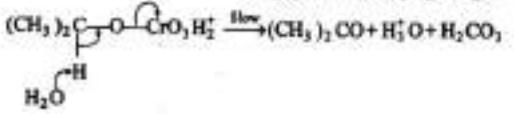
the $-IE$ of two Cl-atoms is greater than that of one. Consequently, the proton of $CHCl_3$ is removed more easily by OH^-, than a proton of CH_2Cl. Thus, the E^2 mechanism.

$$\bar{H}O + H-CCl_2-CH_2-Cl \longrightarrow CCl_2=CH_2$$

45.

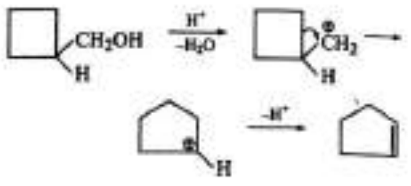
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons HCrO_4^-$$

$$(CH_3)_2CHOH + HCrO_4^- + 2H^+ \rightleftharpoons (CH_3)_2CH\cdot O\cdot CrO_3H_2^+ + H_2O$$

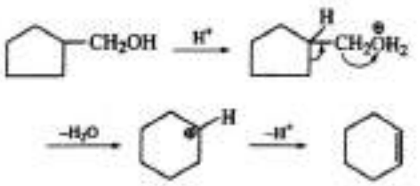


$$(CH_3)_2C-O-CrO_3H_2^+ \xrightarrow{Slow} (CH_3)_2CO + H_3^+O + H_2CO_3$$

46.



47.



48. (a) $Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet$ Chain initiation

$$\left.\begin{array}{l} Cl^\bullet + RH \longrightarrow R^\bullet + HCl \\ R^\bullet + SO_2 \longrightarrow RSO_2^\bullet \\ RSO_2^\bullet + Cl_2 \longrightarrow RSO_2Cl + Cl^\bullet \end{array}\right\} \text{Chain propagation}$$

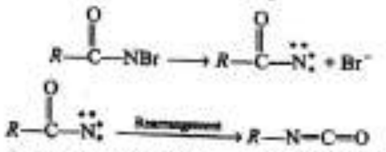
This is Reed reaction having free radical chain mechanism.

(b) $Br_2 + 2NaOH \longrightarrow NaBr + \overset{+}{Na}BrO^- + H_2O$

This is Hoffmann's bromamide reaction.

$$RCONH_2 \xrightarrow[NaOH]{BrO^-} \underset{N\text{-bromoethanamide}}{RCONHBr} + NaBr + H_2O$$

$$RCONHBr \xrightarrow{OH^-} RCONBr + H_2O$$

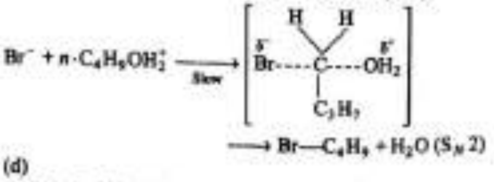


$$R-\overset{O}{\overset{\|}{C}}-NBr \longrightarrow R-\overset{O}{\overset{\|}{C}}-\ddot{N}: + Br^-$$

$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}: \xrightarrow{\text{Rearrangement}} R-N=C=O$$

$$R-N=C=O + 2KOH \longrightarrow RNH_2 + K_2CO_3$$

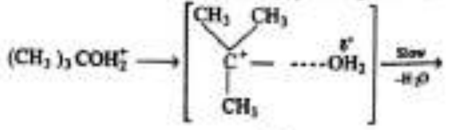
(c) $n\text{-}C_4H_9OH \xrightarrow{HBr} n\text{-}C_4H_9OH_2^+ + Br^-$ (Fast)



$$Br^- + n\text{-}C_4H_9OH_2^+ \xrightarrow[Slow]{} \left[\overset{\delta^-}{Br}\cdots\underset{C_3H_7}{\overset{H\ \ H}{C}}\cdots\overset{\delta^+}{OH_2}\right] \longrightarrow Br-C_4H_9 + H_2O\ (S_N2)$$

(d)

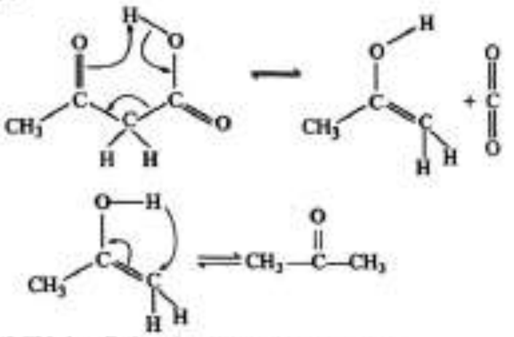
$(CH_3)_3C\cdot OH + HBr \longrightarrow (CH_3)_3C\cdot OH_2^+ + Br^-$ (Fast)



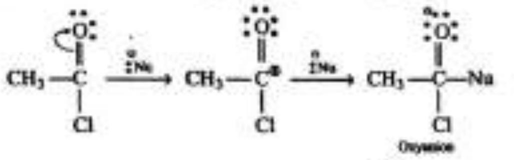
$$(CH_3)_3COH_2^+ \longrightarrow \left[\underset{CH_3}{\overset{CH_3\ \ CH_3}{C^+}}-\ \cdots\overset{\delta^+}{OH_2}\right] \xrightarrow[-H_2O]{Slow}$$

$$(CH_3)_3C^+ \xrightarrow[Fast]{Br^-} (CH_3)_3CBr\ (S_N1)$$

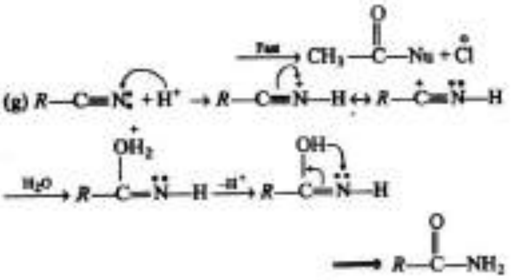
(e)



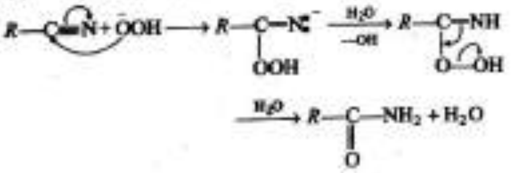
(f) This is called nucleophilic acyl substitution.



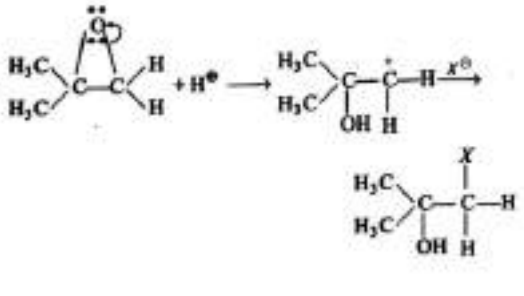
(g)



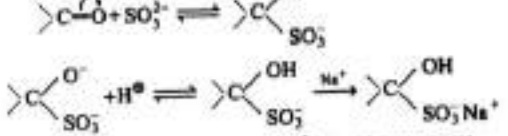
(h) HOOH + OH⁻ ⟶ H₂O + ⁻OOH



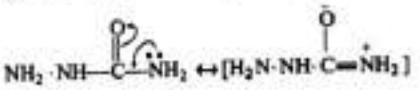
49.



50. $NaHSO_3 \longrightarrow Na^+ + HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

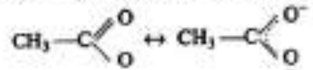


51. $>C{=}O + H_2N{\cdot}NHCONH_2 \longrightarrow >C{=}N{\cdot}NHCONH_2$



resonance stabalization of —C(=O)—NH₂.

52. Acetic acid : CH₃COOH ⇌ CH₃—C(=O)—O⁻ + H⁺



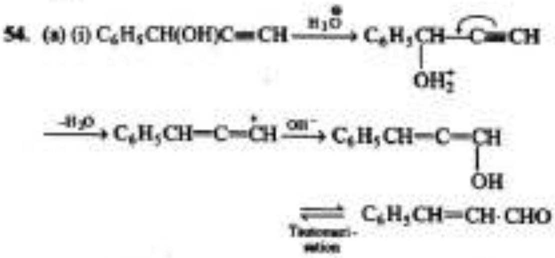
Peroxy acetic acid : $CH_3CO_3H \rightleftharpoons CH_3COOO^- + H^+$;

Negative charge is not delocalised with —C(=O)— gp.

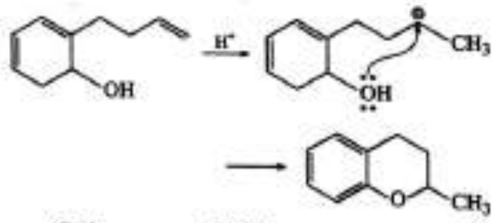
53. $(CH_3)_3C{\cdot}CHOH{\cdot}CH_3 \xrightarrow[\text{(ii) }-H_2O]{\text{(i) }H^+} (CH_3)_3C{\cdot}CH^+{\cdot}CH_3$

$\xrightarrow[\text{shift}]{CH_3^-} (CH_3)_2C^+CH(CH_3)_2 \xrightarrow{-H^+} (CH_3)_2C{=}C(CH_3)_2$

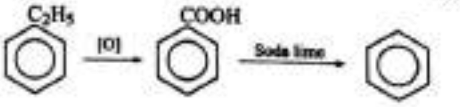
54. (a) (i)



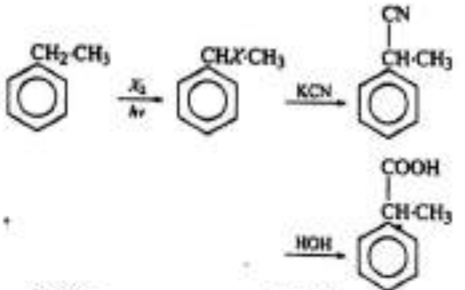
(ii)



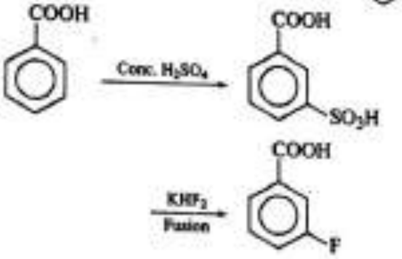
(b) (i)



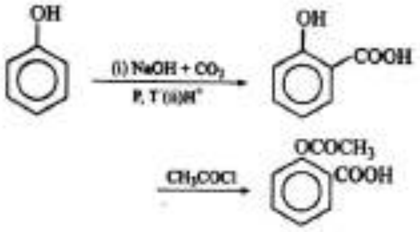
(ii)



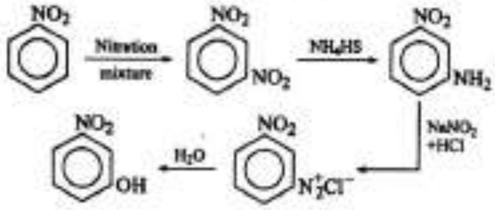
(iii)



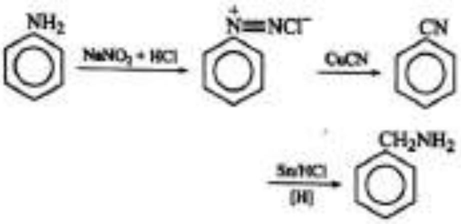
(iv)



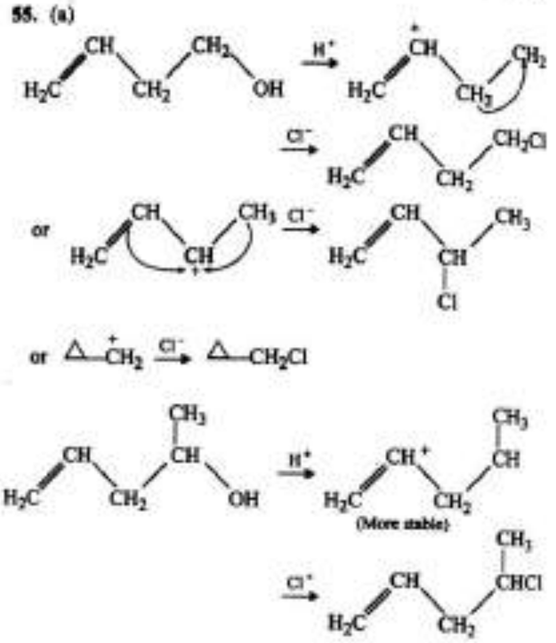
(v)



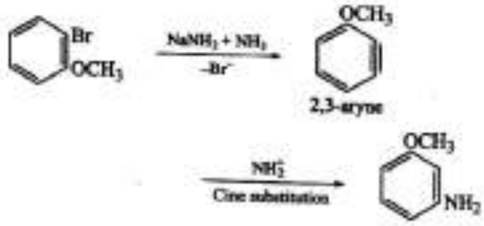
(vi)



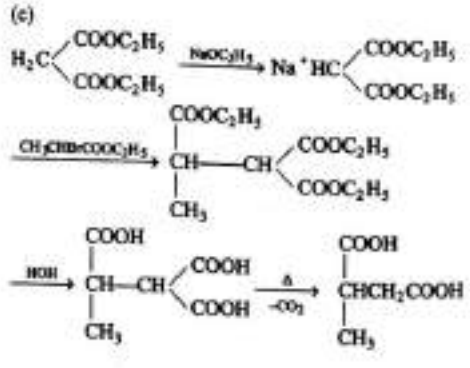
55. (a)



(b)



(c)



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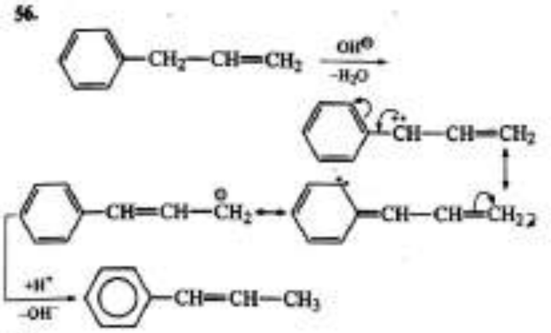

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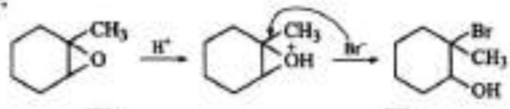
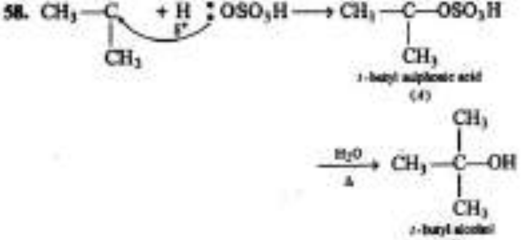
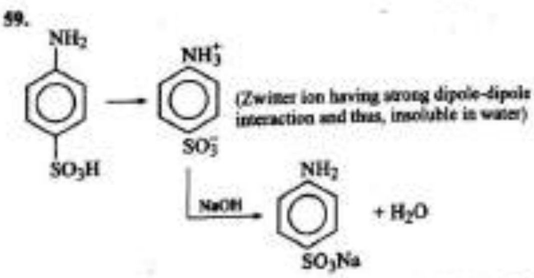


58.



59.

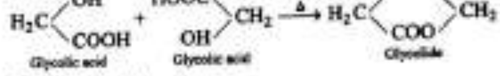


(Zwiter ion having strong dipole-dipole interaction and thus, insoluble in water)

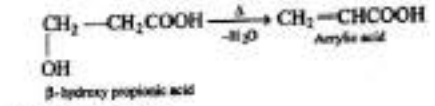
In acid, SO_3^- fails to accept H^+ and thus insoluble in acid whereas in alkalies the strong basic OH^- abstracts a proton from $-NH_3^+$ to make it a water soluble salt.

60. The carbon atoms in $-C\equiv C-$ are *sp*-hybridised and better electron withdrawing group than $>C=C<$ where carbon atoms are sp^2-hybridised. Thus, 3-butynoic acid (pK_a = 3.32) is stronger acid than 3-butenoic acid (pK_a = 4.35).

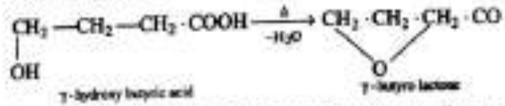
61. **α-hydroxy acid :**



β-hydroxy acids:

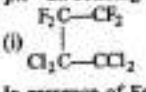


γ-hydroxy acids:



62. $:\!CCl_3^-$ is less basic than $:\!CF_3^-$ because fluorine can disperse charge by inductive effect only while chlorine (having empty 3*d*-orbital) can disperse charge by *–IE* as well as by *p*π – *d*π bonding delocalization.

63. (i)



(ii)

64. In presence of $FeBr_3$, Br_2 produces Br^+ (an electrophile) which attacks the benzene ring at *o*-, *p*-position to give *p*-bromotoluene. In presence of light, side chain is attacked to produce benzyl bromide.

65. (i) *t*-butyl benzene does not contain benzylic hydrogen and thus, this side chain [$-C(CH_3)_3$] cannot be oxidised to $-COOH$ group.

(ii) $CH_2=CH_2$ is less acidic than $CH\equiv CH$ since the latter has *sp*-hybridised carbon atoms which increases the electronegativity of carbon atom and hence acidic character in C—H bond increases. Also, weaker is the acid (C_2H_4), stronger is its conjugate base ($CH_2=CH^-$).

(iii) Benzene has resonance stabilization due to delocalisation of π-electrons. Also, during electrophilic addition reactions, it loses its aromaticity. In electrophilic substitution reactions aromaticity is retained.

(iv) Diethyl ether is Lewis base and anhy. $AlCl_3$ is Lewis acid, thus oxygen atom of diethyl ether readily donates the lone pair to 3*p*-orbital Al-atom of anhydrous $AlCl_3$. In case of hydrated $AlCl_3$, Al-atom is already coordinated by oxygen atom of H_2O. Thus, anhydrous $AlCl_3$ is more soluble in diethyl ether.

66. (a) Wrong; Tollens reagent converts $CH_3CH=CH\cdot CHO$ to $CH_3\cdot CH=CH\cdot COOH$

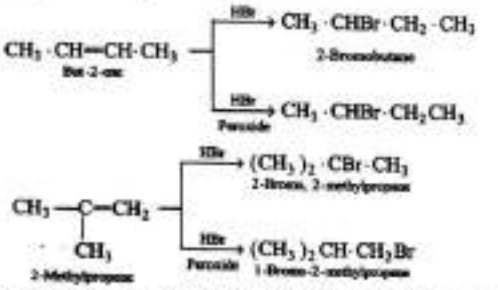
(b) True

(c) Wrong; Desulphonation occurs to give C_6H_6

(d) Wrong ; It not only gives 3-iodo-2,2-dimethyl butane but also 2-iodo-2,3-dimethyl butane or 3-iodo-2,3-dimethyl butane.

67. 7-bromo-1,3,5-cycloheptatriene forms aromatic ion, a stable ion and thus exists in ionic form

5-bromo-1,3-cycloheptatriene forms antiaromatic ion even in presence of Ag^+.

68. 

$$CH_3\cdot CH{=}CH\cdot CH_3 \xrightarrow{HBr} CH_3\cdot CHBr\cdot CH_2\cdot CH_3$$

But-2-ene; 2-Bromobutane

$$CH_3\cdot CH{=}CH\cdot CH_3 \xrightarrow[\text{Peroxide}]{HBr} CH_3\cdot CHBr\cdot CH_2CH_3$$

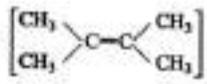
$$CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{HBr} (CH_3)_2\cdot CBr\cdot CH_3$$

2-Methylpropene; 2-Bromo, 2-methylpropane

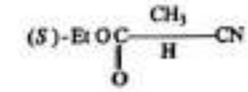
$$CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} (CH_3)_2CH\cdot CH_2Br$$

1-Bromo-2-methylpropane

Note : See only one product is formed in symmetrical alkene, *i.e.*, but-2-ene.

69. 2,3-dimethyl but-2-ene  has no olefinic H-atom and thus it does not decolorise Br_2/CCl_4 as the reaction following free radical addition does not take place. On the other hand reaction of 2,3-dimethyl but-2-ene with Br_2/H_2O involves electrophilic addition and thus Br_2-water is decolorised.

70. These are S_N2 reactions which invert configuration and the product is

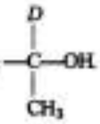


$$(S)\text{-EtO}\underset{\underset{O}{\|}}{C}\overset{CH_3}{\underset{H}{\text{———}}}CN$$

Although inversion occurs, the priority order changes and the product is (R)

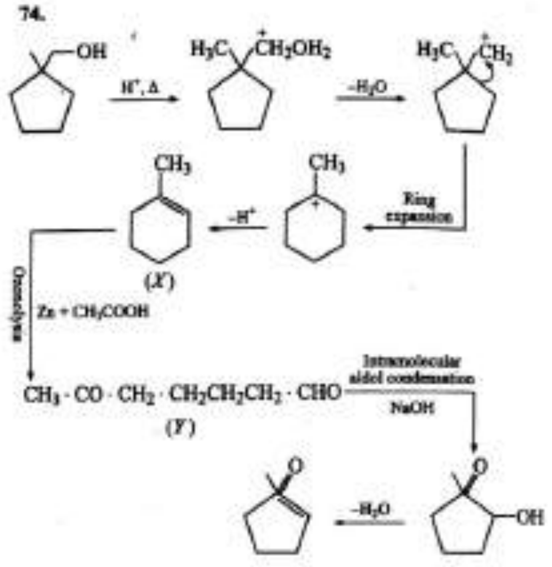
71. $CH_3CH_2CH_2CH_2CHBr_2 \xrightarrow[200°C]{KOH(alc)} CH_3CH_2C{\equiv}CCH_3$

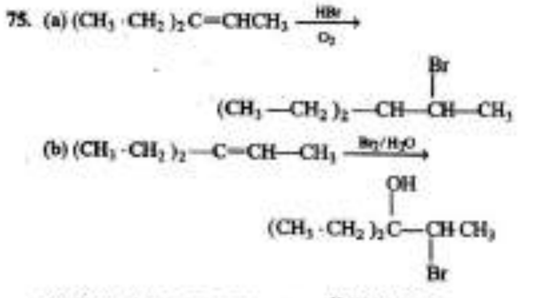
72. $C_6H_5CH_2CH_2OH$

73. (A) and (B) are 

$$C_6H_5{-}\overset{\overset{D}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH$$

74.



75. 

(a) $(CH_3\cdot CH_2)_2C{=}CHCH_3 \xrightarrow[O_2]{HBr}$

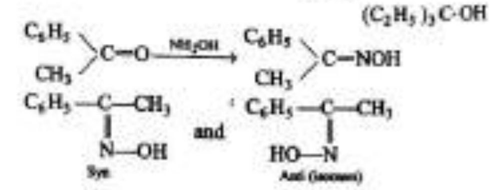
$$(CH_3{-}CH_2)_2{-}CH{-}\overset{\overset{Br}{|}}{CH}{-}CH_3$$

(b) $(CH_3\cdot CH_2)_2{-}C{=}CH{-}CH_3 \xrightarrow{Br_2/H_2O}$

$$(CH_3\cdot CH_2)_2\overset{\overset{OH}{|}}{C}{-}\underset{\underset{Br}{|}}{CH}CH_3$$

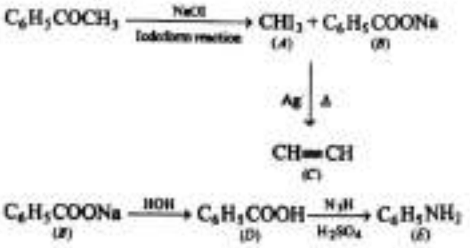
(c) $(CH_3\cdot CH_2)_2C{=}CH{-}CH_3 \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O}$

$$(C_2H_5)_3C\cdot OH$$

76. 

$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!C{=}O \xrightarrow{NH_2OH} \begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!C{=}NOH$$

$$\underset{\text{Syn}}{C_6H_5{-}\underset{\underset{N-OH}{\|}}{C}{-}CH_3} \quad \text{and} \quad \underset{\text{Anti (isomer)}}{C_6H_5{-}\underset{\underset{HO-N}{\|}}{C}{-}CH_3}$$

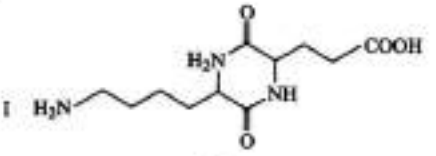
77. 

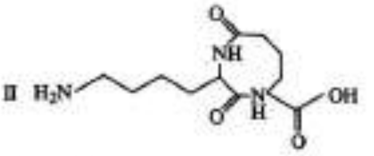
$$C_6H_5COCH_3 \xrightarrow[\text{Iodoform reaction}]{NaOI} \underset{(A)}{CHI_3} + \underset{(B)}{C_6H_5COONa}$$

$$\underset{(A)}{CHI_3} \xrightarrow{Ag\ |\ \Delta} \underset{(C)}{CH{\equiv}CH}$$

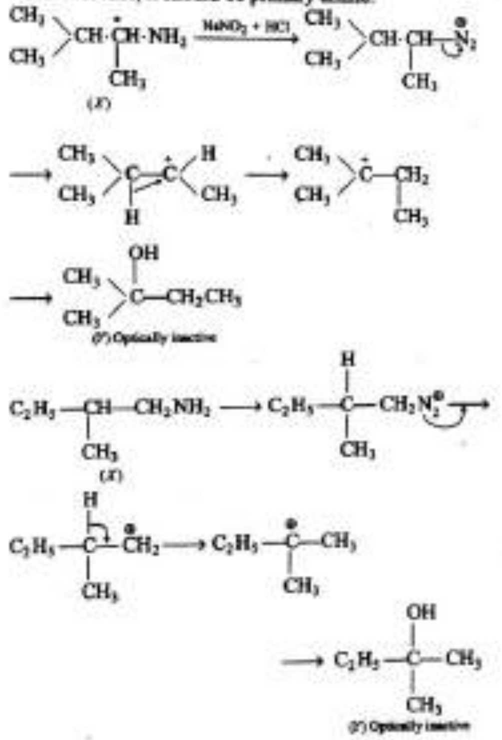
$$\underset{(B)}{C_6H_5COONa} \xrightarrow{HOH} \underset{(D)}{C_6H_5COOH} \xrightarrow[H_2SO_4]{N_3H} \underset{(E)}{C_6H_5NH_2}$$

78.

I 

II 

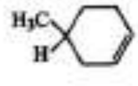
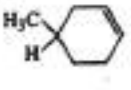
79. (*X*) is optically active and also it gives alcohol with $NaNO_2$ + HCl and thus, it should be primary amine.



80.

(a) 

The two optically active forms are

 and 

(b) (i) Aniline no doubt undergoes Friedel-Crafts reaction. It is nitrobenzene which does not show Friedel-Crafts reaction. Question is wrong. However, the yield is poor because aniline being a base reacts with Lewis acid $AlCl_3$ to give $C_6H_5NH_2 \cdot AlCl_3$ and thus, resists the attack of carbocation. Also, formation of carbocation is hindered since $AlCl_3$ reacts with aniline.

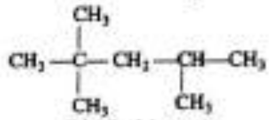
(ii) $C_6H_5NH_2 \xrightarrow{NaNO_2 + 2HCl} C_6H_5N{=}NCl$

The reaction requires HNO_2 + HCl and thus the mineral acid (HCl) is needed in more amount. Also, excess of mineral acid resists the hydrolysis of salt formed.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

Also, excess of HCl prevents coupling of aniline with diazonium salt formed.

(c) $(CH_3)_2C{=}CH_2 + (CH_3)_2CHCH_3 \xrightarrow[\Delta]{HF}$



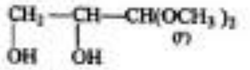
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(2,2,4-dimethyl pentane)

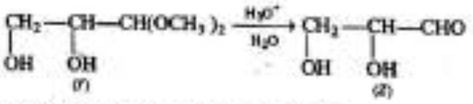
81. $CH_2{=}CH{-}CH_2OH \xrightarrow[CH_2Cl_2]{CrO_3,\ 2C_5H_5N} \underset{(W)}{CH_2{=}CHCHO}$

$\underset{(W)}{CH_2{=}CHCHO} \xrightarrow{CH_3OH,\ H^+} \underset{(X)}{CH_2{=}CH{-}CH(OCH_3)_2}$

$CH_2{=}\underset{(X)}{CH}{-}CH(OCH_3)_2 \xrightarrow[(cold,\ dil.)]{KMnO_4,\ OH^-}$

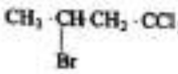


$$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH}-\underset{(Y)}{CH(OCH_3)_2}$$

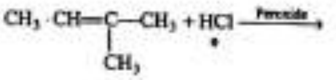


$$\underset{\underset{(Y)}{\underset{OH}{|}}}{CH_2}-\underset{\underset{OH}{|}}{CH}-CH(OCH_3)_2 \xrightarrow[H_2O]{H_3O^+} \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{\underset{(Z)}{OH}}{|}}{CH}-CHO$$

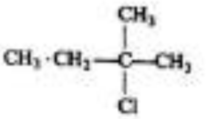
82. (i) $CH_3 \cdot CH{=}CH_2 + Br \cdot CCl_3 \xrightarrow{Peroxide}$



$$CH_3 \cdot \underset{\underset{Br}{|}}{CH}\,CH_2 \cdot CCl_3$$

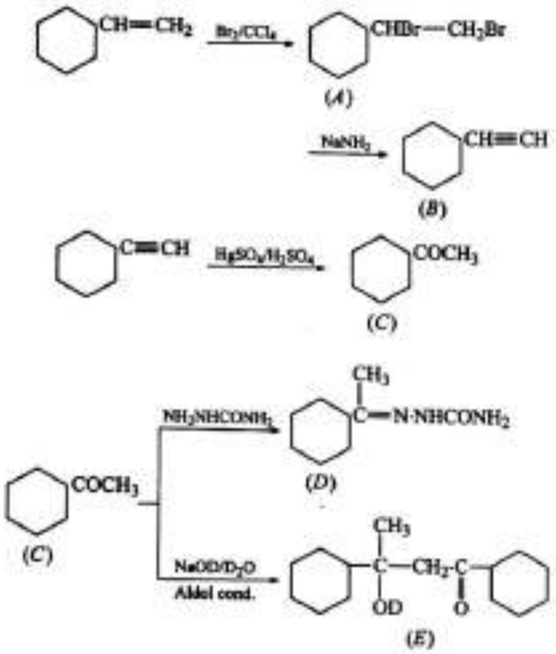
(ii) 

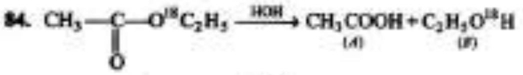
$$CH_3 \cdot CH{=}\underset{\underset{CH_3}{|}}{C}-CH_3 + HCl \xrightarrow{Peroxide}$$



$$CH_3 \cdot CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

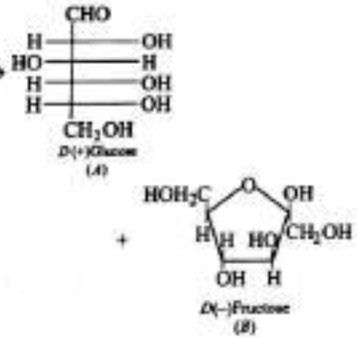
83.



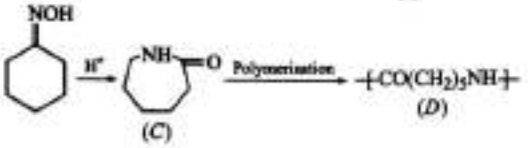


84. $CH_3-\underset{\underset{O}{\|}}{C}-O^{18}C_2H_5 \xrightarrow{HOH} \underset{(A)}{CH_3COOH} + \underset{(B)}{C_2H_5O^{18}H}$

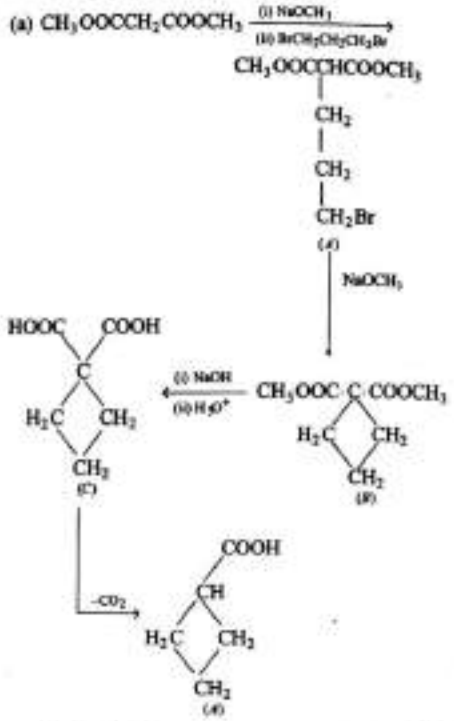
85. (i) Sucrose ⟶



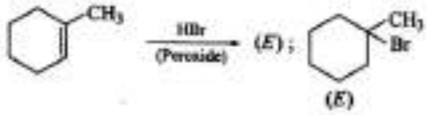
(ii)



86. (a)

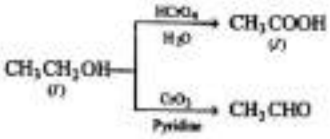


(b)

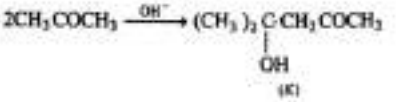


(c)

(d)



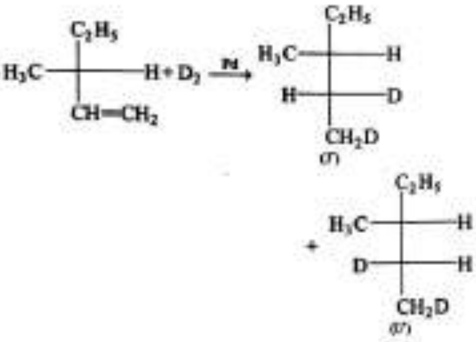
(e)



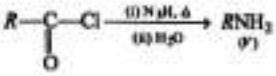
$2CH_3COCH_3 \xrightarrow{OH^-} \underset{(K)}{(CH_3)_2\underset{\underset{OH}{|}}{C}CH_2COCH_3}$

$(K) \xrightarrow[\Delta]{NaHSO_4} (CH_3)_2C{=}CHCOCH_3$

87. (a)

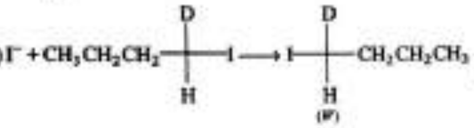


(b)

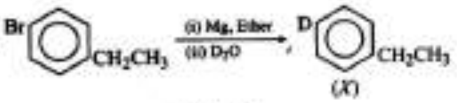


$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{(ii) }H_2O]{\text{(i) }N_3H,\ \Delta} RNH_2$ (V)

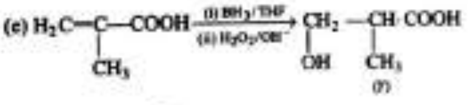
(c)



(d)



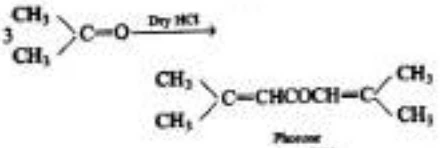
(e)



$H_2C=\underset{\underset{CH_3}{|}}{C}-COOH \xrightarrow[\text{(ii) }H_2O_2/OH^-]{\text{(i) }BH_3/THF} \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{CH_3}{|}}{CH}\,COOH$ (Y)

(f) $2CH\equiv CH \xrightarrow[O_2]{Cu^{2+}} HC\equiv C-C\equiv CH$ (Z)

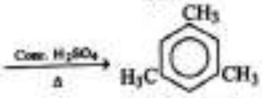
88. (i)



$3\,(CH_3)_2C=O \xrightarrow{\text{Dry HCl}} (CH_3)_2C=CHCOCH=C(CH_3)_2$

Phorone

or $3CH_3COCH_3 \xrightarrow[\Delta]{\text{Conc. }H_2SO_4}$

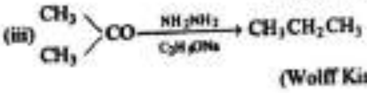


(Mesitylene)

(ii) $CH_3COCl + H_2 \xrightarrow[\text{Quinoline}]{Pd/BaSO_4} CH_3CHO + HCl$

(Rosenmund's reaction)

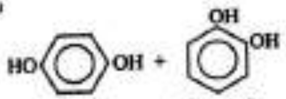
(iii)



$(CH_3)_2CO \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3$

(Wolff Kishner reaction)

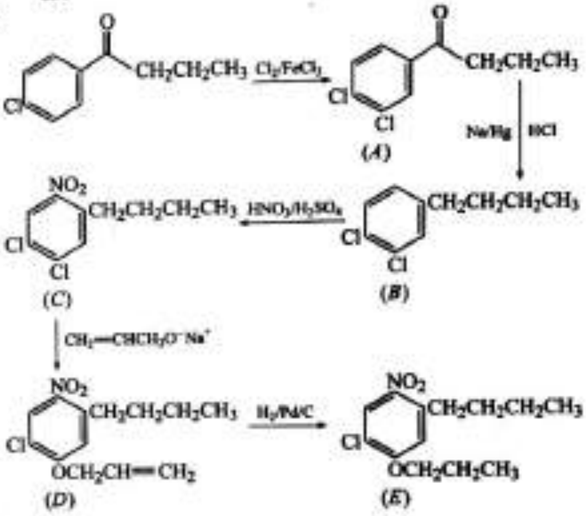
(iv) $C_6H_5OH \xrightarrow[K_2S_2O_8\text{ (alk.)}]{\text{Elb's oxidation}}$



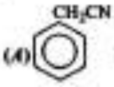
(Quinol) (Catechol)

(v) $C_6H_5N_2Cl \xrightarrow[HCl]{Cu} C_6H_5Cl$ (Gattermann reaction)

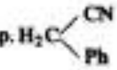
89.



90. (A)



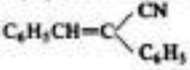
This has reactive methylene group.



$H_2C\begin{smallmatrix}CN\\Ph\end{smallmatrix}$

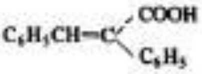
and C_6H_5CHO attacks on CH_2 group giving (B)

(B)



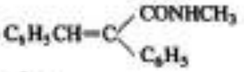
$C_6H_5CH=C\begin{smallmatrix}CN\\C_6H_5\end{smallmatrix}$

(C)



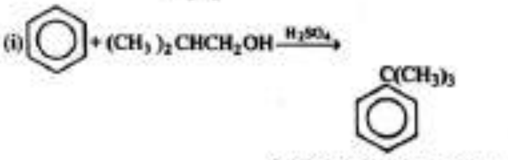
$C_6H_5CH=C\begin{smallmatrix}COOH\\C_6H_5\end{smallmatrix}$

(D)



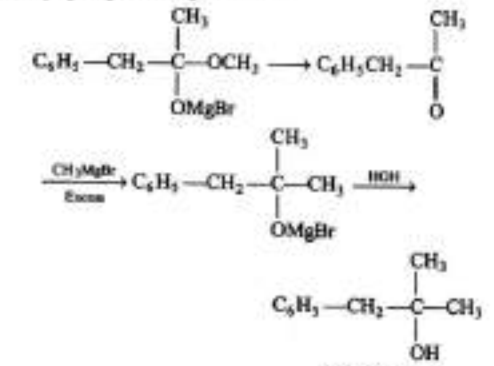
$C_6H_5CH=C\begin{smallmatrix}CONHCH_3\\C_6H_5\end{smallmatrix}$

91. (i)



2-Methyl, 2-phenylpropane

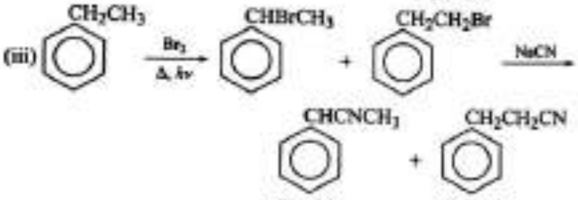
(ii) $C_6H_5CH_2COOCH_3 \xrightarrow{CH_3MgBr}$



$$C_6H_5-CH_2-\underset{OMgBr}{\overset{CH_3}{C}}-OCH_3 \longrightarrow C_6H_5CH_2-\underset{O}{\overset{CH_3}{C}} \xrightarrow[\text{Excess}]{CH_3MgBr} C_6H_5-CH_2-\underset{OMgBr}{\overset{CH_3}{C}}-CH_3 \xrightarrow{HOH} C_6H_5-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

2-Methyl,1-phenyl propan-2-ol

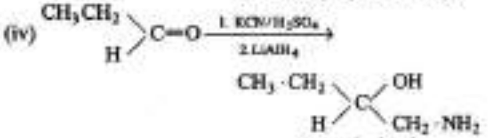
(iii)



(Major) (Minor)

(2-Phenylpropane nitrile)

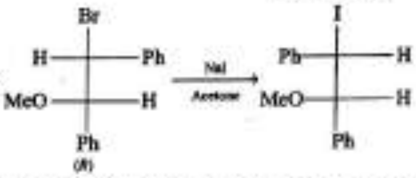
(iv)



$$\begin{matrix}CH_3CH_2\\H\end{matrix}\!\!>C=O \xrightarrow[2.\ LiAlH_4]{1.\ KCN/H_2SO_4} \begin{matrix}CH_3\cdot CH_2\\H\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CH_2\cdot NH_2\end{matrix}$$

(a racemic mixture)

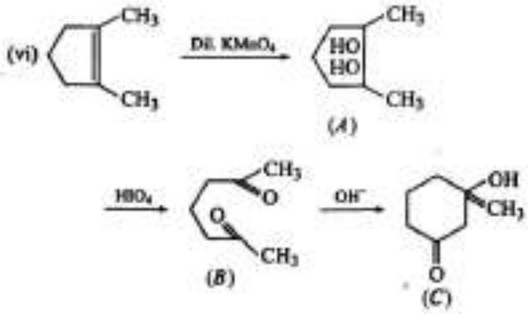
(v)



(R)

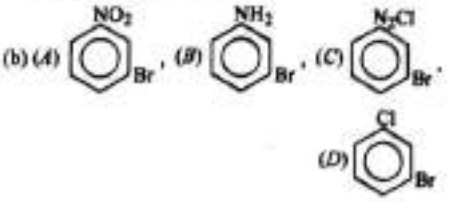
enantiomer of the original compound is formed following S_N2 mechanism (S)

(vi)



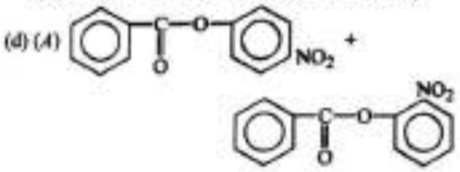
92. (a) (A) CH_3Cl, (B) $C_6H_5CH_2Cl$, (C) KCN,
(D) $C_6H_5CH_2COOH$

(b)



(c) (A) $CH_3CH_2\cdot CH_2Br$, (B) $CH_3\cdot CH=CH_2$,
(C) $CH_3CHBr\cdot CH_3$, (D) $CH_3CHNH_2\cdot CH_3$

(d) (A)



(e) (A) C_6H_5CN (B) C_6H_5COOH

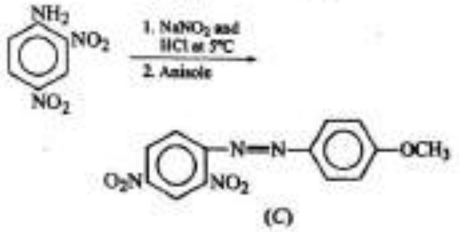
(f) (A)

(g) (A) $C_6H_4<\!\begin{matrix}CH_2OH\\OCH_3\end{matrix}$ (B) HCOOK

(h) $CH_3\cdot CH_2\cdot COOH \xrightarrow[\text{Bromine}]{\text{P and}} \underset{(A)}{CH_3\cdot CHBr\cdot COBr}$

$CH_3CHBr\cdot COBr \xrightarrow[\text{(ii) }H^+]{\text{(i) KOH (alc.)}} \underset{(B)}{CH_2=CH\cdot COOH} + HBr$

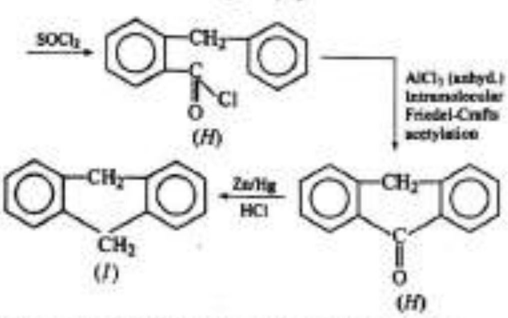
(i)



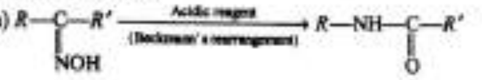
(C)

(j) $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[\text{(Claisen condensation)}]{NaOC_2H_5 \text{ in absolute } C_2H_5OH,\ \Delta} \underset{(D)}{C_6H_5CH=CHCOOC_2H_5}$

(k) o-HOOC—C_6H_4—CH_2—C_6H_5



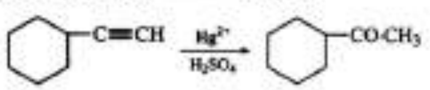
(l) (A) CH_3COOH, (B) CH_3COCl, (C) CH_3CH_2OH, (D) $CH_3 \cdot CH_2Br$

(m)


$$R-\underset{\substack{\| \\ NOH}}{C}-R' \xrightarrow[\text{(Beckmann's rearrangement)}]{\text{Acidic reagent}} R-NH-\underset{\substack{\| \\ O}}{C}-R'$$

(n) $R-COCl + H_2 \xrightarrow{Pd/BaSO_4} R \cdot CHO$

(o) $Br \cdot CH_2 \cdot CH_2Br \xrightarrow{KOH(alc.)} C_2H_2$

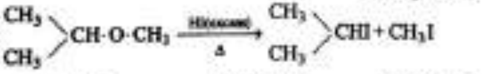
(p)


(q)

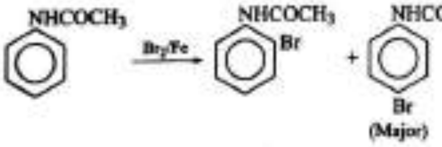

1,4-Dihydronaphthalene

(r) $C_6H_5CH_2 \cdot CHClC_6H_5 \xrightarrow[\Delta]{KOH(alc.)} C_6H_5 \cdot CH{=}CHC_6H_5$ (Cis and Trans-forms)

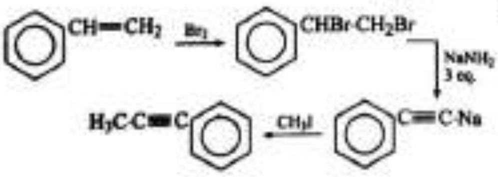
(s) $CH_3 \cdot CH_2 \cdot NH_2 \xrightarrow[\Delta]{(CH_3CO)_2O} CH_3 \cdot CH_2NHCOCH_3 + CH_3COOH$

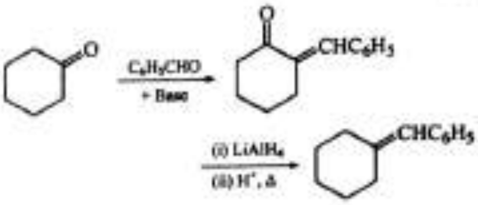
(t)


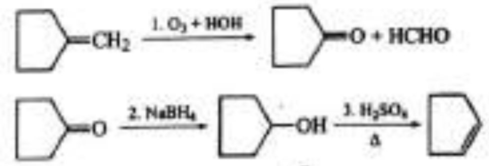
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\! CH \cdot O \cdot CH_3 \xrightarrow[\Delta]{HI(excess)} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\! CHI + CH_3I$$

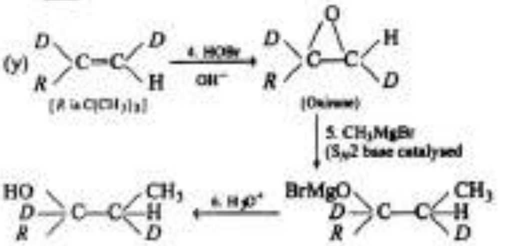
(u)


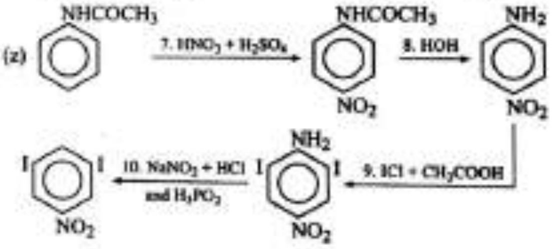
(Major)

(v)


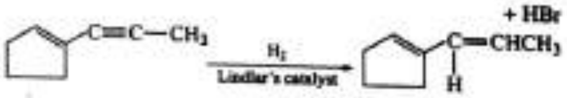
(w)


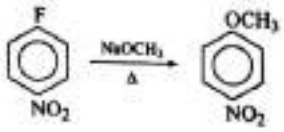
(x)


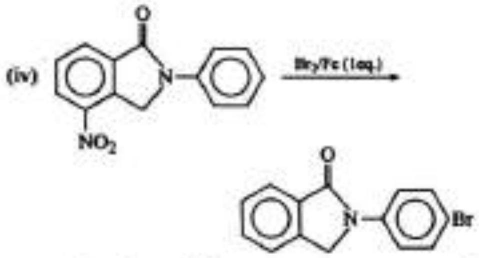
(y)


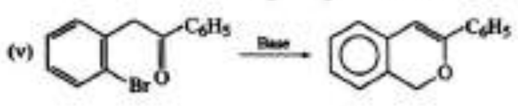
(z)


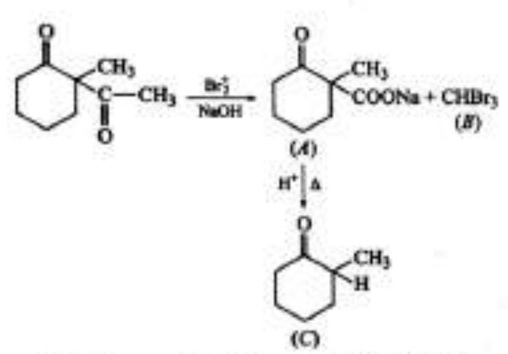
93. (i) $(CH_3)_3 \cdot C \cdot CH_2Br \xrightarrow[\Delta]{C_2H_5OH} (CH_3)_2C{=}CH—CH_3 + HBr$

(ii)


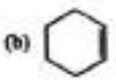
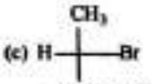
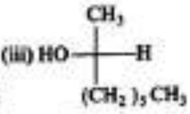
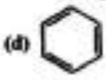
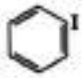
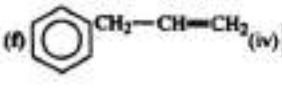
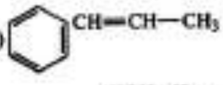
(iii)


(iv) 

(v) 

94. 

95.

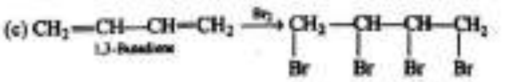
Reagent	Product	Other reagent
(a) $R—CH = CH_2$	(vi) $R\underset{\displaystyle Cl}{\underset{\mid}{C}}H—CH_2\cdot CCl_3$	CCl_4/Peroxide
(b) 	(i) 	Baeyer's reagent or HCOOH or OsO_4 / (aq.) $NaHSO_3$
(c) 	(iii) 	KOH(aq.)
(d) 	(ii) 	($I_2 + HNO_3$ or ICl)
(e) 	(v) 	C_2H_5OH/dry HCl
(f) 	(iv) 	
		KOH + Heat

96.

List I	List II
1	(B)
2	(C)
3	(D)
4	(E)
5	(A)

97. (a) $\underset{\text{1-Butyne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[\text{(A test for terminal alkyne)}]{\text{Amm. }AgNO_3} CH_3CH_2C{\equiv}C\cdot Ag$

(b) $\underset{\text{2-Butyne}}{CH_3—C{\equiv}C—CH_3} \xrightarrow{\text{Alk. }KMnO_4,\ \Delta} 2CH_3COOH$

(c) 

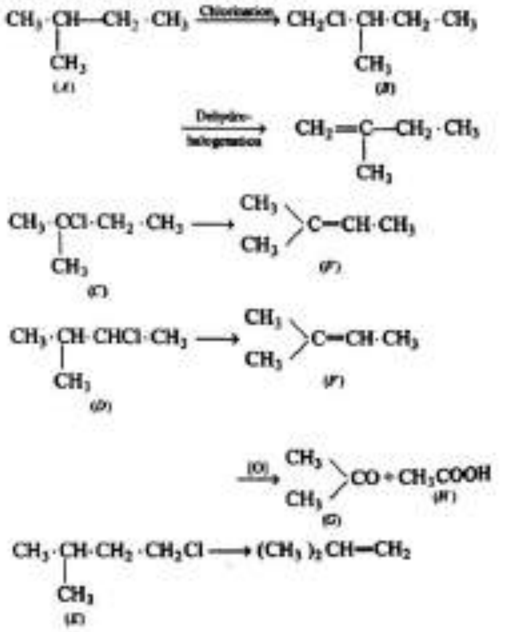
$\underset{\text{1,3-Butadiene}}{CH_2{=}CH—CH{=}CH_2} \xrightarrow{Br_2} \underset{\displaystyle Br}{\underset{\mid}{C}}H_2—\underset{\displaystyle Br}{\underset{\mid}{C}}H—\underset{\displaystyle Br}{\underset{\mid}{C}}H—\underset{\displaystyle Br}{\underset{\mid}{C}}H_2$

Addition of 1 mole of H_2 follows 1,4 addition a characteristic reaction of conjugated alkadienes.

$CH_2{=}CH—CH{=}CH_2 \xrightarrow{H_2,\ 1\text{ mole}} \underset{\text{2-Butene}}{CH_3—CH{=}CH—CH_3}$

(d) 

98. Alkane (*A*) C_5H_{12} on chlorination gives four mono chloro product and thus, (*A*) is isopentane



$\underset{(A)}{CH_3\cdot \underset{\displaystyle CH_3}{\underset{\mid}{C}}H—CH_2\cdot CH_3} \xrightarrow{\text{Chlorination}} \underset{(B)}{CH_2Cl\cdot \underset{\displaystyle CH_3}{\underset{\mid}{C}}H\cdot CH_2\cdot CH_3}$

$\xrightarrow[\text{halogenation}]{\text{Dehydro-}} CH_2{=}\underset{\displaystyle CH_3}{\underset{\mid}{C}}—CH_2\cdot CH_3$

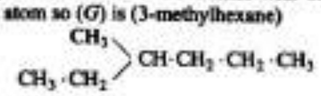
$\underset{(C)}{CH_3\cdot \underset{\displaystyle CH_3}{\underset{\mid}{C}}Cl\cdot CH_2\cdot CH_3} \longrightarrow \underset{(F)}{(CH_3)_2C{=}CH\cdot CH_3}$

$\underset{(D)}{CH_3\cdot \underset{\displaystyle CH_3}{\underset{\mid}{C}}H\cdot CHCl\cdot CH_3} \longrightarrow \underset{(F)}{(CH_3)_2C{=}CH\cdot CH_3}$

$\xrightarrow{[O]} \underset{(G)}{(CH_3)_2CO} + \underset{(H)}{CH_3COOH}$

$\underset{(E)}{CH_3\cdot \underset{\displaystyle CH_3}{\underset{\mid}{C}}H\cdot CH_2\cdot CH_2Cl} \longrightarrow (CH_3)_2CH{=}CH_2$

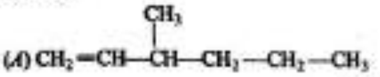
99. (1) (*G*) is lowest mol. mass alkane with one asymmetric carbon atom so (*G*) is (3-methylhexane)



$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\end{matrix}\Big\rangle CH\cdot CH_2\cdot CH_2\cdot CH_3$$

(2) Thus, possible alkenes which can produce (*G*) on hydrogenation are (also none of them on ozonolysis gives acetone).

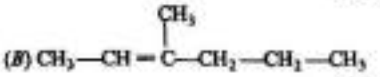
(*A*)



$$CH_2{=}CH-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

3-Methylhex-1-ene

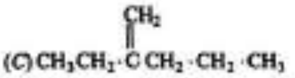
(*B*)



$$CH_3-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-CH_2-CH_3$$

3-Methylhex-2-ene

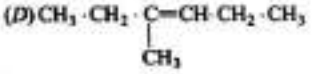
(*C*)



$$CH_3CH_2\cdot\overset{\displaystyle CH_2}{\overset{\|}{C}}\,CH_2\cdot CH_2\cdot CH_3$$

2-Ethylpent-1-ene

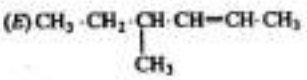
(*D*)



$$CH_3\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\cdot CH_2\cdot CH_3$$

3-Methylhex-3-ene

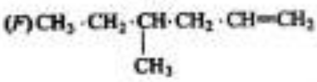
(*E*)



$$CH_3\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH{=}CH\cdot CH_3$$

4-Methylhex-2-ene

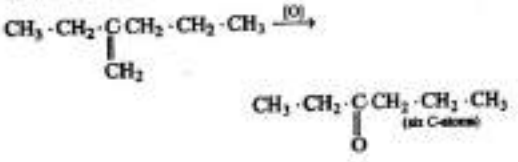
(*F*)



$$CH_3\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2\cdot CH{=}CH_3$$

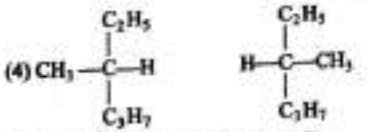
4-Methylhex-1-ene

(3) Only alkene (*C*) gives a ketone containing more than five C-atoms on treatment with warm conc. alk. $KMnO_4$.



$$CH_3\cdot CH_2\cdot\underset{\displaystyle CH_2}{\underset{\|}{C}}\,CH_2\cdot CH_2\cdot CH_3\xrightarrow{[O]}\underset{\text{(six C-atoms)}}{CH_3\cdot CH_2\cdot\underset{\displaystyle O}{\underset{\|}{C}}\,CH_2\cdot CH_2\cdot CH_3}$$

(4)



$$CH_3-\begin{array}{c}C_2H_5\\ |\\ C\\ |\\ C_3H_7\end{array}-H\qquad H-\begin{array}{c}C_2H_5\\ |\\ C\\ |\\ C_3H_7\end{array}-CH_3$$

These are Fischer projections of (*G*).

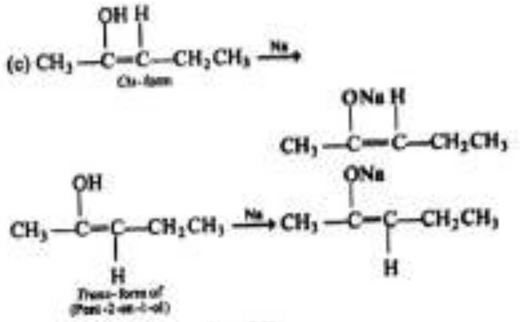
100. (a) Aldehydes lacking with α-H-atom undergoes Cannizzaro's reaction:

$$\underset{\text{2,2-Dimethyl propanal}}{(CH_3)_3C\cdot CHO}\xrightarrow{KOH}(CH_3)_3C\cdot COOK+(CH_3)_3\cdot C\cdot CH_2OH$$

(b)

$$\underset{\text{3-Methyl butan-2-one}}{CH_3COCH(CH_3)_2}\xrightarrow{I_2+KOH}\underset{\text{Iodoform}}{CHI_3}+\underset{\text{Isobutyric acid salt}}{(CH_3)_2CHCOOK}$$

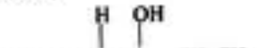
(c)



$$\underset{\text{Cis-form}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-CH_2CH_3}\xrightarrow{Na}CH_3-\overset{\displaystyle ONa}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-CH_2CH_3$$

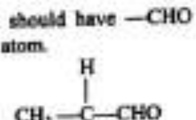
$$\underset{\text{Trans-form of (Pent-2-en-3-ol)}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-CH_2CH_3}\xrightarrow{Na}CH_3-\overset{\displaystyle ONa}{\overset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-CH_2CH_3$$

It may also be,



$$\underset{\text{(Pent-2-en-3-ol)}}{CH_3-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle OH}{\overset{|}{C}}-CH_2CH_3}$$

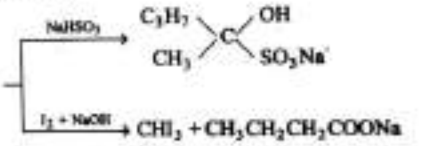
(d) (*A*) should have —CHO gp. and at least one chiral carbon atom.



$$CH_3-\begin{array}{c}H\\ |\\ C\\ |\\ CH_2CH_3\end{array}-CHO$$

(e) (*A*) should be methyl ketone,

$$\underset{\text{Pentan-2-one}}{CH_3\cdot COCH_2CH_2CH_3}$$



$$\xrightarrow{NaHSO_3}\begin{matrix}C_3H_7\\ CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\ SO_3Na^+\end{matrix}$$

$$\xrightarrow{I_2+NaOH}CHI_3+CH_3CH_2CH_2COONa$$

(f) (*A*) should be a carbonyl compound and not a methyl ketone or aldehyde. $NaHSO_3$ gives white solid with all aldehydes and methyl ketones.

$$\underset{\text{Pentan-3-one}}{CH_3CH_2COCH_2CH_3}$$

101. (a)

$$\underset{\substack{\text{Pent-1-ene}\\ \text{(molar mass = 70 g mol}^{-1}\text{)}}}{CH_3\cdot CH_2\cdot CH_2\cdot CH{=}CH_2}+Br_2\longrightarrow\underset{\text{1,2-Dibromopentane}}{CH_3\cdot CH_2\cdot CH_2CHBr\cdot CH_2Br}$$

∵ 70 g C_5H_{10} requires 160 g Br_2

∴ 5 g C_5H_{10} requires $\frac{160\times5}{70}$ g Br_2 = **11.43 g Br_2**

(b)

$$\underset{\substack{\text{Pent-1-yne}\\ \text{(molar mass = 68 g mol}^{-1}\text{)}}}{CH_3\cdot CH_2\cdot CH_2\cdot C{\equiv}CH}+2Br_2\longrightarrow\underset{\text{1,1,2,2-Tetrabromopentane}}{CH_3\cdot CH_2\cdot CH_2\cdot CBr_2\cdot CHBr_2}$$

∵ 68 g C_5H_8 requires 320 g Br_2

∴ 5 g C_5H_8 requires $\frac{320\times5}{68}$ g Br_2 = **23.53 g Br_2**

(c) $\underset{\text{Pentane (molar mass = 72 g mol}^{-1})}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3} \xrightarrow{Br_2} C_5H_{11}Br + HBr$

$\because$ 72 g C_5H_{12} requires 160 g Br_2

$\therefore$ 5 g C_5H_{12} requires $\frac{160 \times 5}{72}$ g Br_2 = **11.11 g Br_2**

102. (a) (1) Given,

$$C_5H_{11}X \xrightarrow[-HX]{KOH(alc.)} \underset{\text{Pent-1-ene}}{CH_3 \cdot CH_2 \cdot CH_2CH{=}CH_2}$$

(2) Thus, possible structure of halide may be (I) or (II). However, elimination of HX, according to Saytzeff's rule, suggests that structure (II) is correct as it gives only pent-1-ene.

$$\underset{(I)}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CHX \cdot CH_3}$$
$$\big\downarrow \text{(alc.) KOH}$$
$$CH_3 \cdot CH_2CH{=}CH \cdot CH_3 \text{ Major}$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH{=}CH_2 \text{ Minor}$$

or
$$\underset{(II)}{CH_3CH_2 \cdot CH_2CH_2 \cdot CH_2X}$$
$$\big\downarrow \text{(alc.) KOH}$$
$$\underset{\text{Pent-1-ene (only)}}{CH_3 \cdot CH_2 \cdot CH_2CH{=}CH_2}$$

Thus, halide is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2X$ *i.e.*, 1-halopentane.

(b) (1) Given, $C_5H_{11}X \xrightarrow[-HX]{KOH(alc.)} CH_3 \cdot CH_2 \cdot CH{=}CH \cdot CH_3$

(2) Thus, possible structure of halide may be (I) or (II). However elimination of HX according to Saytzeff's rule (the major product is one from which elimination of H occurs from less hydrogenated C-atom) structure (II) is correct as it gives only pent-2-ene.

$$\underset{(I)}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CHX \cdot CH_3} \xrightarrow{\text{(alc.) KOH}} \underset{\text{Major}}{CH_3 \cdot CH_2 \cdot CH{=}CH \cdot CH_3} + \underset{\text{Minor}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH{=}CH_2}$$

$$\underset{(II)}{CH_3 \cdot CH_2 \cdot CHX \cdot CH_2 \cdot CH_3} \xrightarrow{\text{(alc.) KOH}} \underset{\text{Pent-2-ene (only)}}{CH_3 \cdot CH{=}CH \cdot CH_2 \cdot CH_3}$$

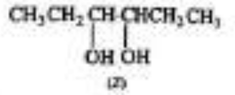
Thus, halide is $CH_3 \cdot CH_2 \cdot CHXCH_2 \cdot CH_3$, *i.e.*, 3-halopentane.

103. $CH_3CH_2C{\equiv}CH \xrightarrow{NaNH_2} CH_3CH_2C{\equiv}C^-Na^+ \xrightarrow{CH_3CH_2Br} \underset{(X)}{CH_3CH_2C{\equiv}CCH_2CH_3}$

$$\underset{(X)}{CH_3CH_2C{\equiv}CCH_2CH_3} \xrightarrow{H_2/Pd\text{-}BaSO_4} \underset{\text{Cis-hexene (Y)}}{CH_3CH_2CH{=}CHCH_2CH_3}$$

$$\underset{(Y)}{CH_3CH_2CH{=}CHCH_2CH_3} \xrightarrow{\text{Alkaline }KMnO_4} \underset{(Z)\text{ Pot. salt of propanoic acid}}{2CH_3CH_2COOK}$$

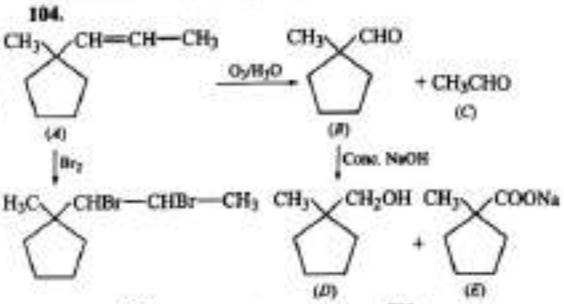
or $\underset{(Y)}{CH_3CH_2CH{=}CHCH_2CH_3} \xrightarrow{\text{if Baeyer's reagent}}$



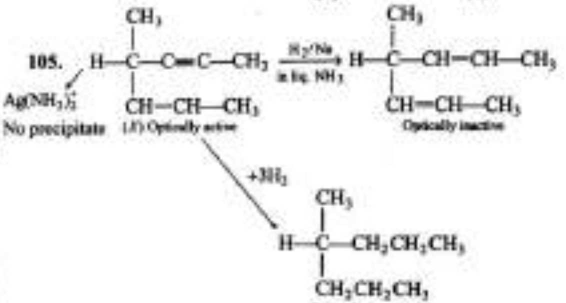
$$\underset{(Z)}{CH_3CH_2\underset{OH}{CH}\underset{OH}{CH}CH_2CH_3}$$

In both cases (Z) is optically inactive.

104.



105.



106. Mole of H_2 taken up $= \frac{8.40 \times 10^{-3}}{22.4} = 3.75 \times 10^{-4}$

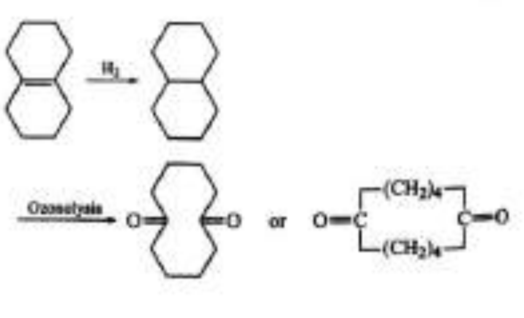
Mole of compound $= \frac{10.02 \times 10^{-3}}{80} = 1.253 \times 10^{-4}$

Thus, mole of H_2 taken up by

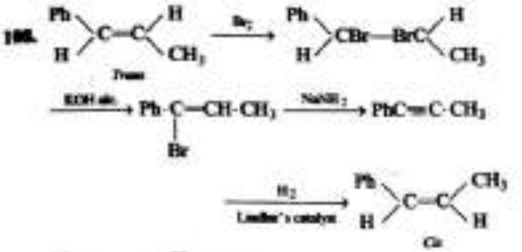
1 mole of compound $= \frac{3.75 \times 10^{-4}}{1.253 \times 10^{-4}} = 3$

Therefore, molecule has three double bond and it may be 1,3,5-hexatriene $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$.

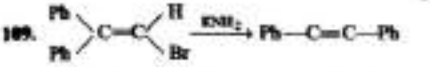
107.



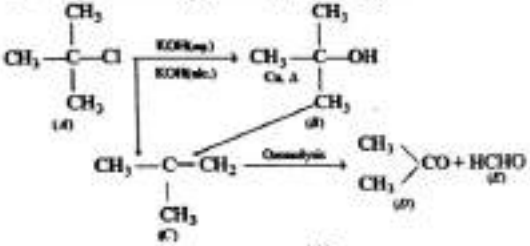
108.

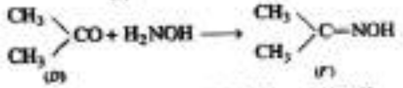


109.



110. The reactions suggest that (*A*) is $(CH_3)_3CCl$





$$\underset{(E)}{2HCHO} + NaOH \longrightarrow \underset{(H)}{HCOONa} + \underset{(G)}{CH_3OH}$$

(Cannizzaro's reaction)

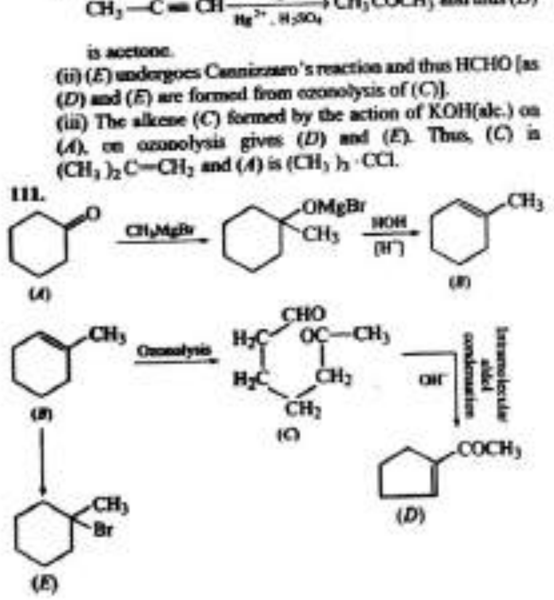
(i) (*D*) is obtained from propyne as

$CH_3—C \equiv CH \xrightarrow[Hg^{2+},\ H_2SO_4]{H_2O} CH_3COCH_3$ and thus (*D*) is acetone.

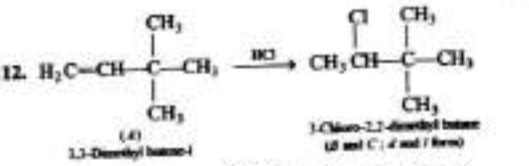
(ii) (*E*) undergoes Cannizzaro's reaction and thus HCHO [as (*D*) and (*E*) are formed from ozonolysis of (*C*)].

(iii) The alkene (*C*) formed by the action of KOH(alc.) on (*A*), on ozonolysis gives (*D*) and (*E*). Thus, (*C*) is $(CH_3)_2C=CH_2$ and (*A*) is $(CH_3)_3\cdot CCl$.

111.



112.



3,3-Dimethyl butene-1

3-Chloro-2,2-dimethyl butane (*B* and *C*; *d* and *l* forms)

$$\underset{(B\ \text{or}\ C)}{CH_3CHClC(CH_3)_3} \xrightarrow{(alc.)\,KOH} \underset{\substack{(D)\\ \text{3,3-Dimethyl but-2-ene}}}{(CH_3)_2C=C(CH_3)_2}$$

$$\underset{(A)}{H_2C=CHC(CH_3)_3} \xrightarrow{Ozonolysis} \underset{\substack{\text{Methanal}\\(F)}}{HCHO} + \underset{\substack{\text{2,2-Dimethyl propanal}\\(G)}}{(CH_3)_3C\cdot CHO}$$

(*F*) and (*G*) both are aldehyde and give Fehling test but do not give iodoform test.

$$\underset{(D)}{(CH_3)_2C=C(CH_3)_2} \xrightarrow{Ozonolysis} \underset{(E)\ \text{Acetone}}{2CH_3COCH_3}$$

Ketone does not give Fehling test. Methyl ketones give iodoform test.

$$\underset{(F)}{HCHO} + \underset{(G)}{(CH_3)_3\cdot CCHO} \xrightarrow[\text{reaction}]{\text{crossed Cannizzaro's}}$$

$$(CH_3)_3C\cdot CH_2OH + HCOONa$$

113. (i) Chlorination of propane gives :

$CH_3\cdot CH_2CH_3 \xrightarrow{2Cl_2} CH_3\cdot CCl_2\cdot CH_3$ 2,2-Dichloropropane
$+ CH_2Cl\cdot CH_2CH_2Cl$ 1,3-Dichloropropane
$+ CH_3CH_2\cdot CHCl_2$ 1,1-Dichloropropane
$+ CH_3\cdot CHCl\,CH_2Cl$ 1,2-Dichloropropane

(ii) Since, (*A*) on further chlorinaton gives one product and thus,

$$\underset{(A)}{CH_3\cdot CCl_2\cdot CH_3} \xrightarrow{Cl_2} CH_3\cdot CCl_2\cdot CH_2Cl$$

(iii) Since, (*B*) on further chlorination gives two products and thus,

$$\underset{(B)}{CH_2Cl\,CH_2\cdot CH_2Cl} \xrightarrow{Cl_2} CH_2Cl\,CHCl\cdot CH_2Cl$$

$$+ CH_2Cl\cdot CH_2\cdot CHCl_2$$

(iv)Since, (*C*) and (*D*) give three products on further chlorination and thus,

$$\underset{(C)}{CH_3CH_2CHCl_2} \xrightarrow{Cl_2} CH_3CHClCHCl_2 + CH_3CH_2\cdot CCl_3$$

$$+ CH_2Cl\cdot CH_2\cdot CHCl_2 \text{ or } \underset{(D)}{CH_3CHClCH_2Cl}$$

114. (i) Molar mass of (*A*) suggest it to be C_4H_6, *i.e.*, molar mass = 54

(ii) C_4H_6 has terminal triple bond as it reacts with CH_3CH_2Br in presence of $NaNH_2$.

(iii) $\underset{(A)}{CH_3\cdot CH_2\cdot C\equiv CH} \xrightarrow{Br_2} \underset{(B)}{CH_3\cdot CH_2\cdot CBr_2\cdot CHBr_2}$

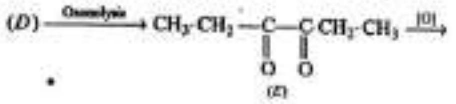
Molar mass = 54 Molar mass = 374

Thus, molar mass of $(B) = \dfrac{593 \times 54}{100} + 54 = 320 + 54 = 374$

(iv) $CH_3-CH_2 \cdot C \equiv CH \xrightarrow{H_2} \underset{\substack{(C)\\ \text{Mol. wt.} = 58}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3}$

Thus, molar mass of $(C) = \frac{7.4}{100} \times 54 + 54 = 58$

(v) $\underset{(A)}{CH_3 \cdot CH_2 \cdot C \equiv CH} \xrightarrow[CH_3 \cdot CH_2Br]{NaNH_2} \underset{(D)}{CH_3 \cdot CH_2 \cdot C \equiv C \cdot CH_2 \cdot CH_3}$



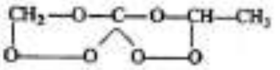
$(D) \xrightarrow{\text{Ozonolysis}} \underset{(E)}{CH_3 \cdot CH_2 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} CH_2 \cdot CH_3} \xrightarrow{[O]}$

$\underset{(F)}{CH_3 \cdot CH_2 \cdot COOH}$

115. (1) Since, 3 molecules are present and thus, rupture of C_4H_6 at two places occurs during ozonolysis so, C_4H_6 has two double bonds.

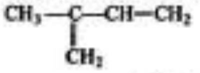
(2) Keeping in view of above facts, C_4H_6 is

$\underset{\substack{\text{Buta-1,2-diene}\\ [C_4H_6]}}{CH_2=C=CH \cdot CH_3} \xrightarrow[\text{(II) HOH}]{\text{(I) } O_3}$

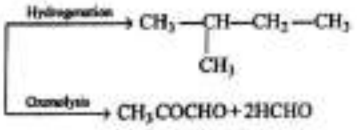


$\underset{\text{Methanal}}{HCHO} + CO_2 + \underset{\text{Ethanal}}{CH_3CHO}$

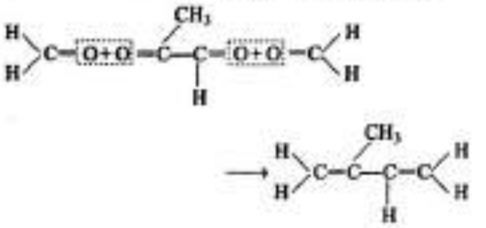
116. Compound (*E*) gives (*F*) on hydrogenation. Also, (*E*) on ozonolysis gives HCHO and 2-ketopropanal. Thus, (*E*) (C_5H_8) having two double bonds may be



$CH_3-\underset{\underset{CH_2}{\|}}{C}-CH=CH_2$

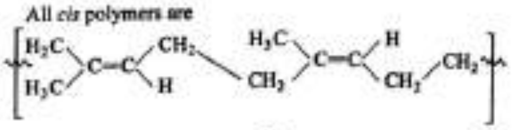


117.

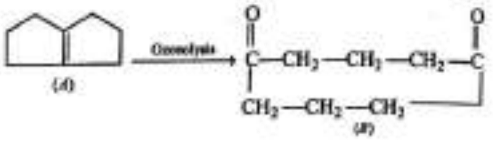


Thus, alkene is $CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$ which on ozonolysis will give two moles of HCHO and one mole of CH_3COCHO.

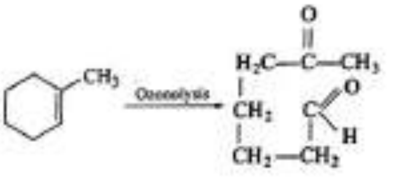
All *cis* polymers are

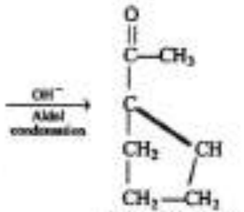


118.



119.

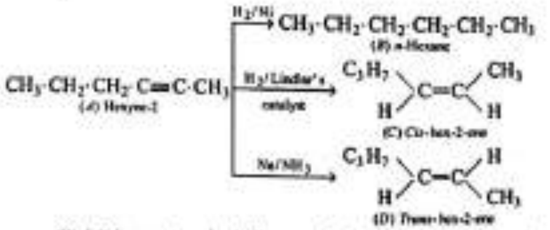




1-Acetyl cyclopentene

120. The given compound (*A*) is $CH_3 \cdot CH_2 \cdot CH_2 \cdot C \equiv C \cdot CH_3$. This is confirmed by the following findings.

(i)



(ii) (*A*) is non-terminal alkyne as it does not give white salt with ammoniacal $AgNO_3$.

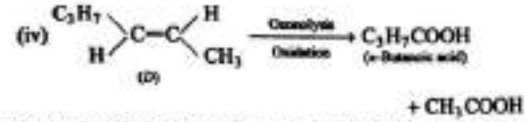
(iii) (*A*) forms (*E*) with $NaNH_2$ which reacts with CH_3I to give (*F*).

$\underset{\text{Hexyne-2}}{CH_3 \cdot CH_2 \cdot CH_2C \equiv C \cdot CH_3} \xrightarrow[\Delta]{NaNH_2}$

$\underset{(E)}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \equiv CNa}$

$\downarrow CH_3I$

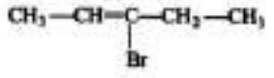
$\underset{(F)}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \equiv C \cdot CH_3}$

(iv)


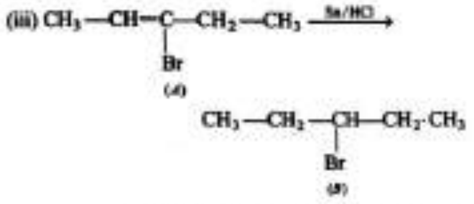
$$\underset{(D)}{C_3H_7(H)C{=}C(H)CH_3} \xrightarrow[\text{Oxidation}]{\text{Ozonolysis}} \underset{(n\text{-Butanoic acid})}{C_3H_7COOH} + CH_3COOH$$

121. (i) (*A*) Decolorises bromine water and $KMnO_4$, thus it has unsaturation.

(ii) The reactions suggest (*A*) to be

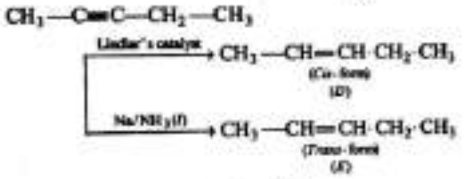


$$CH_3-CH{=}\underset{Br}{\underset{|}{C}}-CH_2-CH_3$$

(iii)


$$CH_3-CH{=}\underset{\underset{(A)}{Br}}{\underset{|}{C}}-CH_2-CH_3 \xrightarrow{Sn/HCl} CH_3-CH_2-\underset{\underset{(B)}{Br}}{\underset{|}{CH}}-CH_2\cdot CH_3$$

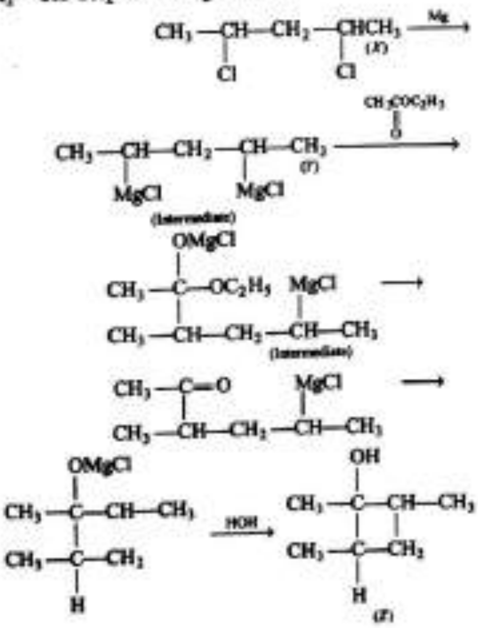
$$(A) \xrightarrow{NaNH_2} \underset{(C)}{CH_3-C\equiv C-CH_2-CH_3}$$



$$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow{\text{Lindlar's catalyst}} \underset{\underset{(D)}{(Cis\text{-}form)}}{CH_3-CH{=}CH\cdot CH_2\cdot CH_3}$$

$$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow{Na/NH_3(l)} \underset{\underset{(E)}{(Trans\text{-}form)}}{CH_3-CH{=}CH\cdot CH_2\cdot CH_3}$$

122. $CH_3-CH\cdot CH_2\cdot CH{=}CH_2 \xrightarrow{HCl}$



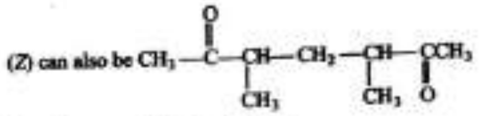
$$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}CH_3\ (X) \xrightarrow{Mg}$$

$$\underset{(\text{Intermediate})}{CH_3-\underset{MgCl}{\underset{|}{CH}}-CH_2-\underset{MgCl}{\underset{|}{CH}}-CH_3}\ (Y) \xrightarrow{CH_3\overset{\overset{O}{\|}}{C}OC_2H_5}$$

$$\underset{(\text{Intermediate})}{CH_3-\overset{OMgCl}{\overset{|}{C}}(OC_2H_5)-\underset{}{CH(CH_3)}-CH_2-\underset{}{CH(MgCl)}-CH_3} \longrightarrow$$

$$CH_3-C(=O)-CH(CH_3)-CH_2-CH(MgCl)-CH_3 \longrightarrow$$

$$CH_3-\overset{OMgCl}{\overset{|}{C}}-CH-CH_3,\ CH_3-\underset{\underset{H}{|}}{C}-CH_2 \xrightarrow{HOH} CH_3-\overset{OH}{\overset{|}{C}}-CH-CH_3,\ CH_3-\underset{\underset{H}{|}}{C}-CH_2\ (F)$$



$$(Z) \text{ can also be } CH_3-\overset{\overset{O}{\|}}{C}-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{\underset{O}{\|}}{C}CH_3$$

123. The given reactions suggest that:

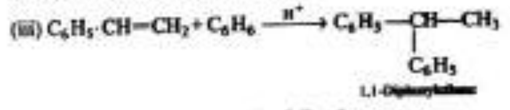
(i) (*B*) is $C_6H_5CHBr\cdot CH_3 \xrightarrow[KOH\,(alc.)]{-HBr} \underset{(C)}{C_6H_5CH{=}CH_2}$

$\xrightarrow{HBr} \underset{(B)}{C_6H_5CHBrCH_3} \xrightarrow{HOH} \underset{(E)}{C_6H_5CHOH\cdot CH_3}$

and (*A*) is $C_6H_5\cdot CH_2\cdot CH_2Br \xrightarrow[KOH\,(alc.)]{-HBr} \underset{(C)}{C_6H_5CH{=}CH_2}$

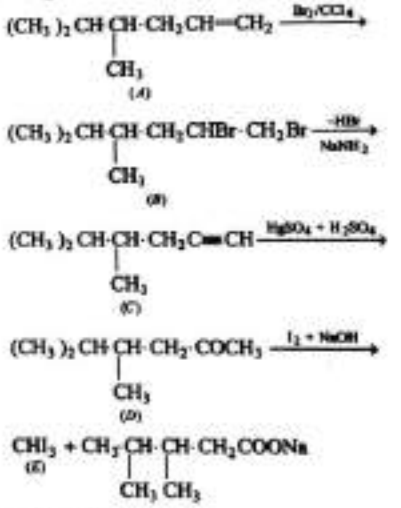
$\xrightarrow[\text{Peroxide}]{HBr} \underset{(A)}{C_6H_5CH_2-CH_2Br} \xrightarrow{HOH} \underset{(D)}{C_6H_5CH_2CH_2OH}$

(ii) (*D*) and (*E*) are isomeric alcohols

(iii)


$$C_6H_5\cdot CH{=}CH_2 + C_6H_6 \xrightarrow{H^+} \underset{\text{1,1-Diphenylethane}}{C_6H_5-\underset{C_6H_5}{\underset{|}{CH}}-CH_3}$$

124. The given reactions suggest the following :



$$\underset{(A)}{(CH_3)_2CH\,\underset{CH_3}{\underset{|}{CH}}\cdot CH_2CH{=}CH_2} \xrightarrow{Br_2/CCl_4}$$

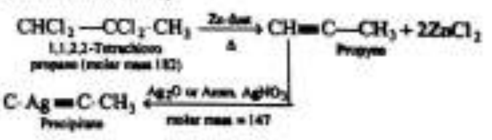
$$\underset{(B)}{(CH_3)_2CH\,\underset{CH_3}{\underset{|}{CH}}\cdot CH_2CHBr\cdot CH_2Br} \xrightarrow[NaNH_2]{-HBr}$$

$$\underset{(C)}{(CH_3)_2CH\cdot\underset{CH_3}{\underset{|}{CH}}\cdot CH_2C\equiv CH} \xrightarrow{HgSO_4 + H_2SO_4}$$

$$\underset{(D)}{(CH_3)_2CH\,\underset{CH_3}{\underset{|}{CH}}\cdot CH_2\cdot COCH_3} \xrightarrow{I_2 + NaOH}$$

$$\underset{(E)}{CHI_3} + CH_3\cdot\underset{CH_3}{\underset{|}{CH}}\cdot\underset{CH_3}{\underset{|}{CH}}\cdot CH_2COONa$$

125. Given reactions are,



$$\underset{\text{1,1,2,2-Tetrachloro propane (molar mass 182)}}{CHCl_2-CCl_2\cdot CH_3} \xrightarrow[\Delta]{\text{Zn dust}} \underset{\text{Propyne}}{CH\equiv C-CH_3} + 2ZnCl_2$$

$$\underset{\text{Precipitate}}{C\cdot Ag\equiv C\cdot CH_3} \xleftarrow[\text{molar mass} = 147]{Ag_2O \text{ or Amm. } AgNO_3} CH\equiv C-CH_3$$

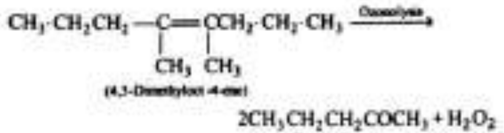
∵ 182 g compound (1,1,2,2-tetrachloropropane) gives = 147 g precipitate

∴ 36.4 g compound (1,1,2,2-tetrachloropropane) gives

$$= \frac{147 \times 36.4}{182}\,g = 29.4g$$

∴ Weight of precipitate = **29.4 g**

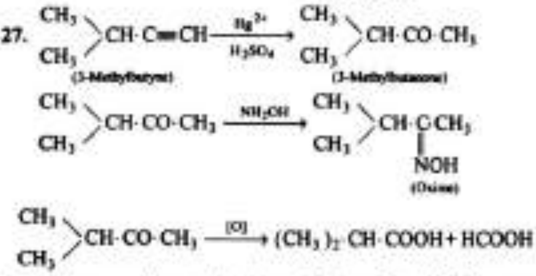
126.



$$CH_3\cdot CH_2CH_2-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}CH_2\cdot CH_2\cdot CH_3 \xrightarrow{\text{Ozonolysis}} \underset{\text{(Pentan-2-one)}}{2CH_3CH_2CH_2COCH_3} + H_2O_2$$

(4,5-Dimethyloct-4-ene)

127.



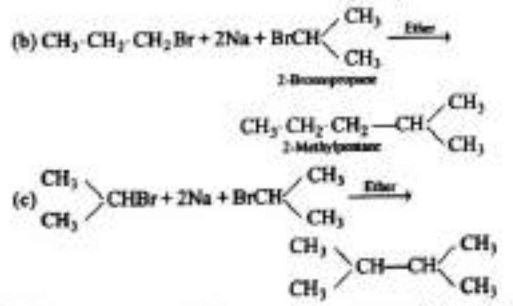
$$\underset{\text{(3-Methylbutyne)}}{(CH_3)_2CH\cdot C\equiv CH} \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{\text{(3-Methylbutanone)}}{(CH_3)_2CH\cdot CO\cdot CH_3}$$

$$(CH_3)_2CH\cdot CO\cdot CH_3 \xrightarrow{NH_2OH} \underset{\text{(Oxime)}}{(CH_3)_2CH\cdot \underset{NOH}{\underset{\|}{C}}CH_3}$$

$$(CH_3)_2CH\cdot CO\cdot CH_3 \xrightarrow{[O]} (CH_3)_2\cdot CH\cdot COOH + HCOOH$$

Note : However, the step showing oxidation of 3-methyl butanone will yield acetic acid and acetone and not dimethyl acetic acid according to Popf's rule. The step given in problem is not appropriate.

128. (1) The given reaction is **Wurtz reaction,** *i.e.*, reaction of alkyl halides with Na in presence of ether. When a mixture of halide reacts with Na in presence of ether, all possible alkanes are formed.



(a) $\underset{\text{1-Bromopropane}}{CH_3\cdot CH_2\cdot CH_2Br} + 2Na + Br\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow{\text{Ether}} \underset{\text{(Hexane)}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3}$

(b) $CH_3\cdot CH_2\cdot CH_2Br + 2Na + \underset{\text{2-Bromopropane}}{BrCH(CH_3)_2} \xrightarrow{\text{Ether}} \underset{\text{2-Methylpentane}}{CH_3\cdot CH_2\cdot CH_2-CH(CH_3)_2}$

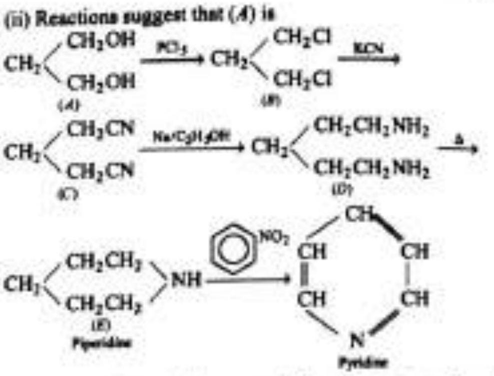
(c) $(CH_3)_2CHBr + 2Na + BrCH(CH_3)_2 \xrightarrow{\text{Ether}} (CH_3)_2CH-CH(CH_3)_2$

129. 1-butyne has more dipole moment because *sp*-hybridised carbon has more electronegativity in comparison to 1-butene (sp^2-hybridised carbon). It is evidenced by acidic nature of butyne-1.

$$CH_3CH_2\underset{sp}{C}\equiv\underset{sp}{CH} \qquad CH_3CH_2\underset{sp^2}{CH}=\underset{sp^2}{CH_2}$$

130. (i) (*A*) gives characteristic colour with ceric ammonium nitrate and thus, it has OH group.

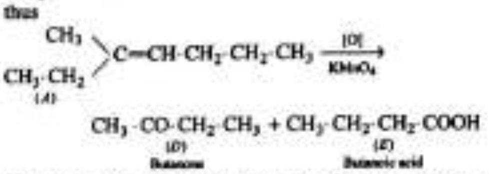
(ii) Reactions suggest that (*A*) is



$$\underset{(A)}{CH_2(CH_2OH)_2} \xrightarrow{PCl_5} \underset{(B)}{CH_2(CH_2Cl)_2} \xrightarrow{KCN} \underset{(C)}{CH_2(CH_2CN)_2} \xrightarrow{Na/C_2H_5OH} \underset{(D)}{CH_2(CH_2CH_2NH_2)_2} \xrightarrow{\Delta}$$

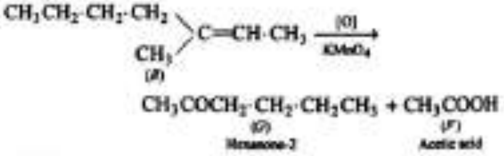
$$\underset{\text{Piperidine}}{\underset{(E)}{CH_2(CH_2CH_2)_2NH}} \longrightarrow \text{Pyridine}$$

131. (i) Since, alkene (*A*) on oxidation gives a carbonyl compound (*D*) and acid (*E*) of four carbon atoms each and thus



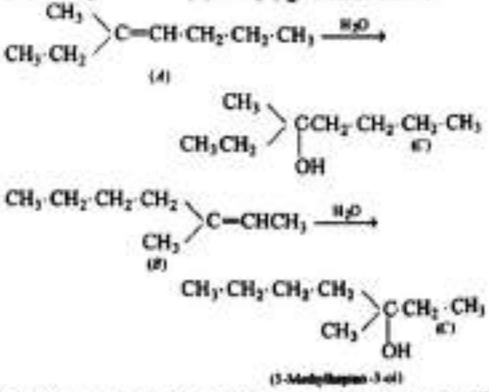
$$\underset{(A)}{(CH_3)(CH_3\cdot CH_2)C=CH\cdot CH_2\cdot CH_2\cdot CH_3} \xrightarrow[KMnO_4]{[O]} \underset{\text{Butanone}}{\underset{(D)}{CH_3\cdot CO\cdot CH_2\cdot CH_3}} + \underset{\text{Butanoic acid}}{\underset{(E)}{CH_3\cdot CH_2\cdot CH_2\cdot COOH}}$$

(ii) Alkene (*A*) and (*B*) give same alcohol on hydration and thus, (*B*) can only be (Also not two groups on same carbon atom).



$$\underset{(B)}{(CH_3CH_2\cdot CH_2\cdot CH_2)(CH_3)C=CH\cdot CH_3} \xrightarrow[KMnO_4]{[O]} \underset{\text{Hexanone-2}}{\underset{(G)}{CH_3COCH_2\cdot CH_2\cdot CH_2CH_3}} + \underset{\text{Acetic acid}}{\underset{(F)}{CH_3COOH}}$$

(iii) The hydration of (*A*) and (*B*) give same alcohol



$$\underset{(A)}{(CH_3)(CH_3\cdot CH_2)C=CH\cdot CH_2\cdot CH_2\cdot CH_3} \xrightarrow{H_2O} \underset{(C)}{(CH_3)(CH_3CH_2)\underset{OH}{\underset{|}{C}}CH_2\cdot CH_2\cdot CH_2\cdot CH_3}$$

$$\underset{(B)}{(CH_3\cdot CH_2\cdot CH_2\cdot CH_2)(CH_3)C=CHCH_3} \xrightarrow{H_2O} \underset{\text{(3-Methylheptan-3-ol)}}{\underset{(C)}{(CH_3\cdot CH_2\cdot CH_2\cdot CH_2)(CH_3)\underset{OH}{\underset{|}{C}}CH_2\cdot CH_3}}$$

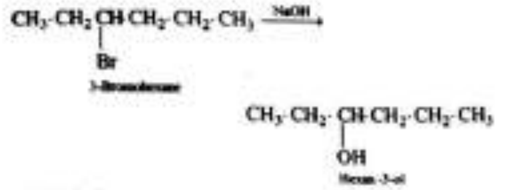
132. (1) (*A*) contains carbon and hydrogen, decolorises Br_2 in CCl_4 and so (*A*) is unsaturated hydrocarbon.

(2) $(A) \xrightarrow{HBr} \underset{\text{Bromide}}{(B)} \xrightarrow{NaOH} \underset{\text{Alcohol}}{(C)} \xrightarrow{\text{Oxidation}}$ Hexanone-3

(3) Since, oxidation of (*C*) gives ketone and thus, (*C*) should be secondary alcohol.

(4) The position of OH in (*C*) should be at '3' because hexan-3-one is formed.

(5) (*C*) is obtained by hydrolysis of (*B*) and thus, (*B*) and *C* are



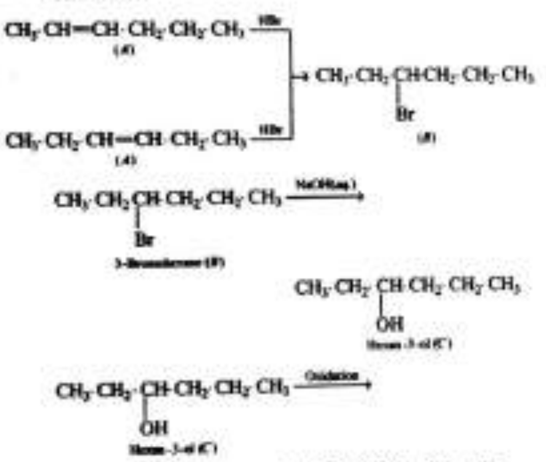
$$\underset{\text{3-Bromohexane}}{\text{CH}_3\cdot\text{CH}_2\underset{\underset{\text{Br}}{|}}{\text{CH}}\,\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{NaOH}} \underset{\text{Hexan-3-ol}}{\text{CH}_3\cdot\text{CH}_2\cdot\underset{\underset{\text{OH}}{|}}{\text{CH}}\,\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

(6) (*B*) is formed by the action of HBr on (*A*) and thus, (*A*) can be

$$\underset{(A)\ \text{Hex-2-ene}}{\text{CH}_3\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

or $$\underset{(A)\ \text{Hex-3-ene}}{\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3}$$

Reactions:



$$\underset{(A)}{\text{CH}_3\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{HBr}} \underset{(B)}{\text{CH}_3\cdot\text{CH}_2\underset{\underset{\text{Br}}{|}}{\text{CH}}\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

$$\underset{(A)}{\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{HBr}} \underset{(B)}{\text{CH}_3\cdot\text{CH}_2\underset{\underset{\text{Br}}{|}}{\text{CH}}\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

$$\underset{\text{3-Bromohexane}\ (B)}{\text{CH}_3\cdot\text{CH}_2\underset{\underset{\text{Br}}{|}}{\text{CH}}\,\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{NaOH(aq.)}} \underset{\text{Hexan-3-ol}\ (C)}{\text{CH}_3\cdot\text{CH}_2\cdot\underset{\underset{\text{OH}}{|}}{\text{CH}}\,\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

$$\underset{\text{Hexan-3-ol}\ (C)}{\text{CH}_3\cdot\text{CH}_2\cdot\underset{\underset{\text{OH}}{|}}{\text{CH}}\text{-}\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{Oxidation}} \underset{\text{Hexan-3-one}}{\text{CH}_3\cdot\text{CH}_2\cdot\underset{\underset{\text{O}}{\|}}{\text{C}}\,\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3}$$

133. (1) (*A*) reacts with HBr to give mono bromo alkane (*B*), so (*A*) is alkene.

(2) (*A*) gives same product on addition of HBr in absence and presence of peroxide and thus, (*A*) is symmetrical alkene.

(3) Now 2 g Br_2 reacts with 0.7 g of (*A*)

$\therefore$ 160 g Br_2 reacts with $\frac{0.7\times160}{2} = 56$ g of (*A*)

$\therefore$ Molar mass of alkene = 56 g mol^{-1}

or $C_nH_{2n} = 56$

$\therefore$ $n = 4$

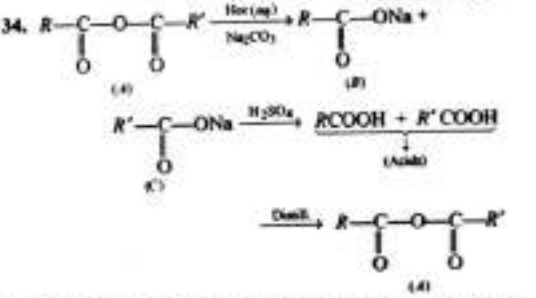
(4) Thus, alkene is C_4H_8 having structure

$$\underset{(A)}{\underset{\text{But-2-ene}}{\text{CH}_3\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_3}}$$

Reactions:

$$\underset{(A)}{\text{CH}_3\text{—CH}{=}\text{CH—CH}_3} \xrightarrow[\text{HBr}]{\text{Presence or absence of peroxide}} \underset{\text{2-Bromobutane}\ (B)}{\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_3}$$

134.



$$\underset{(A)}{R\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—O—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—}R'} \xrightarrow[\text{Na}_2\text{CO}_3]{\text{Hot (aq.)}} \underset{(B)}{R\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—ONa}} + \underset{(C)}{R'\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—ONa}} \xrightarrow{\text{H}_2\text{SO}_4} \underset{\text{(Acids)}}{\underline{R\text{COOH} + R'\text{COOH}}} \xrightarrow{\text{Distill.}} \underset{(A)}{R\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—O—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—}R'}$$

135. (i) (*A*) gives positive test with Br_2 in CCl_4 and thus, it is alkene.

(ii) Oxidation of (*A*) with alkaline $KMnO_4$ yields only one salt of an acid and thus, (*A*) is symmetrical alkene, *i.e.*, hex-3-ene.

$$\underset{(A)}{\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3}$$

Reactions:

(i) $$\underset{(A)}{\underset{\text{Hex-3-ene}}{\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3}} \xrightarrow[\text{CCl}_4]{\text{Br}_2\ \text{in}} \underset{\text{3,4-Dibromohexane}}{\text{CH}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_3}$$

(ii) $$\underset{(A)}{\text{CH}_3\text{CH}_2\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3} \xrightarrow{\text{alk. KMnO}_4} \underset{(B)\ \text{Pot. propanoate}}{\text{CH}_3\text{CH}_2\text{COOK}}$$

136. (1) Alkyne is terminal as it gives Ag salt. Let alkyne be $R\text{—C}\equiv\text{CH}$ and so formula of Ag salt is $R\text{—C}\equiv\text{C}\cdot\text{Ag}$

$\because$ 67.08 g Ag then mass of silver salt = 100

$\therefore$ 108 g Ag then mass of silver salt = $\frac{100\times108}{67.08} = 161.00$

$\therefore$ Molar mass of silver salt = 161.00 g mol^{-1}

Note : If it would have acetylene then molar mass would have been determined by 216 g Ag.

$\therefore$ $R\text{—C}\equiv\text{C}\cdot\text{Ag} = 161$

$R + 12 + 12 + 108 = 161$

$\therefore$ $R = 29$

or $C_nH_{2n+1} = 29$

$\therefore$ $n = 2$

$\therefore$ Alkyne is $\underset{\text{But-1-yne}}{\text{CH}_3\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}}$

137. (1) (*A*) decolorises Br_2 in CCl_4 and absorbs H_2 and thus, (*A*) is unsaturated molecule having double or triple bond.

(2) (*A*) gives a precipitate with ammonical Cu_2Cl_2 and thus, it has terminal alkyne linkage, *i.e.*, triple bond at corner.

(3) Molar mass of (*A*) $= \frac{22400 \times 1.49}{448} = 74.5$

(4) Since, (*A*) has Cl and one $\equiv$ bond at terminal so (*A*) may be

$$RCl \cdot C \equiv CH$$

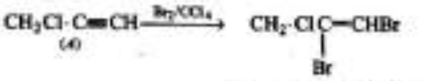
$\therefore \quad R + 35.5 + 12 + 12 + 1 = 74.5$

$\therefore \quad R = 14$

$\therefore \quad R$ is CH_2

(5) Thus, (*A*) is $CH_2Cl \cdot C \equiv CH$, *i.e.*, 3-chloropropyne

Reactions:



$$\underset{(A)}{CH_2Cl \cdot C \equiv CH} \xrightarrow{Br_2/CCl_4} CH_2 \cdot Cl\underset{\underset{Br}{|}}{C} = CHBr$$

1,2-Dibromo, 3-chloroprop-1-ene

$$\underset{(A)}{CH_2Cl \cdot C \equiv CH} \xrightarrow{H_2} \underset{\text{1-Chloropropane}}{CH_2Cl \cdot CH_2 - CH_3}$$

$$2\underset{(A)}{CH_2Cl \cdot C \equiv CH} \xrightarrow[\text{or Am. } Cu_2Cl_2]{Cu_2O} \underset{\text{Red ppt.}}{2CH_2Cl \cdot C \equiv C \cdot Cu} + H_2O$$

138. (1) (*D*) gives 2,2-dimethylpropanal and 1-butanal on ozonolysis and thus,

$$\underset{(D)}{(CH_3)_3C} - \underset{\text{(2,2-Dimethylhept-3-ene)}}{CH = CHCH_2CH_2CH_3} \xrightarrow{\text{Ozonolysis}}$$

$$(CH_3)_3C \cdot CHO + CH_3CH_2CH_2CHO$$

(2) (*D*) is formed by partial hydrogenation (in presence of Lindlar's catalyst) of (*C*) and thus, (*C*) is

$$\underset{\text{(2,2-Dimethylhept-3-yne) (C)}}{(CH_3)_3C \equiv CCH_2CH_2CH_3} \xrightarrow[\text{Lindlar's catalyst}]{H_2}$$

$$(CH_3)_3C - \underset{(D)}{CH = CHCH_2CH_2CH_3}$$

(3) (*A*) reacts with $NaNH_2/NH_3$ to give (*B*) which indicates a terminal triple bond in (*A*)

$$\underset{(A)}{C_6H_{10}} \xrightarrow[NH_3]{NaNH_2} \underset{(B)}{C_4H_9C \equiv C \cdot Na}$$

(4) (*B*) reacts with 1-chloropropane to give (*C*)

$$\underset{(B)}{C_4H_9C \equiv C \cdot Na} + Cl \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow$$

$$\underset{(C)}{C_4H_9C \equiv C \cdot CH_2 \cdot CH_2 \cdot CH_3}$$

But (*C*) is $(CH_3)_3C - C \equiv C \cdot CH_2 \cdot CH_2 \cdot CH_3$

A comparison of two structures of (*C*) suggests that (*B*) and (*A*) are

$$(CH_3)_3C - C \equiv CNa, \quad \underset{\underset{(A)}{\text{(3,3-Dimethylbut-1-yne)}}}{(CH_3)_3C - C \equiv CH}$$

139. (1) (*A*), C_6H_{10} either has one triple bond or two double bonds.

(2) Ozonolysis of (*A*) suggests that it has two double bonds.

$$\underset{(A)}{C_6H_{10}} \xrightarrow{\text{Ozonolysis}} \underset{(D)}{C_2H_4O} + \underset{(E)}{C_2H_2O_2}$$

Since, (*D*) and (*E*) are aldehydes, *i.e.*, $\underset{\text{Ethanal (D)}}{CH_3CHO}$ and $\underset{\text{Ethane-1,2-dial (E)}}{CHO \cdot CHO}$

$\therefore$ (*A*) is $\quad \underset{\text{Hexa-2,4-diene}}{CH_3CH = CH - CH = CH \cdot CH_3}$

(3) (*A*) gives (*B*) on reduction and finally gives (*C*).

$$\underset{(A)}{CH_3 \cdot CH = CH - CH = CH - CH_3} \xrightarrow{H_2}$$

$$\underset{\text{(B) Hex-2-ene}}{CH_3 \cdot CH_2 \cdot CH_2CH = CH \cdot CH_3} \xrightarrow{H_2}$$

$$\underset{\text{Hexane}}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3}$$

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH = CH \cdot CH_3 \xrightarrow{[O]}$$

$$\underset{(F)}{CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH} + CH_3COOH$$

Note : The above problem may also be given as : If acid (*F*) should have been given $C_3H_6O_2$. Then it would have been solved as :

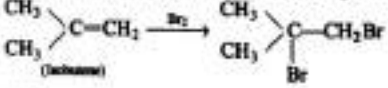
$$\underset{(A)}{CH_3 \cdot CH = CH - CH = CH - CH_3} \xrightarrow{H_2}$$

$$\underset{(B)}{CH_3 \cdot CH_2 \cdot CH = CH \cdot CH_2 \cdot CH_3} \xrightarrow{\text{Oxidation}} \underset{\underset{(F)}{\text{Propanoic acid}}}{CH_3CH_2COOH}$$

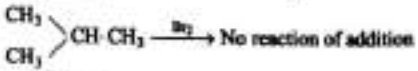
Note : Conjugated alkadienes, *i.e.*, alkenes with alternate single and double bonds, show 1 addition at 1,4 position giving rise to double bond at 2,3 positions.

$$CH_2 = CH - CH = CH_2 \xrightarrow{X_2} \underset{\underset{X}{|}}{CH_2} \cdot CH = CH - \underset{\underset{X}{|}}{CH_2}$$

140. Let isobutane be *a* g and isobutene be *b* g. Thus, $a + b = 10$



$$\underset{\text{(Isobutene)}}{(CH_3)_2C = CH_2} \xrightarrow{Br_2} (CH_3)_2\underset{\underset{Br}{|}}{C} - CH_2Br$$



$$\underset{\text{(Isobutane)}}{(CH_3)_2CH \cdot CH_3} \xrightarrow{Br_2} \text{No reaction of addition}$$

Now, $\because$ 160 g Br_2 is needed for 56 g isobutene

$\therefore$ 20 g Br_2 is needed for $\frac{56 \times 20}{160} = 7$ g

Thus, isobutene, *i.e.*, $b = 7$ g
isobutane, *i.e.*, $a = 3$ g

Now, 7 g isobutene is converted to isobutane by reduction to give $\frac{58 \times 7}{56}$ g isobutane $= 7.25$ g.

Now isobutane reacts with Br_2 to give monobromo product in light.

$$C_4H_{10} + Br_2 \longrightarrow C_4H_9Br + HBr$$

$\because$ 58 g C_4H_{10} gives product $= 137$ g C_4H_9Br

$\therefore$ $(7.25 + 3)$ g C_4H_{10} gives product

$$= \frac{137 \times 10.25}{58} \text{ g } C_4H_9Br$$

$$= \mathbf{24.21 \text{ g } C_4H_9Br}$$

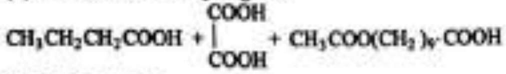
141. (a) $\underset{\text{Bombykol}}{C_{16}H_{30}O} \xrightarrow{\text{Hydrogenation}} \underset{(A)}{C_{16}H_{34}O}$

Thus, Bombykol has two double bonds or one triple bond.

(b) (i) Bombykol reacts with acetic anhydride to give an ester, thus, it has —OH group.

$$C_{16}H_{29}OH + (CH_3CO)_2O \longrightarrow \underset{\text{Ester}}{C_{16}H_{29}OOC \cdot CH_3} + CH_3COOH$$

(ii) The ester on ozonolysis gives



$$CH_3CH_2CH_2COOH + \begin{matrix} COOH \\ | \\ COOH \end{matrix} + CH_3COO(CH_2)_9 \cdot COOH$$

Therefore, ester is

$CH_3CH_2CH_2 \cdot CH{=}CH{-}CH{=}CH(CH_2)_9 \cdot OOC \cdot CH_3$

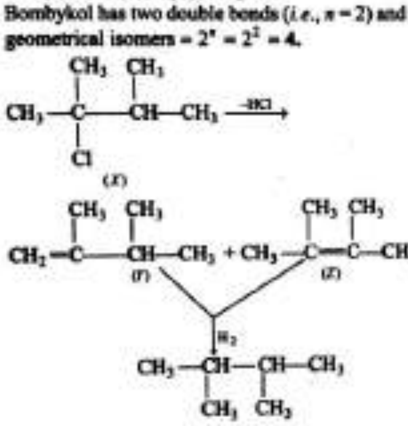
Thus, Bombykol is

$CH_3CH_2CH_2CH{=}CH{-}CH{=}CH(CH_2)_8CH_2OH$

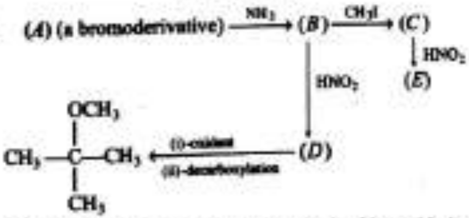
and (A) is $CH_3(CH_2)_{14}CH_2OH$

Bombykol has two double bonds (*i.e.*, $n = 2$) and thus, it has geometrical isomers $= 2^n = 2^2 = 4$.

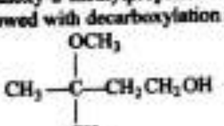
142.



143.

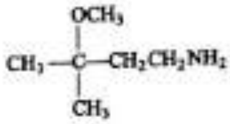


(i) 2-methoxy-2-methylpropane is obtained by oxidation of (D) followed with decarboxylation and thus, (D) is



$$CH_3-\overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2CH_2OH$$

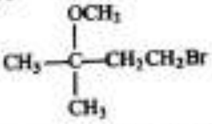
(ii) (D) is formed by the action of HNO_2 on (B) and thus, (B) is



$$CH_3-\overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2CH_2NH_2$$

(iii) (B) is formed by the action of NH_3 over (A) a bromoderivative

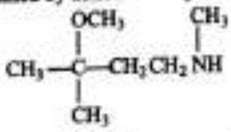
∴ (A) is



$$CH_3-\overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2CH_2Br$$

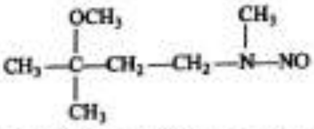
(iv) (C) is obtained by action of CH_3I over (B)

∴ (C) is



$$CH_3-\overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2CH_2\overset{\displaystyle CH_3}{NH}$$

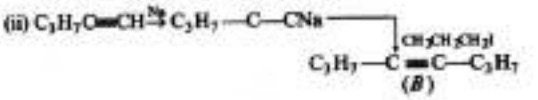
∴ (E) is



$$CH_3-\overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_2-\overset{\displaystyle CH_3}{N}-NO$$

144. (i) (A) reacts with sodium in ammonia and thus, it is terminal alkyne, *i.e.*, $C_3H_7C \equiv CH$

(ii)



$$C_3H_7C{\equiv}CH \xrightarrow{Na} C_3H_7-C{\equiv}CNa \xrightarrow{CH_3CH_2CH_2I} \underset{(B)}{C_3H_7-C{\equiv}C-C_3H_7}$$

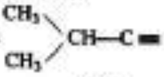
(iii) $C_3H_7-C \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} C_3H_7-\underset{(C)}{CO}-CH_3$

(iv) $C_3H_7-C \equiv C-CH_2-CH_2-CH_3 \xrightarrow[KMnO_4]{[O]}$

$$\underset{(D)}{CH_3CH_2CH_2COOH} + \underset{(E)}{C_3H_7COOH}$$

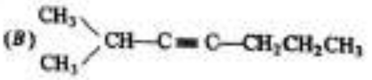
Since, (D) and (E) are isomers and thus, (E) is $(CH_3)_2CH \cdot COOH$

∴ (A) is



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH-C \equiv CH;$$

(B)



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH-C \equiv C-CH_2CH_2CH_3$$

145. (A) is ozone as it reacts with but-2-ene to show ozonolysis

$$CH_3-CH=CH-CH_3 + \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2CH_3CHO$$

The deep red coloured compound is potassium ozonide, KO_3 and gas is O_2

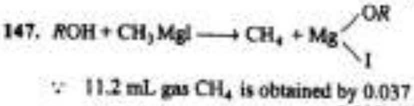
$$\underset{(A)}{5O_3} + 2KOH \longrightarrow \underset{(B)}{2KO_3} + H_2O(v) + \underset{(C)}{5O_2}$$

146. The alcohol is readily oxidised by dil. $KMnO_4$ and thus, primary alcohol, *i.e.*, *n*-butanol. Tertiary alcohols are not oxidized by dil. $KMnO_4$.

$$CH_3CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2CHO$$

$$\downarrow [O]$$

$$CH_3CH_2CH_2COOK + \underset{\text{(Brown ppt.)}}{MnO_2} + KOH$$

147. 

$$ROH + CH_3MgI \longrightarrow CH_4 + Mg\begin{matrix}OR\\ I\end{matrix}$$

∵ 11.2 mL gas CH_4 is obtained by 0.037 g ROH

∴ 22400 mL gas is obtained by $\frac{0.037 \times 22400}{11.2} = 74$ g

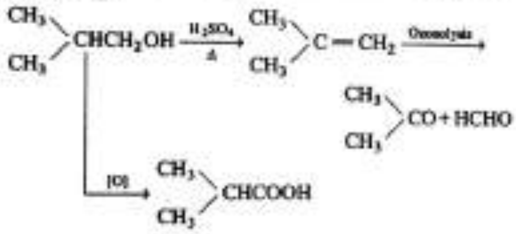
∴ Molar mass of $ROH = 74$ g mol^{-1}

Since, ROH on oxidation gives acid of same number of carbon atoms and thus, ROH is primary alcohol, *i.e.*, $C_nH_{2n+1}CH_2OH$.

∴ $12n + 2n + 1 + 12 + 2 + 16 + 1 = 74$

∴ $n = 3$

∴ Alcohol is $C_3H_7CH_2OH$. The reactions suggest the structure as



148. The given reactions suggest the following

(i) $(A) \xrightarrow{\text{Ozonolysis}} \underset{(B)}{RCHO} + R'\underset{(C)}{CHO}$

(B) cannot be HCHO however it gives Cannizzaro's reaction because then (A) must have $R'C{=}CH_2$ structure which will not give geometrical isomer.

(ii) $\underset{(X)}{C_7H_{12}} \xrightarrow[CH_3COOH]{B_2H_6} \underset{(A)}{C_7H_{14}}$

The reaction of alkyne to give alkene takes place through vinylic boranes as intermediate and *cis* alkene predominates.

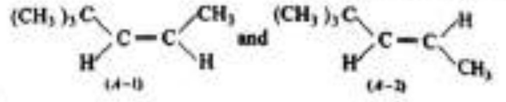
(iii) Thus, (A) is

$$\underset{(A)}{(CH_3)_3CCH{=}CHCH_3} \xrightarrow{\text{Ozonolysis}} \underset{(B)}{(CH_3)_3C\cdot CHO} + \underset{(C)}{CH_3CHO}$$

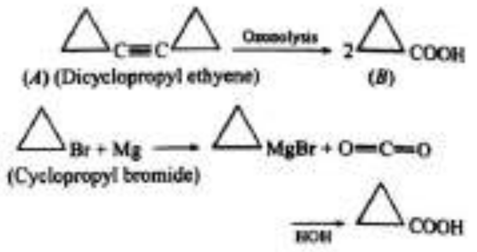
(B) does not have α-H atom and will show Cannizzaro's reaction.

(iv) (X) is therefore $(CH_3)_3C\cdot C{\equiv}C\cdot CH_3$

(v) Two geometrical isomers of (A) are



149.



150. (i) (A) reacts with H_2 to give (B) and (C) successively and thus, it has either two double bonds or one triple bond.

(ii) Ozonolysis of (A) gives (D), an aldehyde C_2H_4O, *i.e.*, CH_3CHO and (E) $C_2H_2O_2$, *i.e.*, $\begin{matrix}CHO\\ |\\ CHO\end{matrix}$ and thus,

$$CH_3\cdot CH \underset{(A)}{=} CH\cdot CH = CH\cdot CH_3 \xrightarrow{\text{Ozonolysis}} 2CH_3CHO + \begin{matrix}CHO\\ |\\ CHO\end{matrix}$$

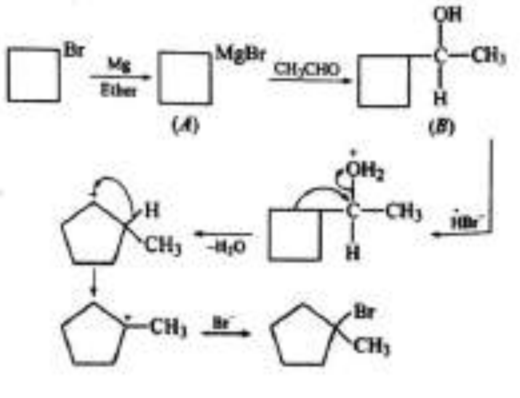
$$H_2 \downarrow (I)$$

$$CH_3\cdot CH_2\cdot CH \underset{(B)}{=} CH\cdot CH_2\cdot CH_3 \xrightarrow[(II)]{H_2} \underset{\text{Hexane}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3}$$

(iii) $CH_3\cdot \underset{(B)}{CH_2}\cdot CH = \underset{\text{(Hexene-3)}}{CH\cdot CH_2}\cdot CH_3 \xrightarrow{\text{Ozonolysis}} 2\underset{\text{Propanal}}{CH_3\cdot CH_2\cdot CHO}$

Note : Addition of H_2 in I case is a characteristic reaction of conjugated (alternate single and double bond) alkadienes where it occurs at 1,4-position and double bond is shifted to 2,3 position.

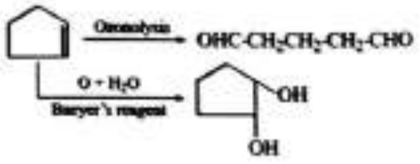
151.



152. Unsaturated ether (divinyl ether) will decolourise Br_2 water or Baeyer's reagent.

153. V < IV < III < II < I; The reactivity for E_2 dehydrohalogenation depends chiefly on the stability of the alkenes being formed.

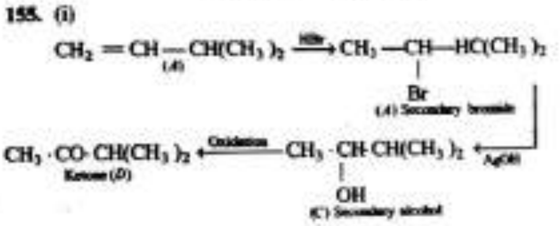
154. (a)



(b) NaI reacts with *R*Cl to form *R*I. The alkyl iodides having larger C—I bond length are more reactive than *R*Cl and thus readily hydrolysis.

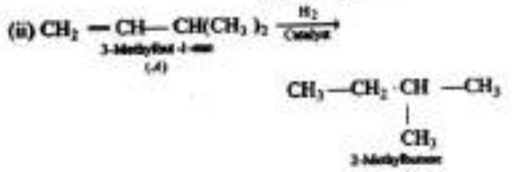
$$RCl + NaI \longrightarrow RI + NaCl$$
$$RI + HOH \longrightarrow ROH + HI$$

155. (i)



$$CH_2=\underset{(A)}{CH}-CH(CH_3)_2 \xrightarrow{HBr} CH_3-\underset{\underset{(A)\ \text{Secondary bromide}}{Br}}{CH}-HC(CH_3)_2$$
$$\underset{\text{Ketone }(D)}{CH_3\cdot CO\cdot CH(CH_3)_2} \xleftarrow{\text{Oxidation}} CH_3\cdot\underset{\underset{(C)\ \text{Secondary alcohol}}{OH}}{CH}\cdot CH(CH_3)_2 \xleftarrow[AgOH]{}$$

(ii)



$$\underset{\underset{(A)}{\text{3-Methylbut-1-ene}}}{CH_2=CH-CH(CH_3)_2} \xrightarrow[\text{Catalyst}]{H_2} \underset{\text{2-Methylbutane}}{CH_3-CH_2\cdot\underset{CH_3}{\underset{|}{CH}}-CH_3}$$

156. (1) Molar mass of bromo-derivative

$$(A)=\frac{0.369\times 22400}{67.2}=123$$

(2) Let bromo-derivative be *R*Br

Then, molar mass of $R = 123 - 80 = 43$

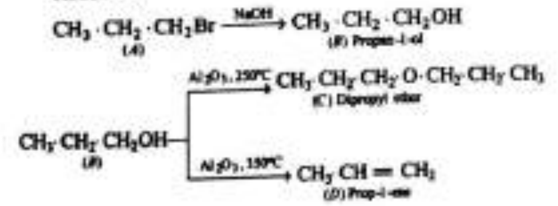
$\therefore$ $C_nH_{2n+1} = 43$

$\therefore$ $n = 3,$

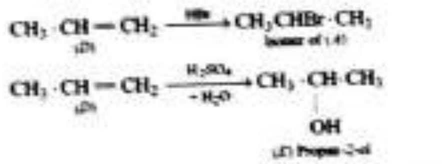
Thus, bromo-derivative is C_3H_7Br

Reactions:

$$\underset{(A)}{CH_3\cdot CH_2\cdot CH_2Br} \xrightarrow{NaOH} \underset{(B)\ \text{Propan-1-ol}}{CH_3\cdot CH_2\cdot CH_2OH}$$



$$\underset{(B)}{CH_3\cdot CH_2\cdot CH_2OH} \xrightarrow{Al_2O_3,\ 250^\circ C} \underset{(C)\ \text{Dipropyl ether}}{CH_3\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot CH_3}$$
$$\underset{(B)}{CH_3\cdot CH_2\cdot CH_2OH} \xrightarrow{Al_2O_3,\ 350^\circ C} \underset{(D)\ \text{Prop-1-ene}}{CH_3\cdot CH=CH_2}$$

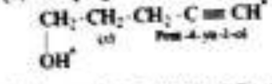


$$CH_3\cdot\underset{(D)}{CH}=CH_2 \xrightarrow{HBr} \underset{\text{Isomer of }(A)}{CH_3CHBr\cdot CH_3}$$
$$CH_3\cdot\underset{(D)}{CH}=CH_2 \xrightarrow[-H_2O]{H_2SO_4} CH_3\cdot\underset{\underset{(E)\ \text{Propan-2-ol}}{OH}}{CH}\cdot CH_3$$

157. (1) (*x*), C_5H_8O does not react with Lucas reagent appreciably at room temperature but gives precipitate with ammoniacal $AgNO_3$ and thus, (*x*) has terminal alkyne linkage as well as primary alcoholic gp.

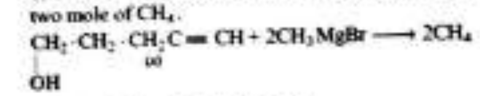
(2) (*x*) on hydrogenation and then reacting with HI gives pentane and thus, (*x*) is straight chain compound.

(3) Keeping in view of the above facts (*x*) may be



$$\underset{\underset{OH^*}{|}}{CH_2}\cdot\underset{(x)}{CH_2}\cdot CH_2\cdot \underset{\text{Pent-4-yn-1-ol}}{C\equiv CH^*}$$

(4) Its reaction with MeMgBr gives CH_4. (It has two acidic or active H^*-atoms) and thus, 1 mole of (*x*) will give two mole of CH_4.



$$\underset{\underset{OH}{|}}{CH_2}\cdot CH_2\cdot\underset{(x)}{CH_2}C\equiv CH + 2CH_3MgBr \longrightarrow 2CH_4$$

$\because$ 84 g (*x*) gives 2×22.4 litre CH_4

$\therefore$ 0.42 g (*x*) will give $\dfrac{2\times 22.4\times 0.42}{84}=$ **224 mL CH_4**

Given fact is confirmed.

158. $C_2H_5OH + CH_3CHO = 0.535\ g$

Let *a* g C_2H_5OH and *b* g CH_3CHO be present in mixture

$\therefore$ $a + b = 0.535$

Now mixture reacts with Fehling solution to give a red precipitate, which suggests a characteristic reaction for aldehyde, *i.e.*,

$$CH_3CHO + \underset{\text{Fehling solution}}{2CuO} \longrightarrow CH_3COOH + \underset{\text{Red ppt.}}{Cu_2O}$$

$\because$ 143.6 g Cu_2O is given by 44 g CH_3CHO

$\therefore$ 1.2 g Cu_2O is given by $\dfrac{44\times 1.2}{143.6}=0.368\ g\ CH_3CHO$

$\therefore$ $b = 0.368\ g$

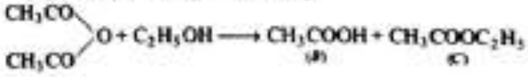
$\therefore$ % of $CH_3CHO=\dfrac{0.368}{0.535}\times 100=$ **68.78%**

159. The given statements suggest the following :

(i) (*B*) is acetic acid since it reacts with $Ca(OH)_2$ which on dry distillation gives (*E*) C_3H_6O, *i.e.*, acetone.

$$CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca$$
$$(CH_3COO)_2Ca \xrightarrow[\text{distillation}]{\text{dry}} \underset{(E)}{CH_3COCH_3} + CaCO_3$$

(ii) (*A*) reacts with ethanol to give (*B*), *i.e.*, CH_3COOH and (*C*), thus, (*A*) is $CH_3COOOCCH_3$



$$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O + C_2H_5OH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

(iii) (*C*) on acid hydrolysis gives (*B*), *i.e.*, CH_3COOH and (*D*); oxidation of (*D*) gives (*B*). Thus,

$$CH_3COOC_2H_5 + HOH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

$$\underset{(D)}{C_2H_5OH} \xrightarrow{[O]} \underset{(B)}{CH_3COOH}$$

160. (1) (*A*) gives Lucas test within 5 minutes and thus, (*A*) is secondary alcohol.

(2) (*A*) contains one O-atom and thus, only one OH gp. in (*A*). Thus, (*A*) is $C_nH_{2n+1}OH$.

(3) $\because$ 1120 mL H_2 is given by the action of Na over 6 g (*A*).

$$\therefore \quad 11200 \quad " \quad " \quad \frac{6 \times 11200}{1120} = 60 g\ (A)$$

$$\therefore \qquad \text{Molar mass of } (A) = 60 \text{ g mol}^{-1}$$

Since, one mole of an alcohol having one OH gp. gives 11200 mL H_2 at STP with Na.

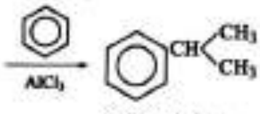
(4) Thus, $\qquad C_nH_{2n+1}OH = 60$

$\therefore \qquad n = 3$

or (*A*) is C_3H_7OH; being secondary alcohol its formula is $CH_3 \cdot CHOH \cdot CH_3$

Reactions:

$$\underset{\substack{(A)\\ \text{(Propan-2-ol)}}}{CH_3 \cdot CHOH \cdot CH_3} \xrightarrow{PBr_3} \underset{\substack{(B)\\ \text{(2-Bromopropane)}}}{CH_3CHBr \cdot CH_3}$$



(*C*) 2-Phenylpropane

This is Friedel-Crafts reaction.

161. (1) Molar mass of $A = \frac{1000 \times K' \times w}{\Delta T \times W}$

$$= \frac{1000 \times 40 \times 0.0088}{8 \times 0.5} = 88 \text{ g mol}^{-1}$$

(2) For empirical formula

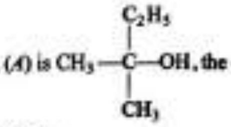
Element	**%**	**Relative no. of atoms**	**Simplest ratio**
C	68.18	5.68	4.8≃5
H	13.16	13.16	11.2≃11
O	18.66	1.17	1 1

$\therefore$ Empirical formula of (*A*) = $C_5H_{11}O$; Empirical formula mass = 87 but molar mass = 88 and therefore, molecular formula = $C_5H_{12}O$.

(3) (*A*) reacts with acetyl chloride and gives H_2 with Na so, (*A*) is alcohol.

(4) (*A*) reacts with Lucas reagent ($HCl + ZnCl_2$), a dense oily layer separated immediately hence, (*A*) is a tertiary alcohol.

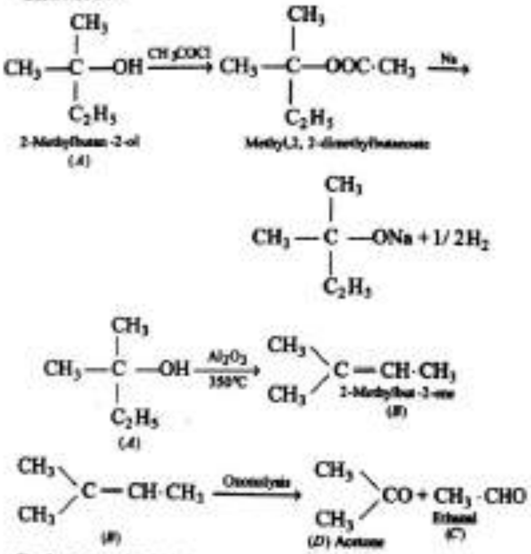
(5) Thus, (*A*) is



$$CH_3-\overset{\overset{\large C_2H_5}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH$$

, the only tertiary alcohol of 5 carbon atoms.

Reactions :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OH \xrightarrow{CH_3COCl} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OOC \cdot CH_3 \xrightarrow{Na} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-ONa + 1/2H_2$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OH \xrightarrow[350°C]{Al_2O_3} (CH_3)_2C{=}CH \cdot CH_3$$

$$(CH_3)_2C{=}CH \cdot CH_3 \xrightarrow{\text{Ozonolysis}} (CH_3)_2CO + CH_3 \cdot CHO$$

Both (*C*) and (*D*) give test with carbonyl reagents such as HCN, $NaHSO_3$ forming addition products but only (*C*) gives test with Fehling solution. Thus, (*C*) is aldehyde and (*D*) is ketone, each having $CH_3CO—$ unit.

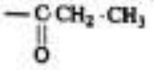
162. (i) (*X*) forms semicarbazone and thus possesses carbonyl gp.

$$>C{=}O + H_2N \cdot NHCONH_2 \longrightarrow\ >C{=}N \cdot NHCONH_2$$

(ii) It does not give Tollen's reagent test and thus it is ketone.

(iii) It does not give iodoform test and thus it is not methyl ketone.

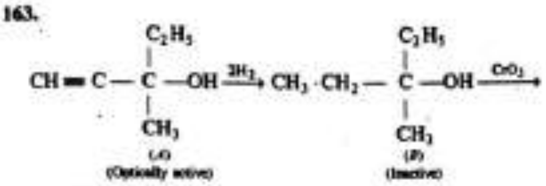
(iv) Keeping in view of the above facts and molecular formula; (*X*) is



$$C_6H_5-\underset{\underset{O}{\|}}{C}CH_2 \cdot CH_3$$

(v) This on reduction will give *n*-propyl benzene.

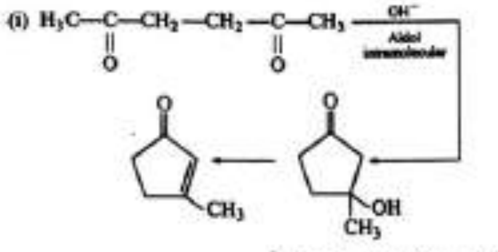
163.



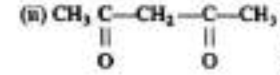
$$\mathrm{CH{\equiv}C-\overset{\displaystyle C_2H_5}{\underset{\displaystyle \underset{\substack{(A)\\(Optically\ active)}}{CH_3}}{C}}-OH \xrightarrow{2H_2} CH_3\cdot CH_2-\overset{\displaystyle C_2H_5}{\underset{\displaystyle \underset{\substack{(B)\\(Inactive)}}{CH_3}}{C}}-OH \xrightarrow{CrO_3}}$$

Resistant to oxidation as it is tertiary alcohol.

164. (i)



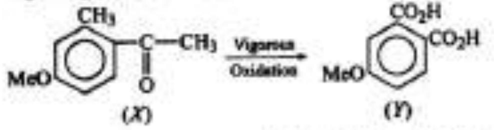
(ii)



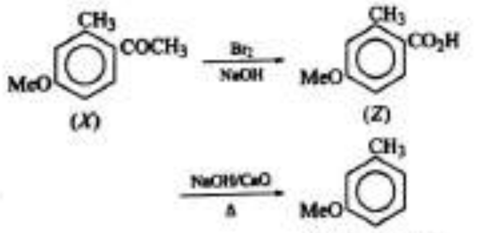
$$\mathrm{CH_3\,\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3}$$

[It would merely form the stable carbonion and react no further. The C^1 carbanion does not add to C^4 because a strained four-membered ring would result.]

165. The statements provides the following informations regarding (X), (Y) and (Z).

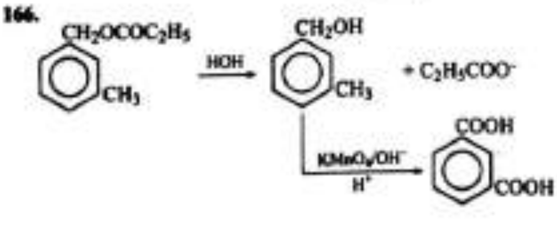


$\xrightarrow{\Delta}$ Can form anhydride



3-Methyl anisole

166.



167. $\mathrm{C_6H_5CHOH\cdot CH_3 \xrightarrow[\text{Iodoform reaction (ii) HOH}]{\text{(i) } I_2 + NaOH} \underset{\substack{(D)\\ White}}{C_6H_5COOH} + \underset{\substack{(E)\\ Yellow}}{CHI_3}}$

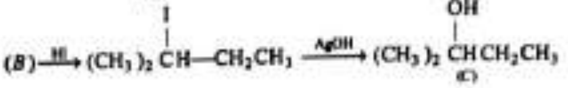
168. The reactions given are :

$$\mathrm{\underset{(A)}{C_5H_{11}OH} \xrightarrow[250°C]{Al_2O_3} \underset{(B)}{C_5H_{10}} \xrightarrow[\text{(ii) AgOH}]{\text{(i) HI}} \underset{\substack{(C)\\ \text{(an isomer of } A)}}{C_5H_{11}OH}}$$

$$\mathrm{C_5H_{11}OH \xrightarrow[150°C]{Al_2O_3} \underset{(B)}{C_5H_{10}} \xrightarrow[H_2O_2,\,OH^-]{B_2H_6} (A)}$$

This is possible only when (A) is $\mathrm{(CH_3)_2CHCHOHCH_3}$.

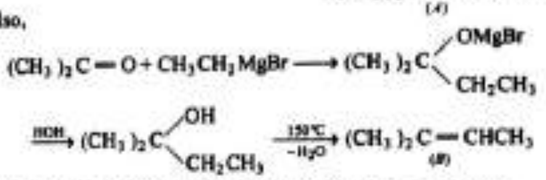
$$\mathrm{\underset{(A)}{(CH_3)_2CHCHOHCH_3} \xrightarrow[250°C]{Al_2O_3} \underset{(B)}{(CH_3)_2CH{=}CHCH_3}}$$



$$\mathrm{(B) \xrightarrow{HI} (CH_3)_2\overset{\overset{\displaystyle I}{|}}{C}H-CH_2CH_3 \xrightarrow{AgOH} (CH_3)_2\underset{(C)}{\overset{\overset{\displaystyle OH}{|}}{C}H}CH_2CH_3}$$

$$\mathrm{(C) \xrightarrow[150°C]{Al_2O_3} (CH_3)_2CH{=}CHCH_3 \xrightarrow[B_2H_6,\,H_2O_2]{OH^-} \underset{(A)}{(CH_3)_2CHCHOHCH_3}}$$

Also,



$$\mathrm{(CH_3)_2C{=}O + CH_3CH_2MgBr \longrightarrow (CH_3)_2C\begin{smallmatrix} OMgBr \\ CH_2CH_3 \end{smallmatrix}}$$

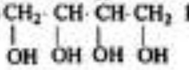
$$\mathrm{\xrightarrow{HOH} (CH_3)_2C\begin{smallmatrix} OH \\ CH_2CH_3 \end{smallmatrix} \xrightarrow[-H_2O]{150°C} \underset{(B)}{(CH_3)_2C{=}CHCH_3}}$$

169. (i) (A) undergoes acetylation and thus, contains OH gps.

$$\mathrm{-OH \xrightarrow{CH_3COCl} -OOCCH_3 + HCl}$$

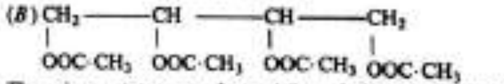
(ii) Presence of one OH gp. enhances $\mathrm{C_2H_2O}$ structure in molecule. Since, (B) shows an increase in $\mathrm{4(C_2H_2O)}$ units and thus, (A) has four OH gps.

(iii) Thus, (A) is



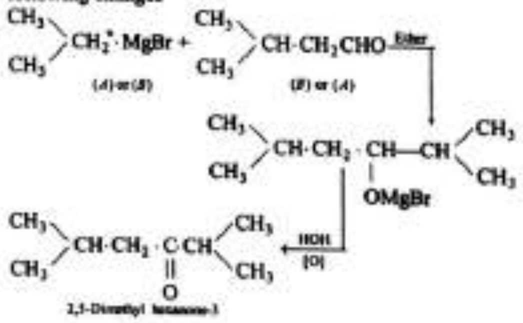
$$\mathrm{\underset{OH}{\underset{|}{CH_2}}\cdot\underset{OH}{\underset{|}{CH}}\cdot\underset{OH}{\underset{|}{CH}}\cdot\underset{OH}{\underset{|}{CH_2}}}$$

Butan-1,2,3,4-tetra-ol



$$\mathrm{(B)\ \underset{OOC\cdot CH_3}{\underset{|}{CH_2}}-\underset{OOC\cdot CH_3}{\underset{|}{CH}}-\underset{OOC\cdot CH_3}{\underset{|}{CH}}-\underset{OOC\cdot CH_3}{\underset{|}{CH_2}}}$$

170. The given statement about (A) and (B) suggests the following changes



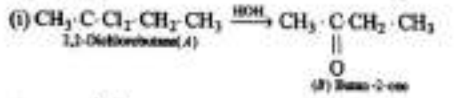
2,3-Dimethyl hexanone-3

171. (i) (*B*) reacts with hydroxyl amine and thus, (*B*) has carbonyl gp. *i.e.*, $>C=O$ gp. either ketonic ($>C=O$) or aldehyde ($-\underset{\underset{H}{|}}{C}=O$) gp.

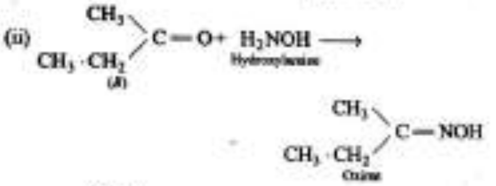
(ii) (*B*) gives negative test with Tollen's reagent and thus, (*B*) is ketone.

(iii) (*B*) is obtained by hydrolysis of (*A*) and thus, both Cl-atoms should be on same carbon atom, *i.e.*, (*A*) must be gem dihalide as well as not on corners. Thus, only possibility of (*A*) is $CH_3\cdot CCl_2\cdot CH_2\cdot CH_3$.

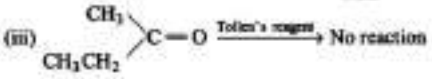
Reactions :



$$\text{(i)}\ \underset{\text{2,2-Dichlorobutane}(A)}{CH_3\cdot C\cdot Cl_2\cdot CH_2\cdot CH_3} \xrightarrow{HOH} \underset{(B)\ \text{Butan-2-one}}{CH_3\cdot \underset{\underset{O}{\|}}{C}\cdot CH_2\cdot CH_3}$$



$$\text{(ii)}\ \underset{(B)}{\begin{matrix}CH_3\diagdown\\ CH_3\cdot CH_2\diagup\end{matrix}}C=O + \underset{\text{Hydroxylamine}}{H_2NOH} \longrightarrow \underset{\text{Oxime}}{\begin{matrix}CH_3\diagdown\\ CH_3\cdot CH_2\diagup\end{matrix}C-NOH}$$



$$\text{(iii)}\ \begin{matrix}CH_3\diagdown\\ CH_3CH_2\diagup\end{matrix}C=O \xrightarrow{\text{Tollen's reagent}} \text{No reaction}$$

172. For empirical formula

$C = 40.7/12$	$= 3.39$	1
$H = 5.1/1$	$= 5.1$	1.5
$O = 54.4/16$	$= 3.4$	1.0

∴ Empirical formula of acid is $C_2H_3O_2$

$$\frac{\text{mass of Ag}}{\text{E. mass of Ag}} = \frac{\text{mass of acid salt}}{\text{E. mass of acid salt}}$$

∴ E. mass of acid salt = $(100 \times 108)/65.1 = 165.89$

∴ E. mass of acid $165.89 - 108 + 1 = 58.89$

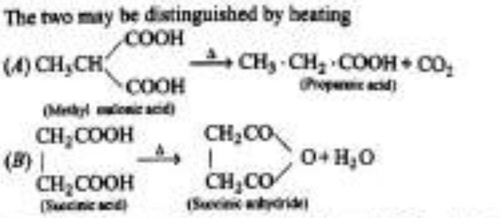
∵ Molar mass of ethyl ester is 174 and thus, acid is dibasic because molar mass of C_2H_5 gp. is only 29.

Thus, Molar mass of acid = $58.89 \times 2 = 177.78$

∴ Molecular formula of acid = $(C_2H_3O_2)_2 = C_4H_6O_4$

Thus, acid (*A*) is $CH_3\cdot CH\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}$; the isomer of (*A*) may be $\begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix}$ or *vice-versa*

The two may be distinguished by heating



$$(A)\ \underset{\text{(Methyl malonic acid)}}{CH_3CH\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}} \xrightarrow{\Delta} \underset{\text{(Propanoic acid)}}{CH_3\cdot CH_2\cdot COOH} + CO_2$$

$$(B)\ \underset{\text{(Succinic acid)}}{\begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix}} \xrightarrow{\Delta} \underset{\text{(Succinic anhydride)}}{\begin{matrix}CH_2CO\diagdown\\ |\\ CH_2CO\diagup\end{matrix}}O + H_2O$$

173. (i) $C_4H_8O_2$ reacts with $NaHCO_3$ to liberate CO_2 and so it contains —COOH group, *i.e.*, (*A*) is C_3H_7COOH.

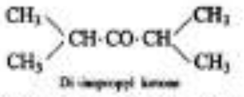
$$\text{(ii)}\ \underset{(A)}{C_3H_7COOH} \xrightarrow{NaOH + CaO} \underset{\text{Propane}}{C_3H_8} + Na_2CO_3$$

Thus, (*A*) may be

$$\underset{\text{Butanoic acid}}{\underset{(I)}{CH_3\cdot CH_2\cdot CH_2COOH}} \quad \text{or} \quad \underset{\text{2-Methylpropanoic acid}}{CH_3\cdot \underset{\underset{CH_3}{|}}{CH}\cdot COOH}\ \text{(II)}$$

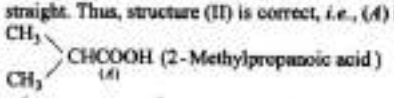
Since, both gives propane on decarboxylation.

(iii) However, $C_8H_{14}O_4Ca$, *i.e.*, Ca salt of acid on heating gives

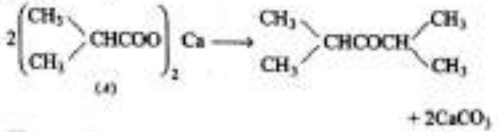


$$\underset{\text{Di-isopropyl ketone}}{\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CH\cdot CO\cdot CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}}$$

Di-isopropyl ketone and thus, chain in acid is also not straight. Thus, structure (II) is correct, *i.e.*, (*A*) is



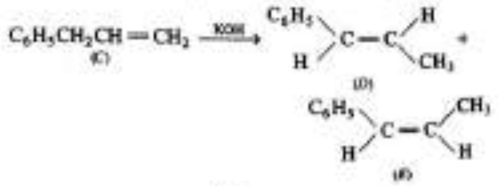
$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}\underset{(A)}{CHCOOH}\ \text{(2-Methylpropanoic acid)}$$



$$2\left(\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CHCOO\right)_2 Ca \longrightarrow \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CHCOCH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} + 2CaCO_3$$

174. The reactions suggest as :

$$\underset{(B)}{CH_2=CH\cdot CH_2X} + \underset{(A)}{C_6H_5MgX} \longrightarrow \underset{(C)}{C_6H_5CH_2\cdot CH=CH_2}$$



$$\underset{(C)}{C_6H_5CH_2CH=CH_2} \xrightarrow{KOH} \underset{(D)}{\begin{matrix}C_6H_5\diagdown\\ H\diagup\end{matrix}C=C\begin{matrix}\diagup H\\ \diagdown CH_3\end{matrix}} + \underset{(E)}{\begin{matrix}C_6H_5\diagdown\\ H\diagup\end{matrix}C=C\begin{matrix}\diagup CH_3\\ \diagdown H\end{matrix}}$$

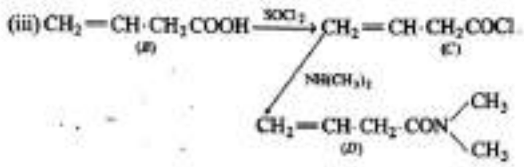
$$\underset{(C)}{C_6H_5CH_2CH=CH_2} \xrightarrow[\text{Peroxide}]{HBr} C_6H_5CH_2CH_2\cdot CH_2Br$$

175. (i) (*A*) $C_4H_8O_3$ loses its optical activity on strong heating and gives (*B*) $C_4H_6O_2$. Thus, (*A*) may be $CH_3\cdot CH_2CHOH\cdot COOH$ or $CH_3\cdot CHOH\cdot CH_2COOH$.

(ii) Since, (*B*) is $C_4H_6O_2$ and thus (*A*) is β-hydroxy acid and not α-hydroxy acid because only β-hydroxy acids lose H_2O on heating.

Thus, (*A*) is

$$\underset{(A)}{CH_3\cdot CHOH\cdot CH_2COOH} \xrightarrow{\Delta} CH_2 = CH\cdot CH_2\cdot COOH$$



$$\text{(iv)}\ \underset{(A)}{CH_3\cdot CHOH\cdot CH_2COOH} \xrightarrow{[O]} \underset{(E)}{CH_3\cdot CO\cdot CH_2COOH}$$

$$(E) \xrightarrow{\text{Decarboxylation}} \underset{(F)}{CH_3COCH_3} \xrightarrow{\text{Zn/HCl}} \underset{(G)}{CH_3CH_2\cdot CH_3}$$

176. (i) (*A*) C_5H_8O adds one Br_2 molecule and thus, has one double bond.

(ii) It forms phenyl hydrazone with phenyl hydrazine and thus, carbonyl group is present in (*A*).

(iii) (*A*) does not reduce Tollen's reagent so carbonyl group is ketone and not aldehyde.

(iv) Ozonolysis of (*A*) gives CH_3CHO and $C_3H_4O_2$ and thus, in consideration of above facts (*A*) is

$$\underset{(A)}{CH_3CH = CH\cdot COCH_3} \xrightarrow{\text{Ozonolysis}} CH_3CHO + \underset{\substack{\downarrow \\ CH_3CHO + CO}}{CH_3COCHO}$$

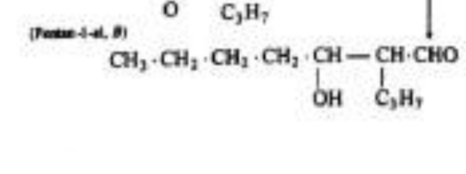
Note : α-keto aldehydes lose CO moderately to form aldehydes.

177. (i) $C_5H_{10}O$ has two isomers (*A*) and (*B*). Molecular formula suggests that they may be carbonyl compounds.

(ii) (*A*) on treating with NaOH(*aq.*) gives 2,2-dimethylpropanol and 2,2-dimethylpropanoic acid salts. Thus, (*A*) is an aldehyde lacking α-C-atom; since this is Cannizzaro's reaction.

$$\underset{\substack{\text{2, 2-Dimethylpropanal} \\ (A)}}{(CH_3)_3\cdot C\cdot CHO} \xrightarrow{\text{NaOH}} (CH_3)_3\cdot C\cdot CH_2OH + (CH_3)_3\cdot C\cdot COONa$$

(iii) Isomer (*B*) reacts with NaOH to show aldol condensation product 3-hydroxy-2-propylheptanal and thus, (*B*) is pentanal-1, as condensation occurs at α-carbon atom.



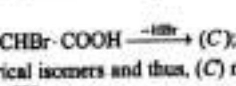
$$\underset{\text{(Pentan-1-al, B)}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot \underset{\underset{O}{\|}}{C}H} + \underset{\underset{C_3H_7}{|}}{CH_2}\cdot CHO \xrightarrow{\text{NaOH (aq)}} CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot \underset{\underset{OH}{|}}{CH} - \underset{\underset{C_3H_7}{|}}{CH}\cdot CHO$$

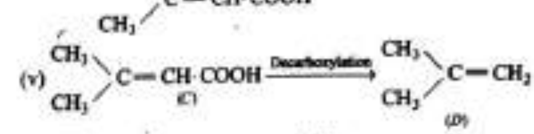
178. (i) (*A*) is an acid showing HVZ reaction in presence of $P + Br_2$. It suggests that (*A*) is $R\cdot CH_2\cdot COOH$.

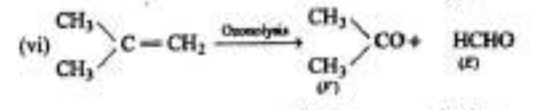
(ii) $R{-}CH_2\cdot COOH \xrightarrow{Br_2/P} RCHBr\cdot COOH$ where *R* is C_3H_7.

(iii) $RCHBrCOOH$ has asymmetric C-atom represented by C*.

(iv) $RCHBr\cdot COOH \xrightarrow{-HBr} (C)$; since *C* has not geometrical isomers and thus, (*C*) may be



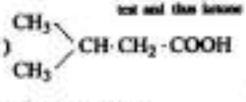




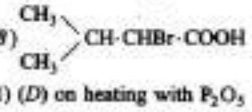
Negative Schiff's reagent test and thus ketone

Positive Schiff's reagent test and thus aldehyde

(vii) Thus, (*A*)



(*B*)



179. (1) (*D*) on heating with P_2O_5 gives 2-methylpropannitrile and so, (*D*) is $\underset{\text{2-Methylpropanamide}}{(CH_3)_2CH\cdot CONH_2}$

$$\underset{(D)}{(CH_3)_2CH\cdot CONH_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{2-Methylpropanenitrile}}{(CH_3)_2CH\cdot CN}$$

(2) (*D*) is formed by heating the compound (*C*), whereas (*C*) is formed by the action of (*B*) over NH_3. Thus, (*B*) is an acid and (*C*) is its ammonium salt.

$$\underset{\substack{(B) \\ \text{2-Methylpropanoic acid}}}{(CH_3)_2CH\cdot COOH} + NH_3 \longrightarrow \underset{\substack{(C) \\ \text{2-Methylammonium-} \\ \text{propanoate}}}{(CH_3)_2CH\cdot COONH_4} \longrightarrow \underset{(D)}{(CH_3)_2CH\cdot CONH_2}$$

(3) Acid (*B*) is formed by the hydrolysis of (*A*) hence all the three halogens must be present on terminal C-atom. Therefore, (*A*) is

$$\underset{\substack{(A) \\ \text{1, 1, 1-Trichloro,} \\ \text{2-methylpropane}}}{(CH_3)_2CH\cdot CCl_3} \xrightarrow{\text{KOH (aq)}} \underset{(B)}{(CH_3)_2CH\cdot COOH}$$

180. (1) $C_3H_6O_2$ has two isomers (*A*) and (*B*). The molecular formula suggests, that they may be an acid or ester.

(2) (*B*) reacts with $NaHCO_3$ whereas (*A*) does not do so, therefore, (*B*) is acid and (*A*) is ester.

$\underset{\text{(Propanoic acid) }(B)}{CH_3CH_2COOH}$ $\underset{(A)}{HCOOC_2H_5}$ or $\underset{(A)}{CH_3COOCH_3}$

(3) (*A*) on reacting with NaOH gives (*C*) and (*D*); (*D*) gives iodoform test and thus, ester is $HCOOC_2H_5$.

$$\underset{\substack{(A)\\ \text{Ethyl formate}}}{HCOOC_2H_5} \xrightarrow{NaOH} \underset{(C)}{HCOONa} + \underset{\substack{(D),\ \text{Ethanol}\\ \text{Gives iodoform test}}}{C_2H_5OH}$$

(4) Also, (*C*) on treating with dil. H_2SO_4 gives (*E*) which reduces Tollen's reagent.

$$HCOONa \xrightarrow[H_2SO_4]{HOH} \underset{\substack{(E)\\ \text{(Reduces Tollen's reagent)}}}{HCOOH} + NaOH$$

181. (i) Compound (*B*) is obtained from pentanol-1 vapours on passing through Cu at 570 K and thus, it is an aldehyde (1° alcohols give aldehyde)

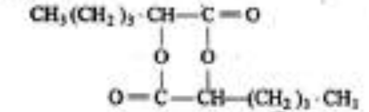
$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH \xrightarrow[570\ K]{Cu} \underset{\text{Pentanal-1 }(B)}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO}$$

(ii) Compound (*B*), *i.e.*, pentanal-1 is also obtained along with CO and H_2O from (*A*) on heating with H_2SO_4. Thus, (*A*) is $CH_3(CH_2)_3\cdot CHOH\cdot COOH$.

$$\underset{(A)}{CH_3(CH_2)_3\cdot CHOH\cdot COOH} \xrightarrow{H_2SO_4} CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO + H_2O + CO$$

(iii) (*A*) on heating gives (*C*), *i.e.*,

$$\underset{(A)}{CH_3(CH_2)_3\cdot CHOH\cdot COOH} \xrightarrow{\Delta}$$



(*C*)
Lactide

182. (1) Ester is $R\text{—}\underset{\underset{O}{\|}}{C}\text{—}OR'$; Molar mass of ester = 102

$\therefore$ Molar mass of $R + R' = 102 - 44 = 58$

(2) Given, $\underset{(A)}{R\text{—}COOR'} \xrightarrow{HOH} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$

mM of acid = mM of NaOH

$$\frac{0.185}{M/1} \times 1000 = 25 \times 0.1$$

$\therefore$ Molar mass of acid $R\text{—}\underset{\underset{O}{\|}}{C}\text{—}OH = 74\ g\ mol^{-1}$

$\therefore$ Molar mass of $R = 74 -$ (Molar mass of COOH)
$= 74 - 45 = 29$

$\therefore$ Molar mass of $R' = 58 - 29 = 29$

Thus, $R = R'$, also R may be $C_nH_{2n+1} = 29$

$\therefore$ $n = 2$

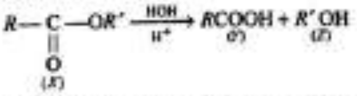
i.e., R' and R is C_2H_5

(3) Thus, ester is $CH_3\cdot CH_2COOCH_2\cdot CH_3$

Reaction :

$$\underset{\substack{\text{Ester}\\ \text{(Ethyl propanoate)}}}{CH_3CH_2COOC_2H_5} + H_2O \longrightarrow \underset{\substack{\text{Acid}\\ \text{(Propanoic acid)}}}{CH_3CH_2COOH} + \underset{\substack{\text{Alcohol}\\ \text{(Ethyl alcohol)}}}{C_2H_5OH}$$

183. (i) Since, (*X*) is hydrolysed to give an acid (*Y*) and an alcohol (*Y*) and thus, (*X*) is ester.



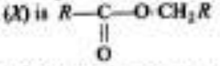
$$\underset{(X)}{R\text{—}\underset{\underset{O}{\|}}{C}\text{—}OR'} \xrightarrow[H^+]{HOH} \underset{(Y)}{RCOOH} + \underset{(Z)}{R'OH}$$

(ii) Oxidation of alcohol (*Z*) gives acid (*Y*), it shows that (*Z*) is a primary alcohol $R\text{—}CH_2OH$.

$$\underset{(Z)}{R'OH} \xrightarrow{\text{Oxidation}} \underset{(Y)}{RCOOH}$$

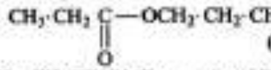
$\therefore$ $R\cdot CH_2\cdot OH \longrightarrow RCOOH$ ($\because$ R' is $R\text{—}CH_2$)

So, (*X*) is



$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}O\cdot CH_2R$

$\therefore$ (*X*) is



$CH_3\cdot CH_2\underset{\underset{O}{\|}}{C}\text{—}OCH_2\cdot CH_2\cdot CH_3$

(Propylpropanoate)

(*Y*) is $CH_3\cdot CH_2COOH$ (Propanoic acid)

(*Z*) is $CH_3\cdot CH_2\cdot CH_2OH$ (Propan-1-ol)

184. (1) (*E*) C_3H_6O does not give Tollen's test, does not reduce Fehling solution but forms hydrazone and so, (*E*) is a ketone. A ketone of 3 C-atoms is only acetone.

$$\underset{(E)}{CH_3\cdot CO\cdot CH_3}$$

(2) (*E*) is formed by heating (*B*) with $Ca(OH)_2$ thus, (*B*) is CH_3COOH (acetic acid).

$$\underset{(B)}{2CH_3COOH} + Ca(OH)_2 \xrightarrow{\Delta} (CH_3COO)_2Ca \xrightarrow{\Delta} \underset{(E)}{CH_3COCH_3}$$

(3) (*B*) is formed by the oxidation of (*D*) and thus, (*D*) is C_2H_5OH (ethyl alcohol).

$$\underset{(D)}{C_2H_5OH} \xrightarrow{\text{Oxidation}} \underset{(B)}{CH_3COOH}$$

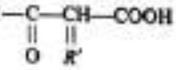
(4) (*B*) and (*D*) both are formed by (*C*) on hydrolysis in acid medium and thus, (*C*) should be an ester $CH_3COOC_2H_5$ (ethyl acetate)

$$\underset{(C)}{CH_3COOC_2H_5} \xrightarrow[H^+]{HOH} \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

(5) Now (*B*) and (*C*) both are formed with action of (*A*) over C_2H_5OH and so, (*A*) can be acetic anhydride.

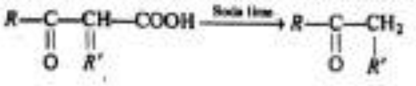
$$\underset{(A)}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{(C)}{CH_3COOC_2H_5} + \underset{(B)}{CH_3COOH}$$

185. (1) (*C*) is β-keto acid and thus, it may be



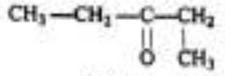
$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{R'}{\|}}{CH}\text{—}COOH$

(2) (*C*) on decarboxylation gives 3-pentanone, *i.e.*,



$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{\|}}{CH}-COOH \xrightarrow{\text{Soda lime}} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{R'}{|}}{CH_2}$$

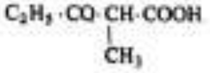
or



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH_2}$$

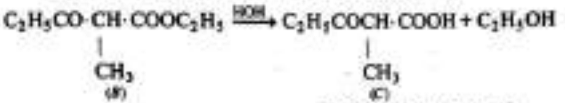
3-Pentanone

Thus, R is C_2H_5 and R' is CH_3



$$\therefore\ (C) \text{ is } \quad C_2H_5\cdot CO\cdot \underset{\underset{CH_3}{|}}{CH}\cdot COOH$$

(3) (*C*) is formed along with ethanol from (*B*) on acid hydrolysis so (*B*) is a β-keto ester (ethyl ester).



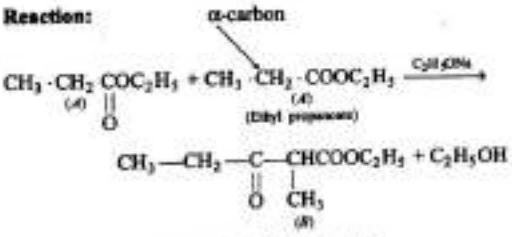
$$\underset{(B)}{C_2H_5CO\cdot\underset{\underset{CH_3}{|}}{CH}\cdot COOC_2H_5} \xrightarrow{\text{HOH}} \underset{(C)}{C_2H_5CO\underset{\underset{CH_3}{|}}{CH}\cdot COOH} + C_2H_5OH$$

(2-Methyl-3-ketopentanoic acid)

(4) (*B*) is formed as a condensation of two mole of ester (*A*), since the condensation occurs at 'α' C-atom, *i.e.*, Claisen condensation or Claisen reaction so, the probable structure of (*A*) is

$$\underset{(A)}{CH_3\cdot CH_2\cdot COOC_2H_5}$$

Reaction:



α-carbon

$$\underset{(A)}{CH_3\cdot CH_2}\underset{\underset{O}{\|}}{C}OC_2H_5 + \underset{\substack{(A)\\ \text{(Ethyl propanoate)}}}{CH_3\cdot CH_2\cdot COOC_2H_5} \xrightarrow{C_2H_5ONa}$$

$$\underset{(B)}{CH_3-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}COOC_2H_5} + C_2H_5OH$$

Ethyl, (2-Methyl, 3-ketopentanoate)

186. (1) Compound (*A*) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (*B*) and (*C*) and thus, it seems to be an ester *RCOOR'*

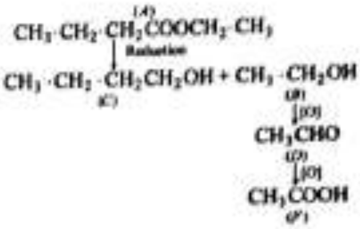
(2) $\underset{(A)}{RCOOR'} \xrightarrow{\text{Reduction}} \underset{(B)}{RCH_2OH} + \underset{(C)}{R'OH}$

(3) (*F*) is monobasic acid of molar mass 60 and hence, (*F*) is CH_3COOH.

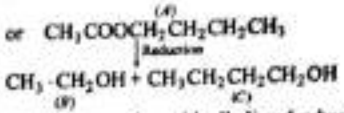
($\because$ $RCOOH = 60$, $\therefore$ $R = 15$, *i.e.*, CH_3COOH)

(4) (*F*) is obtained by oxidation of (*D*) and (*D*) is obtained by oxidation of (*B*) and thus, (*D*) is CH_3CHO and (*B*) is CH_3CH_2OH

(5) Thus, an ester of six C-atoms giving two alcohols, one of 2 carbon atoms, the other alcohol must be of four carbon atoms. Thus, ester (*A*) is

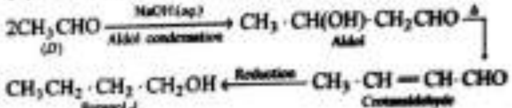


$$\begin{array}{c} \overset{(A)}{CH_3\cdot CH_2\cdot CH_2COOCH_2\cdot CH_3} \\ \big\downarrow \text{Reduction} \\ \underset{(C)}{CH_3\cdot CH_2\cdot CH_2CH_2OH} + \underset{(B)}{CH_3\cdot CH_2OH} \\ \big\downarrow [O] \\ \underset{(D)}{CH_3CHO} \\ \big\downarrow [O] \\ \underset{(F)}{CH_3COOH} \end{array}$$



$$\begin{array}{l} \text{or } \overset{(A)}{CH_3COOCH_2CH_2CH_2CH_3} \\ \qquad \big\downarrow \text{Reduction} \\ \underset{(B)}{CH_3\cdot CH_2OH} + \underset{(C)}{CH_3CH_2CH_2CH_2OH} \end{array}$$

(6) (*D*) on treating with alkali and subsequent heating gives (*E*) which on catalytic hydrogenation gives (*C*)



$$\underset{(D)}{2CH_3CHO} \xrightarrow[\text{Aldol condensation}]{\text{NaOH(aq)}} \underset{\text{Aldol}}{CH_3\cdot CH(OH)\cdot CH_2CHO} \xrightarrow{\Delta}$$

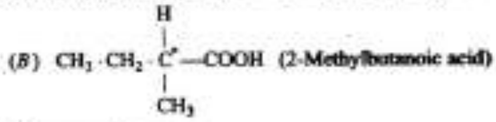
$$\underset{\substack{\text{Butanol-1}\\(C)}}{CH_3CH_2\cdot CH_2\cdot CH_2OH} \xleftarrow{\text{Reduction}} \underset{\substack{\text{Crotonaldehyde}\\(E)}}{CH_3\cdot CH=CH\cdot CHO}$$

187. (1) (*A*) $C_5H_8O_2$ liberates CO_2 with $NaHCO_3$ so, (*A*) is acid, *i.e.*, (*A*) is C_4H_7COOH.

(2) (*A*) seems to be unsaturated and thus shows geometrical isomerism.

(3) $\underset{(A)}{C_4H_7COOH} \xrightarrow{H_2} \underset{(B)}{C_5H_{10}O_2}$;

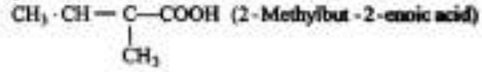
Since, (*B*) is optically active and thus, acid (*B*) may be



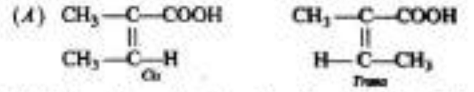
$$(B)\ CH_3\cdot CH_2\cdot \overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C^*}}-COOH \quad \text{(2-Methylbutanoic acid)}$$

*is asymmetric carbon.

(4) Since, (*B*) is formed by hydrogenation of acid (*A*) having geometrical isomers, thus, (*A*) can only be



$$CH_3\cdot CH=\underset{\underset{CH_3}{|}}{C}-COOH \quad \text{(2-Methylbut-2-enoic acid)}$$

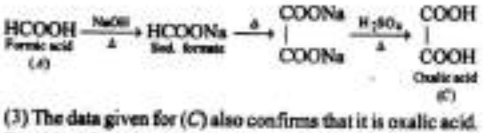


$$(A)\ \underset{Cis}{\begin{array}{c} CH_3-C-COOH \\ \| \\ CH_3-C-H \end{array}} \qquad \underset{Trans}{\begin{array}{c} CH_3-C-COOH \\ \| \\ H-C-CH_3 \end{array}}$$

188. (1) (*A*) is sodium salt of a carboxylic acid produced by a gas (*B*) on reacting with NaOH at high *P* and *T*. The reaction is a characteristic reaction of CO and NaOH at high *P* and *T*.

$$\underset{(B)}{CO} + NaOH \xrightarrow{P,\,T} HCOONa \xrightarrow{\text{HOH}} \underset{(A)}{HCOOH}$$

(2) (*A*) on heating in presence of NaOH followed with H_2SO_4 gives a dibasic acid (*C*)



$$\underset{\underset{(A)}{\text{Formic acid}}}{HCOOH} \xrightarrow[\Delta]{NaOH} \underset{\text{Sod. formate}}{HCOONa} \xrightarrow{\Delta} \begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow[\Delta]{H_2SO_4} \underset{\underset{(C)}{\text{Oxalic acid}}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}}$$

(3) The data given for (*C*) also confirms that it is oxalic acid.

Empirical formula of (*C*)

Element	%	Relative no. of atoms	Simplest ratio
C	$\frac{12}{44}\times\frac{0.39}{0.40}\times100=26.59$	2.21	1
H	$\frac{2}{18}\times\frac{0.08}{0.40}\times100=2.22$	2.22	1
O	$100-(26.59+2.22)=71.19$	4.44	2

∴ Empirical formula of (*C*) is CHO_2; Empirical formula mass = 45

Also, molar mass of (*C*)

$$\frac{\text{Mass of Ag}}{\text{Eq. mass of Ag}}=\frac{\text{Mass of Ag salt}}{E+108}$$

where, *E* is Eq. mass of anion of acid

$$\frac{0.71}{108}=\frac{1}{E+108}$$

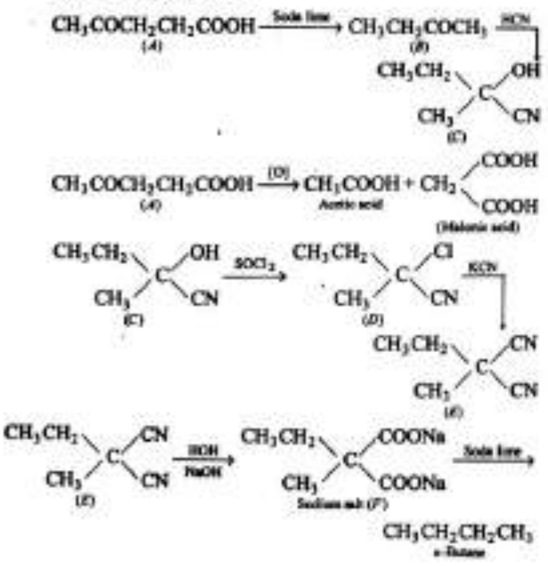
$$\therefore \quad E=44$$

∴ Eq. mass of acid = 44 + 1 = 45

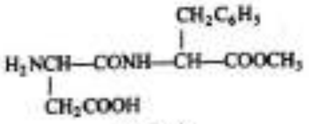
∴ Molar mass of acid = 90 g mol^{-1}

∴ M. formula of $(C)=(CHO_2)_2=COOH\text{-}COOH$

189. The statements given in problem suggest (*A*) to be $CH_3COCH_2CH_2COOH$



190.



$$H_2N\underset{\underset{CH_2COOH}{|}}{C}H-CONH-\overset{\overset{CH_2C_6H_5}{|}}{C}H-COOCH_3$$

Aspartame

(i) The four functional groups are :

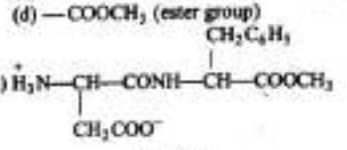
(a) $-NH_2$ (amino group)

(b) $-COOH$ (carboxylic group)

(c) $-CONH-$ (peptide or amide group)

(d) $-COOCH_3$ (ester group)

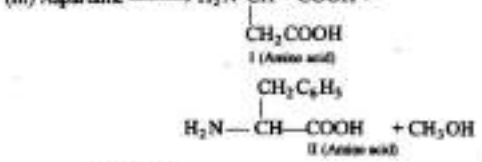
(ii)



$$\overset{+}{H_3}N-\underset{\underset{CH_2COO^-}{|}}{C}H-CONH-\overset{\overset{CH_2C_6H_5}{|}}{C}H-COOCH_3$$

Zwitter ion

(iii)



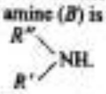
$$\text{Aspartame}\xrightarrow{HOH} \underset{\text{I (Amino acid)}}{H_2N\text{-}\underset{\underset{CH_2COOH}{|}}{C}H-COOH} + \underset{\text{II (Amino acid)}}{H_2N-\overset{\overset{CH_2C_6H_5}{|}}{C}H-COOH} + CH_3OH$$

(iv) $H_2N\text{-}\overset{\overset{CH_2C_6H_5}{|}}{C}H\text{-}COOH$ is more hydrophobic as it has one $-COOH$ and one $-NH_2$ group along with more powerful hydrophobic chain $-CH_2C_6H_5$.

191. (1) (*A*) on hydrolysis gives an amine (*B*) and a carboxylic acid (*C*), *i.e.*, amine and *R*COOH.

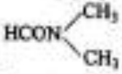
(2) Amine (*B*) reacts with benzene sulphonyl chloride and the product is insoluble in aqueous solution of NaOH and therefore, amine (*B*) is secondary amine,

i.e.,



(3) Acid (*C*) reacts with Tollen's reagent and thus, it may be formic acid HCOOH.

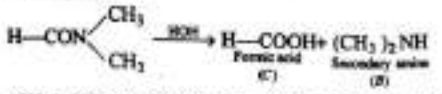
(4) Thus, (*A*) C_3H_7NO can be



(*N*, *N'* – Dimethylformamide)

(5) The structure can be justified by the reactions.

Reactions:



$$\underset{(C)}{(CH_3)_2NH}+\underset{\text{Benzene sulphonyl chloride}}{C_6H_5SO_2Cl}\longrightarrow \underset{\underset{\text{Insoluble in NaOH (aq)}}{\text{(Sulphonamide)}}}{(CH_3)_2N\cdot SO_2\cdot C_6H_5}$$

$$\underset{(C)}{HCOOH}+Ag_2O\longrightarrow \underset{\text{Silver mirror}}{2Ag}+H_2O+CO_2\uparrow$$

192. (1) Compound gives foul odour with $CHCl_3$ and alcoholic KOH and thus, it is primary amine say $R\text{—}NH_2$. The reaction is carbylamine reaction.

(2) $RNH_2 \xrightarrow[0°C]{HCl + NaNO_2} ROH + N_2$

$\because$ 112 mL N_2 is given by 0.295 g

$\therefore$ 22400 mL N_2 is given by $\frac{0.295 \times 22400}{112} = 59$

$\therefore$ Molar mass of $RNH_2 = 59$

$\therefore \quad R = 59 - (14+2) = 43$

i.e., $C_nH_{2n+1} = 43$

$\therefore \quad n = 3$

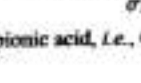
(3) Given,

$$C_3H_7NH_2 \xrightarrow{HCl + NaNO_2} C_3H_7OH \xrightarrow{I_2 + NaOH} \text{yellow precipitate}$$

Since, alcohol gives iodoform test and thus, it is secondary alcohol, *i.e.*,

$CH_3CHOH{\cdot}CH_3$ (Propan -2 -ol)

Thus, original compound should be



$$\underset{\text{Propan-2-amine}}{CH_3\underset{\displaystyle NH_2}{\underset{|}{C}H}{\cdot}CH_3}$$

193. (1) For empirical formula of (*A*)

Element	%	Relative no. of atoms	Simplest ratio
C	49.32	4.11	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.91	1.37	1

$\therefore$ Empirical formula of (*A*) is $\mathbf{C_3H_7NO}$

and Empirical formula mass of (*A*) = 73

(2) Molar mass of acid (*B*) can be derived as:

$$\frac{\text{Mass of Ag}}{\text{Eq. mass of Ag}} = \frac{\text{Mass of salt}}{\text{Eq. mass of salt}}$$

$$\frac{59.67}{108} = \frac{100}{E+108}$$

$\therefore$ $E = 73$, *i.e.*, equivalent mass of anion of salt

$\therefore$ Equivalent mass of acid $= E + 1 = 73 + 1 = 74$

$\therefore$ Molar mass of acid $= 74 \times 1\,\text{g mol}^{-1}$ $\quad \because$ Basicity = 1

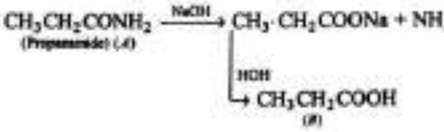
(3) Acid (*B*) is monobasic and thus (*B*) is $C_nH_{2n+1}COOH$

$\therefore$ $12n + 2n + 1 + 12 + 32 + 1 = 74$

$\therefore \quad n = 2$

So, acid (*B*) is $CH_3{\cdot}CH_2COOH$.

(4) Since, (*B*) is obtained by the action of (*A*) with NaOH followed with hydrolysis and so (*A*) is $CH_3CH_2CONH_2$.



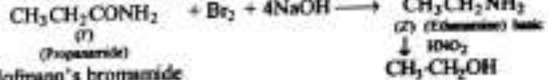
$$\underset{\text{(Propanamide) }(A)}{CH_3CH_2CONH_2} \xrightarrow{NaOH} CH_3{\cdot}CH_2COONa + NH_3 \quad \xrightarrow{HOH} \underset{(B)}{CH_3CH_2COOH}$$

194. (1) For empirical formula of (*Y*)

Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.11	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.91	1.37	1

$\therefore$ Empirical formula of (*Y*) is $\mathbf{C_3H_7NO}$.

(2) (*Y*) reacts with Br_2 and NaOH to give (*Z*) and (*Z*) reacts with HNO_2 to give ethanol and thus, empirical formula of (*Y*) seems to be molecular formula with $\text{—}CONH_2$ group.



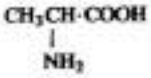
$$\underset{\text{(Propanamide)}}{\underset{(Y)}{CH_3CH_2CONH_2}} + Br_2 + 4NaOH \longrightarrow \underset{(Z)\text{ (Ethanamine) basic}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3{\cdot}CH_2OH}$$

Hofmann's bromamide reaction

(3) (*Y*) is formed from (*X*) having Cl on treatment with NH_3 and so (*X*) is CH_3CH_2COCl, *i.e.*, propanoyl chloride.

$$\underset{(X)}{CH_3{\cdot}CH_2COCl} + NH_3 \longrightarrow \underset{(Y)}{CH_3CH_2CONH_2}$$

195. Alanine is α-amino propionic acid, *i.e.*,



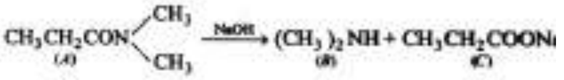
$$CH_3\underset{\displaystyle NH_2}{\underset{|}{C}H}{\cdot}COOH$$

At pH = 2, $CH_3CHNH_2COOH \xrightarrow{H^+} CH_3CH\overset{+}{N}H_3COOH$

At, pH = 10, $CH_3CHNH_2COOH \xrightarrow{OH^-} CH_3CHNH_2COO^-$

196. The given reactions suggest that

(i)



$$\underset{(A)}{CH_3CH_2CON}\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{NaOH} \underset{(B)}{(CH_3)_2NH} + \underset{(C)}{CH_3CH_2COON}$$

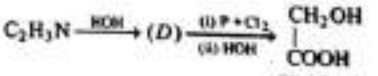
(ii) $\underset{(B)}{(CH_3)_2NH} \xrightarrow{HNO_2} \underset{\text{Yellow oil }(E)}{(CH_3)_2N{\cdot}NO}$

(iii) $\underset{(B)}{(CH_3)_2NH} \xrightarrow{CH_3COCl} \underset{(D)}{(CH_3)_2NCOCH_3}$

197. (1) (*A*) on distillation loses water and forms (*B*) which on further distillation with P_2O_5 gives (*C*)

$$\underset{(A)}{C_2H_7NO_2} \xrightarrow[-H_2O]{\Delta} \underset{(B)}{C_2H_5NO} \xrightarrow[P_2O_5]{\Delta} \underset{(C)}{C_2H_3N}$$

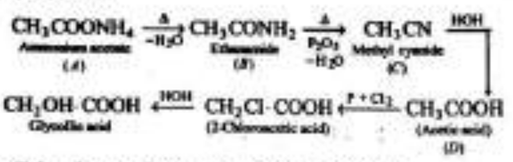
(2) (*C*) on hydrolysis gives (*D*) which on treating with $P + Cl_2$ followed with hydrolysis gives glycollic acid.



$$C_2H_3N \xrightarrow{HOH} (D) \xrightarrow[\text{(ii) HOH}]{\text{(i) }P + Cl_2} \underset{\text{Glycollic acid}}{\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}}$$

(3) All these facts can be explained if (*A*) is ammonium acetate, *i.e.*, CH_3COONH_4.

Reactions:

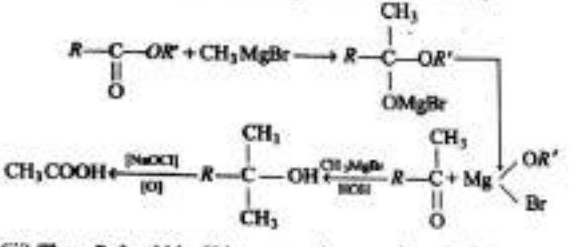


$$\underset{\substack{\text{Ammonium acetate}\\(A)}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{Ethanamide}\\(B)}}{CH_3CONH_2} \xrightarrow[\substack{P_2O_5\\-H_2O}]{\Delta} \underset{\substack{\text{Methyl cyanide}\\(C)}}{CH_3CN} \xrightarrow{HOH}$$

$$\underset{\text{Glycollic acid}}{CH_2OH \cdot COOH} \xleftarrow{HOH} \underset{\text{(2-Chloroacetic acid)}}{CH_2Cl \cdot COOH} \xleftarrow{P + Cl_2} \underset{\substack{\text{(Acetic acid)}\\(D)}}{CH_3COOH}$$

198. (i) Let the ester be $R—\underset{\underset{O}{\|}}{C}—OR'$, *i.e.*, $C_4H_8O_2$

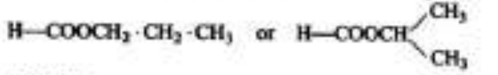
(ii) It reacts with CH_3MgBr; the product (B) on acidification gives an alcohol (B) which on oxidation with NaOCl followed with acidification gives acetic acid. Thus,



$$R—\underset{\underset{O}{\|}}{C}—OR' + CH_3MgBr \longrightarrow R—\overset{\overset{CH_3}{|}}{\underset{\underset{OMgBr}{|}}{C}}—OR'$$

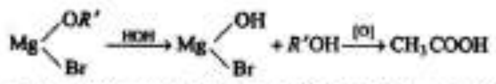
$$CH_3COOH \xleftarrow[{[O]}]{[NaOCl]} R—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—OH \xleftarrow[HOH]{CH_3MgBr} R—\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}} + Mg\begin{matrix} OR' \\ Br \end{matrix}$$

(iii) Thus, R should be H because only secondary alcohol can be oxidised by NaOCl and not tertiary. Thus, the ester may be



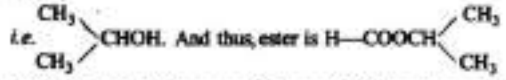
$$H—COOCH_2 \cdot CH_2 \cdot CH_3 \quad \text{or} \quad H—COOCH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

(iv) Also,



$$Mg\begin{matrix} OR' \\ Br \end{matrix} \xrightarrow{HOH} Mg\begin{matrix} OH \\ Br \end{matrix} + R'OH \xrightarrow{[O]} CH_3COOH$$

Thus, $R'OH$ must be secondary alcohol of three carbon atoms,



i.e. $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH$. And thus, ester is $H—COOCH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$

199. Acid anhydride (A) reacts with an acid (B) to give an acid (C) of equivalent mass 74 and an anhydride (D). These may be

$$\underset{(A)}{(CH_3 \cdot CH_2 \cdot CO)_2O} + \underset{(B)}{2CF_3CH_2COOH} \longrightarrow \underset{(C)}{2CH_3 \cdot CH_2COOH} + \underset{(D)}{(CF_3 \cdot CH_2CO)_2O}$$

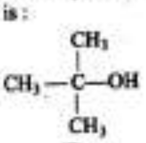
CH_3CH_2COOH has eq. mass = 74

and $CF_3 \cdot CH_2COOH$ has eq. mass = 128.

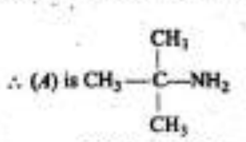
200. (1) Both (A) and (B) lose N_2 on treating with HNO_2 forming alcohols (C) and (D) respectively and thus, (A) and (B) both are primary amines.

$$\underset{(A) \text{ or } (B)}{C_4H_9NH_2} \xrightarrow{HNO_2} \underset{(C) \text{ or } (D)}{C_4H_9OH}$$

(2) (C) reacts with Lucas reagent immediately and thus, (C) is tertiary alcohol. The tertiary alcohol of formula C_4H_9OH is :

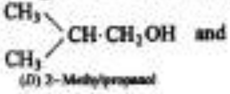


$$\underset{\substack{(C)\\ \text{2-Methylpropanol}}}{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—OH}$$



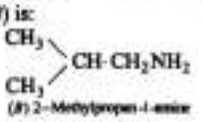
$$\therefore (A) \text{ is } \underset{\text{2-Methylpropan-2-amine}}{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—NH_2}$$

(3) (D) does not react with Lucas reagent and is easily oxidised and thus, it is primary alcohol ($—CH_2OH$). Complete methylation of (B) does not give on decomposition butene-1. Thus, (B) and (D) do not have straight chain. Therefore, (B) is:



$$\underset{(D) \text{ 2-Methylpropanol}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2OH}$$

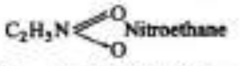
and



$$\underset{(B) \text{ 2-Methylpropan-1-amine}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2NH_2}$$

201. (i) Molecular formula of (A) suggests that it is

either



$C_2H_5N\begin{matrix} \nearrow O \\ \searrow O \end{matrix}$ Nitroethane

or $C_2H_5O—N=O$ Ethyl nitrite

(ii) Since, (A) undergoes hydrolysis to give an alcohol (B) and an acid, it is ethyl nitrite $C_2H_5O—N=O$.

Reactions :

$$\underset{\substack{\text{Ethyl nitrite}\\(A)}}{C_2H_5O—N=O} \xrightarrow[H^+]{H_2O} \underset{(B)}{C_2H_5OH} + HNO_2$$

Molar mass of (B) is = 46

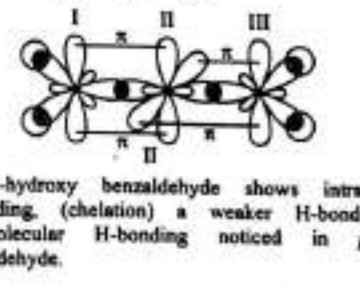
$$C_2H_5O—N=O \xrightarrow{\text{Reduction}} C_2H_5OH + NH_3$$

202. (a)

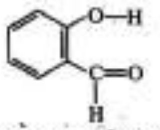
$$CH_3CH_2C \equiv CH \xrightarrow{Na} CH_3CH_2C \equiv CNa \xrightarrow{CH_3X} (A)$$

$$(A) \text{ or } CH_3CH_2C \equiv CCH_3 \xrightarrow[H_2SO_4]{HgSO_4} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$$

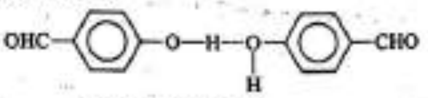
(b) Allene is $\underset{sp^2}{\overset{I}{CH_2}} = \underset{sp}{\overset{II}{C}} = \underset{sp^2}{\overset{III}{CH_2}}$



(c) *o*-hydroxy benzaldehyde shows intramolecular H-bonding, (chelation) a weaker H-bonding than intermolecular H-bonding noticed in *p*-hydroxy benzaldehyde.

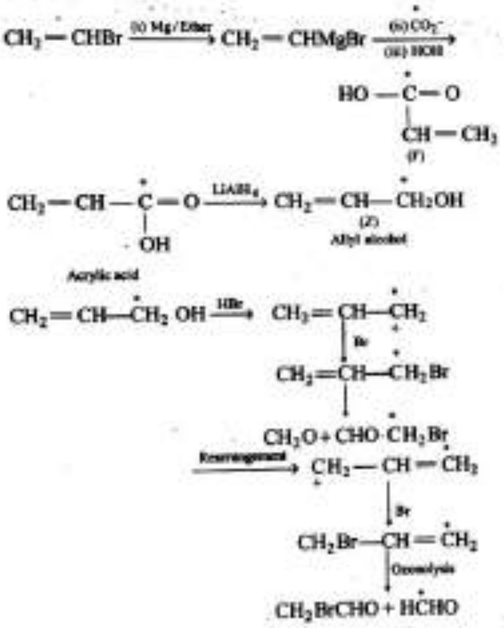


o-Hydroxy benzaldehyde

and 

p-Hydroxy benzaldehyde

203. (a) $\mathrm{Ba\dot{C}O_3 + H_2SO_4 \longrightarrow \underset{gas\,(X)}{\dot{C}O_2} + BaSO_4 + H_2O}$



$$\mathrm{CH_3-CHBr \xrightarrow{(i)\ Mg/Ether} CH_2=CHMgBr \xrightarrow[(ii)\ HOH]{(i)\ \dot{C}O_2^-} \underset{(F)}{HO-\dot{C}(=O)-CH-CH_3}}$$

$$\mathrm{\underset{Acrylic\ acid}{CH_2-CH-\dot{C}(OH)=O} \xrightarrow{LiAlH_4} \underset{\underset{Allyl\ alcohol}{(Z)}}{CH_2=CH-\dot{C}H_2OH}}$$

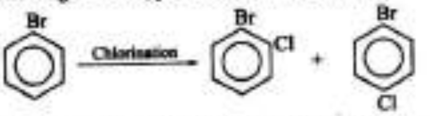
$$\mathrm{CH_2=CH-\dot{C}H_2\,OH \xrightarrow{HBr} CH_3=CH-\overset{+}{\dot{C}H_2} \xrightarrow{Br^-} CH_2=CH-\dot{C}H_2Br \longrightarrow CH_2O + CHO\cdot\dot{C}H_2Br}$$

$$\mathrm{\xrightarrow{Rearrangement} \overset{+}{C}H_2-CH=\dot{C}H_2 \xrightarrow{Br^-} CH_2Br-CH=\dot{C}H_2 \xrightarrow{Ozonolysis} CH_2BrCHO + H\dot{C}HO}$$

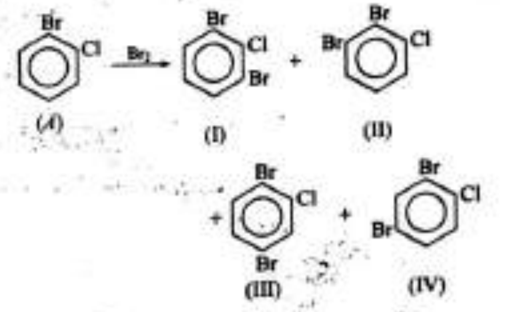
204. (a) $\mathrm{CH_2-CHCH_2OH}$; α,β-unsaturated carbonyl compounds are reduced to unsaturated alcohol by $\mathrm{LiAlH_4}$.

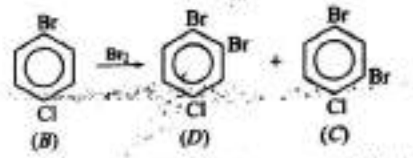
(b) $\mathrm{C_6H_5CH_2CH_2CH_2OH}$; However, if phenyl group is attached to β-carbon atom of α,β-unsaturated carbonyl compounds, both double bond and carbonyl group are reduced by $\mathrm{LiAlH_4}$.

205. (1) Bromobenzene is chlorinated, since bromine is o- and p-directing and thus, products (A) and (B) are,

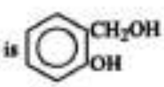


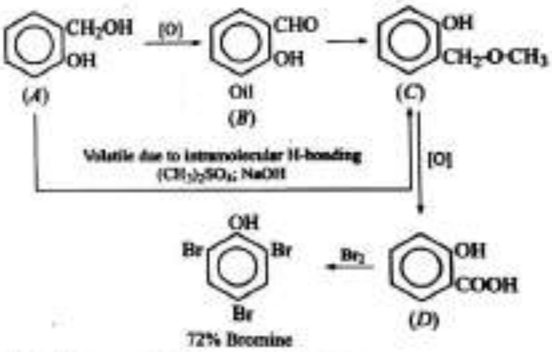
(2) Monobromination of (A) gives several products whereas (B) gives only two isomers and thus, (A) and (B) are,





(3) (C) is identical to (IV) but (D) does not resemble with (I) to (IV).

206. The given reactions suggest that (A) is 



207. (1) For empirical formula of (A), a hydrocarbon (*i.e.*, C and H only)

Element	%	Relative no. of atoms	Simplest ratio
C	90.56	7.55	1 or 4
H	9.44	9.44	1.25 or 5

∴ Empirical formula of (A) = $\mathbf{C_4H_5}$

Empirical formula mass = 53

Given, Molar mass = 53 × 2 = 106 g $\mathrm{mol^{-1}}$

∴ Molecular formula of (A) = $\mathrm{(C_4H_5) = C_8H_{10}}$

(2) $(A) \xrightarrow[\text{oxidation}]{\text{Vigorous}} (B)$ Dibasic acid, $R\begin{smallmatrix}\diagup \mathrm{COOH}\\ \diagdown \mathrm{COOH}\end{smallmatrix}$

Meq. of dibasic acid = Meq. of NaOH

$$\frac{0.1}{E} \times 1000 = 24.1 \times 0.05$$

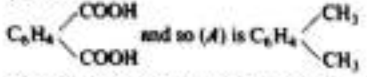
∴ Equivalent mass of dibasic acid = 83

∴ Molar mass of dibasic acid = 166

∴ Molar mass of $R = 166 - 2 \times 45 = 76$

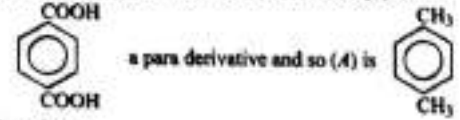
This also suggests R to be C_6H_4.

(3) (B) on heating with soda lime gives benzene and thus, (B) is



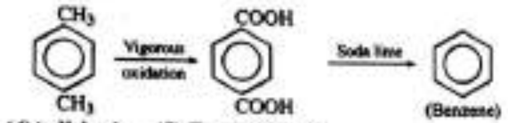
$$C_6H_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} \text{ and so } (A) \text{ is } C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

(4) Also, (B) shows mononitro derivative so (B) is

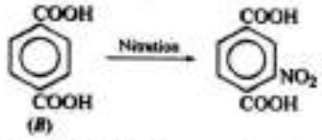


a para derivative and so (A) is

Reactions :

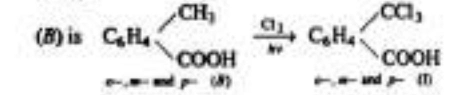


(A) (p-Xylene) (B) (Terephthalic acid) (Benzene)



(B)

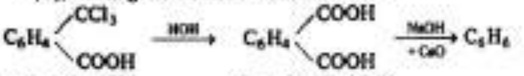
208. (i) Both (B) and (C) $C_8H_8O_2$ are monobasic acids, (B) on chlorination gives a compounds having 3 Cl-atoms whereas (C) on chlorination gives a compounds having 2 Cl-atoms. Thus,



$$(B) \text{ is } \underset{o-,\,m- \text{ and } p-\ (B)}{C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COOH\end{matrix}} \xrightarrow[h\nu]{Cl_2} \underset{o-,\,m- \text{ and } p-\ (I)}{C_6H_4\begin{matrix}\diagup CCl_3\\ \diagdown COOH\end{matrix}}$$

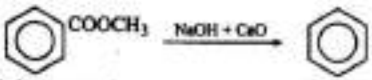
(C) is $\underset{(C)}{C_6H_5CH_2COOH} \xrightarrow[h\nu]{Cl_2} C_6H_5\cdot \underset{(II)}{CCl_3} \cdot COOH$

(ii) Acid (I) formed by (B) on hydrolysis gives dibasic acid (D), which gives benzene with soda lime.



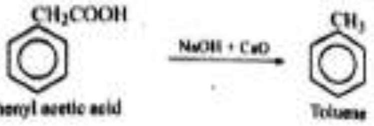
$$\underset{o-,\,m- \text{ and } p-\ (I)}{C_6H_4\begin{matrix}\diagup CCl_3\\ \diagdown COOH\end{matrix}} \xrightarrow{HOH} \underset{o-,\,m- \text{ and } p-\text{dibasic acid}}{C_6H_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}} \xrightarrow[+CaO]{NaOH} C_6H_6$$

(iii) Compound (A) being neutral but gives C_6H_6 with soda lime and thus, (A) is

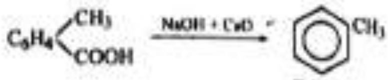


(A) (Methyl benzoate) Benzene

Reactions :

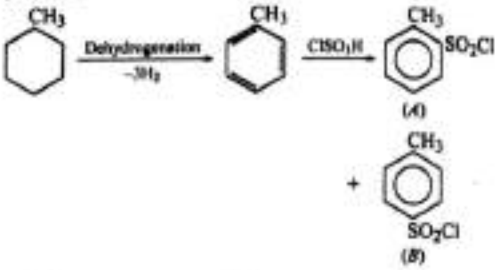


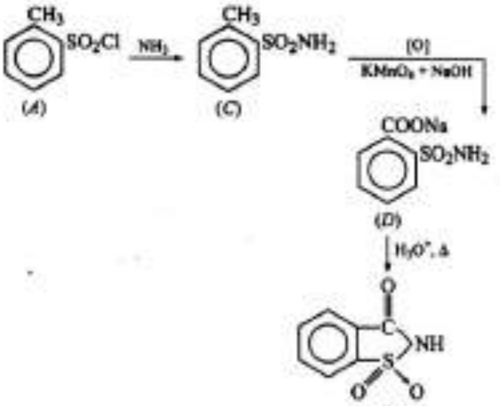
(C) Phenyl acetic acid Toluene



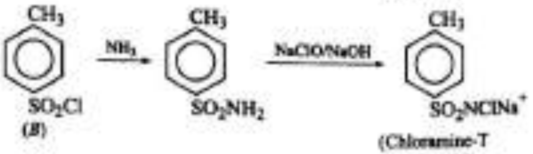
Toluene

209. The given statements suggest that following reactions are possible:



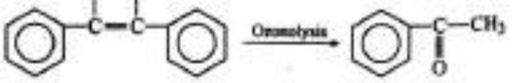


(Saccharin)

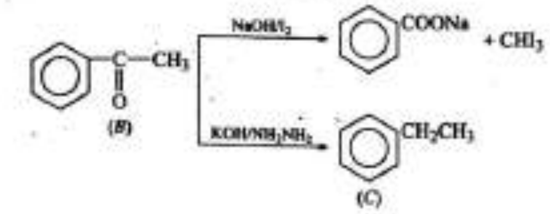


(Chloramine-T antiseptic)

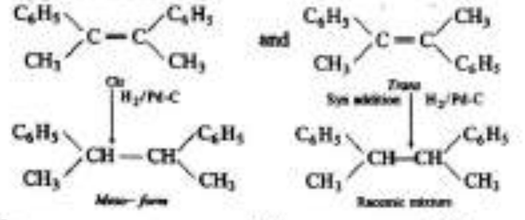
210.



(A) (B)

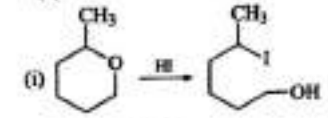


(*A*) has two structures:

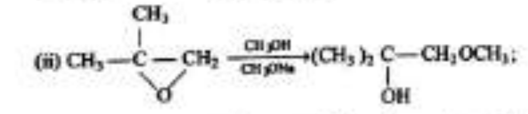


211.

(b)

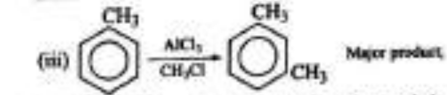


This is acid catalysed cleavage of ether where nucleophile attacks the most substituted carbon.



$$\text{(ii) } CH_3-\overset{\overset{CH_3}{|}}{C}-CH_2 \xrightarrow[CH_3ONa]{CH_3OH} (CH_3)_2\underset{\underset{OH}{|}}{C}-CH_2OCH_3;$$

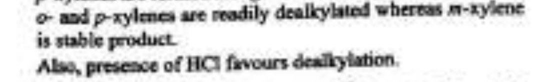
This is base catalysed cleavage of ether where nucleophile attacks least substituted carbon.



Major product.

No doubt CH_3 gp. is *o*- and *p*-directing and thus *o*- and *p*-xylenes are formed along with little *m*-xylene. But at 80°C *o*- and *p*-xylenes are readily dealkylated whereas *m*-xylene is stable product.

Also, presence of HCl favours dealkylation.



212. Given,

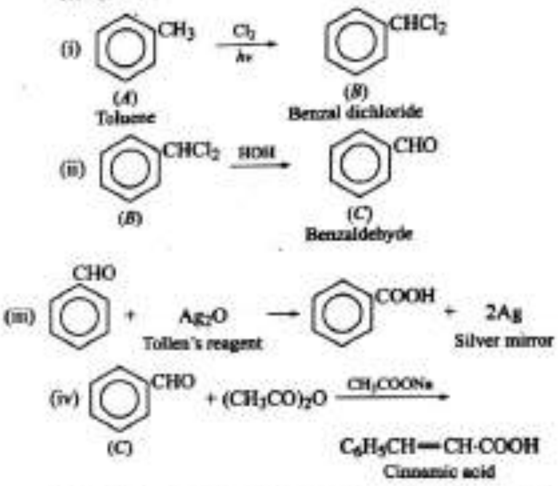
$$C_7H_8 \xrightarrow[h\nu]{Cl_2} \underset{(B)}{\text{Chlorinated product}} \xrightarrow{H_2O} (C)$$

(i) (*C*) gives positive test with Tollen's reagent and thus, (*C*) is aldehyde.

(ii) (*C*) is obtained by hydrolysis of (*B*) and thus, (*B*) is terminal gem dihalide, —$CHCl_2$ group.

(iii) (*B*) is obtained by chlorination of (*A*) thus, (*A*) is $C_6H_5CH_3$.

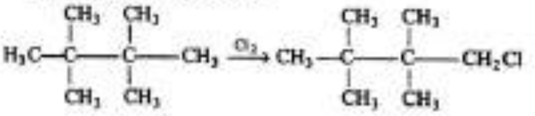
Reactions :



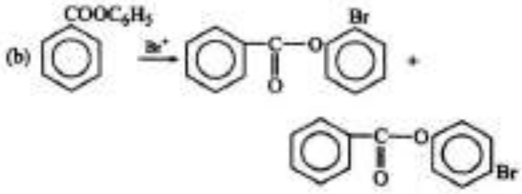
This is Perkins reaction, (*D*) has molar mass 148.15 g mol⁻¹.

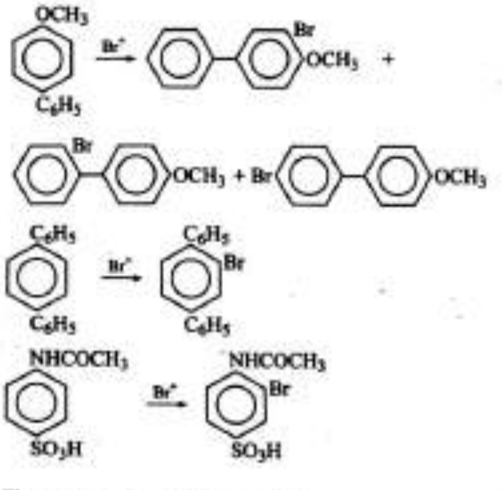
∵ Monobasic acid ∴ E. mass = 148.15

213. (a) The alkane having C_8H_{18} structure gives only single monochloride on substitution and thus, it should be 2,2,3,3-tetra methyl butane.

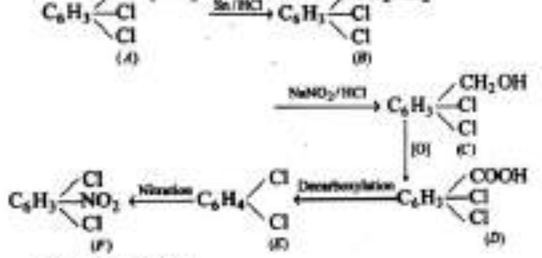


$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{Cl_2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl$$





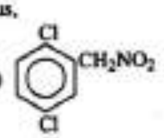
214. The compounds and reactions are :

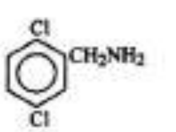


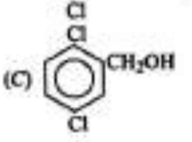
only one product

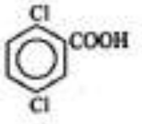
Since, (*F*) is only one product and thus, (*E*) is para derivative.

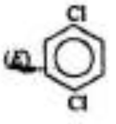
Thus,

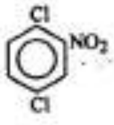
(*A*) 

(*B*) 

(*C*) 

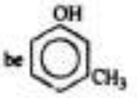
(*D*) 

(*E*) 

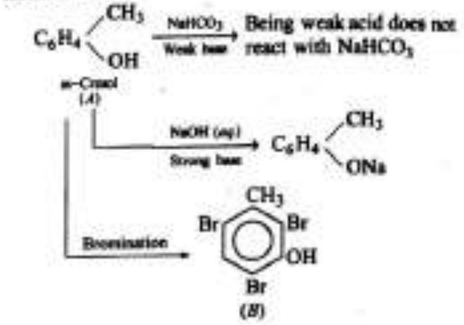
(*F*) 

215. (i) (*A*) gives characteristic colour with aqueous $FeCl_3$ and so it has phenolic group.

(ii) (*A*) on treatment with Br_2 gives $C_7H_5OBr_3$ and thus, taking an account of molecular formula of (*A*); (*A*) seems to be a methyl substituted phenol, *i.e.*, cresol.

(iii) On the basis of bromination, (*A*) can be  because meta position can form tribromo derivative.

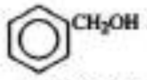
Reactions :



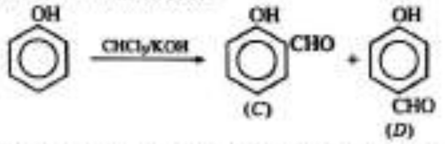
(iv) If (*A*) neither dissolves in aqueous NaOH, nor it gives characteristic colour with $FeCl_3$, it is neutral compound, *i.e.*, either


Anisole

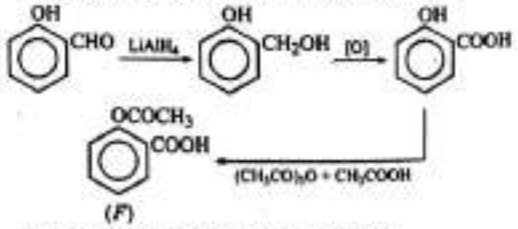
or


Benzyl alcohol

216. (i) The organic compound (*A*) is phenol as it undergoes Reimer-Tiemann reaction.



(ii) (*C*) does not reduce Schiff's reagent due to intramolecular H-bonding and is also steam volatile.

(iii) 

(*F*)

Acetyl salicylic acid or aspirin, a pain killer.

217. (1)

Element	%	Relative no. of atoms	Simplest ratio
C	68.32	5.69	8
H	6.4	6.40	9
Cl	25.26	0.71	1

Hence, Empirical formula of (*A*) = C_8H_9Cl

Empirical formula mass = 140.5

∵ Molar mass = 140.5 g mol^{-1}

∴ Molecular formula = C_8H_9Cl

(2) Given, $\underset{(A)}{C_8H_9Cl} \xrightarrow{HOH} \underset{(B)}{C_8H_9OH} \xrightarrow{\text{Oxidation}} \underset{(C)}{C_8H_8O}$

(3) (*C*) reacts with phenyl hydrazine and thus, a carbonyl compound.

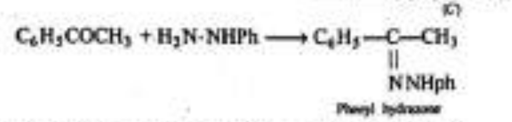
(4) (*C*) gives positive iodoform test and thus, has CH_3CO— unit. Thus, (*C*) is $C_6H_5COCH_3$ (Acetophenone)

(5) Since, (*C*) is formed by the oxidation of (*B*) and thus, (*B*) is $C_6H_5CHOHCH_3$ (1-Phenylethanol)

(6) Since, (*B*) is obtained by hydrolysis of (*A*) so, (*A*) is $C_6H_5CHClCH_3$ (1-Chloro-1-phenylethane)

Reactions : $\underset{(A)}{C_6H_5CHCl \cdot CH_3} \xrightarrow[H^+]{HOH} \underset{(B)}{C_6H_5CHOH \cdot CH_3}$

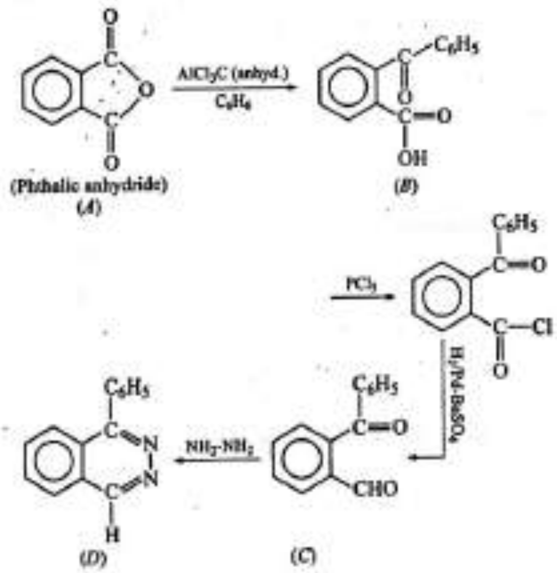
$$\xrightarrow{\text{Oxidation}} \underset{(C)}{C_6H_5COCH_3}$$



$$C_6H_5COCH_3 + H_2N \cdot NHPh \longrightarrow \underset{\text{Phenyl hydrazone}}{C_6H_5-\underset{\underset{NNHph}{\|}}{C}-CH_3}$$

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + \underset{\text{Yellow ppt.}}{CHI_3} + 3NaI + 3H_2O$$

218.



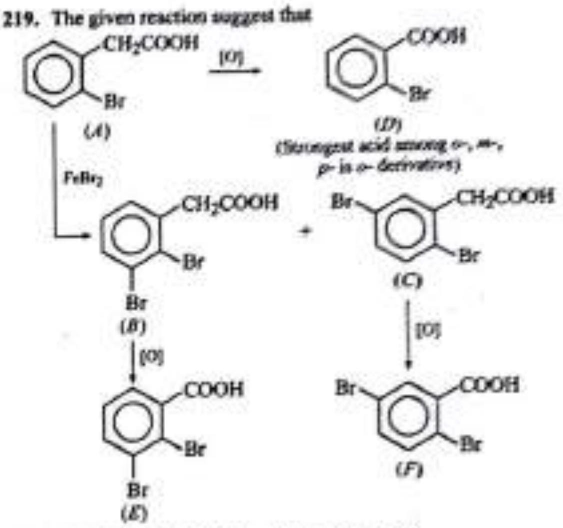
(Phthalic anhydride) (*A*)

(*B*)

(*D*)

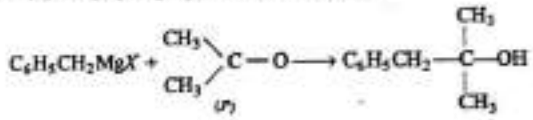
(*C*)

219. The given reaction suggest that

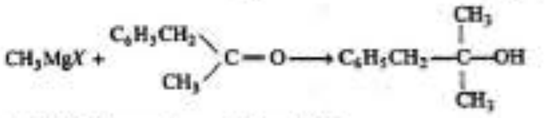


(*D*)
(Strongest acid among *o*-, *m*-, *p*- is *o*- derivative)

220. (*X*) is $C_6H_5CH_2MgX$ and (*Y*) is CH_3MgX



$$C_6H_5CH_2MgX + \underset{(P)}{\overset{CH_3}{\underset{CH_3}{\rangle}}C=O} \longrightarrow C_6H_5CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$



$$CH_3MgX + \overset{C_6H_5CH_2}{\underset{CH_3}{\rangle}}C=O \longrightarrow C_6H_5CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

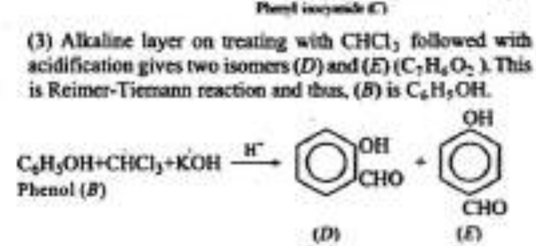
221. (1) Given, mixture of (*A*) and (*B*)

$$\xrightarrow[+KOH(aq.)]{CHCl_3} \underset{(A)}{\text{Organic layer}} + \underset{(B)}{\text{Alkaline aqueous layer}}$$

(2) Organic layer on treating with KOH(alc.) produces (*C*) of unpleasant odour (C_7H_5N) and thus, (*C*) is C_6H_5NC. This is carbylamine reaction. Therefore, (*A*) is $C_6H_5NH_2$.

$$\underset{\text{(Aniline) }(A)}{C_6H_5NH_2} + CHCl_3 + 3KOH(\text{alc.}) \longrightarrow \underset{\text{Phenyl isocyanide }(C)}{C_6H_5NC} + 3KCl + 3H_2O$$

(3) Alkaline layer on treating with $CHCl_3$ followed with acidification gives two isomers (*D*) and (*E*) ($C_7H_6O_2$). This is Reimer-Tiemann reaction and thus, (*B*) is C_6H_5OH.



(*D*) Ortho (*E*) Para

Hydroxybenzaldehydes

222. Since, % of chlorine is fix in each hydrochloride and thus all amines are isomers. Also amine hydrochloride is $C_nH_{2n+3}N \cdot HCl$.

$\because$ 32.42 is chlorine then amine $= (100 - 32.42 - 1) = 66.58$

$\therefore$ 35.5 is chlorine then amine $= \dfrac{66.58 \times 35.5}{32.42} = 72.90$

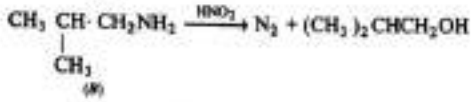
$$\therefore \quad 12n + 2n + 3 = 72.90$$

$$\therefore \quad n = 4$$

Thus, amine is $C_4H_{11}N$.

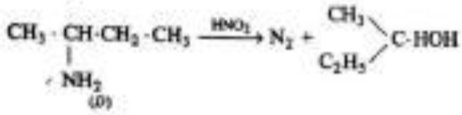
The possible amines are :

$$\underset{(A)}{CH_3CH_2CH_2CH_2NH_2} \xrightarrow{HNO_2} N_2 + CH_3CH_2CH_2CH_2OH$$



$$\underset{(B)}{CH_3\,\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2NH_2} \xrightarrow{HNO_2} N_2 + (CH_3)_2CHCH_2OH$$

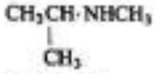
$$\underset{(C)}{(CH_3)_3C \cdot NH_2} \xrightarrow{HNO_2} N_2 + (CH_3)_3C \cdot OH$$



$$\underset{(D)}{CH_3 \cdot \underset{\displaystyle NH_2}{\underset{|}{CH}} \cdot CH_2 \cdot CH_3} \xrightarrow{HNO_2} N_2 + \begin{matrix} CH_3 \diagdown \\ C_2H_5 \diagup \end{matrix} C \cdot HOH$$

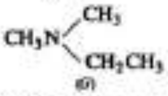
All primary amines give N_2 with HNO_2.

Others are $\underset{(E)}{CH_3CH_2CH \cdot NH \cdot CH_3}$

or 

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot NHCH_3$$

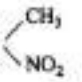
$$\underset{(F)}{CH_3CH_2NHCH_2CH_3}$$

or 

$$\underset{(G)}{CH_3N \begin{matrix} \diagup CH_3 \\ \diagdown CH_2CH_3 \end{matrix}}$$

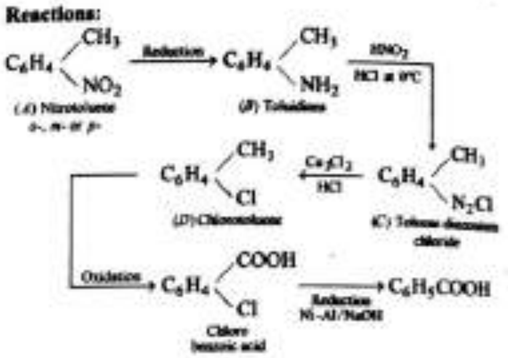
223. (i) (A) $C_7H_7NO_2$ on reduction gives a solid (B) and thus, (A) contains —NO_2 group which is reduced to —NH_2 group.

(ii) (B) undergoes diazotization (since —NH_2 group in it) to give (C) which on treating with Cu_2Cl_2/HCl gives (D) and (D) on reduction with Ni-Al/NaOH gives benzoic acid. This suggests that Cl is present at another position in C_6H_6 ring in (D).

(iii) Keeping these facts into account (A) is 

$$C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown NO_2 \end{matrix}$$

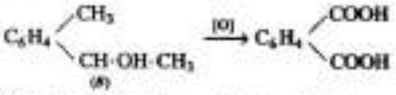
Reactions:



224. (i) (A) releases N_2 with HNO_2 and thus, (A) is primary amine, *i.e.*,

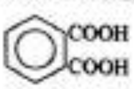
$$\underset{(A)}{C_9H_{11}NH_2} \xrightarrow{HNO_2} \underset{(B)}{C_9H_{11}OH}$$

(ii) (A) forms alcohol (B) with HNO_2 which is optically active and thus, keeping in view of molecular formula of (A) and (B) as well as the fact that (B) on oxidation gives dicarboxylic acid (*i.e.*, two side chains on C_6H_4 ring), (B) can be

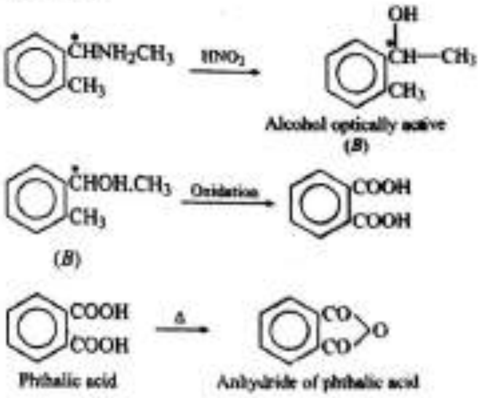


$$\underset{(B)}{C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown CH \cdot OH \cdot CH_3 \end{matrix}} \xrightarrow{[O]} C_6H_4 \begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix}$$

(iii) Since, acid formed on oxidation of (B) forms anhydride and thus, two side chains are at ortho positions, *i.e.*,



Reactions:



*is asymmetric carbon.

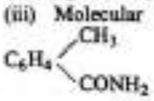
225.

C = 71.11%	$\frac{71.11}{12}$	5.92	8
H = 6.67%	$\frac{6.67}{1}$	6.67	9
N = 10.37%	$\frac{10.37}{14}$	0.74	1
O = 11.85%	$\frac{11.85}{16}$	0.74	1

(i) Empirical formula of (*A*) $\mathbf{C_8H_9NO}$; (*A*) contains only one N-atom in its molecule and thus, molecular formula of (*A*) is C_8H_9NO.

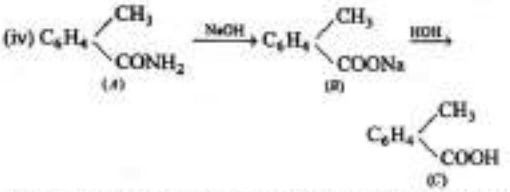
(ii) (*A*) gives NH_3 with NaOH and thus has $CONH_2$ group.

(iii) Molecular formula of (*A*) suggests it to be



$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CONH_2\end{matrix}$

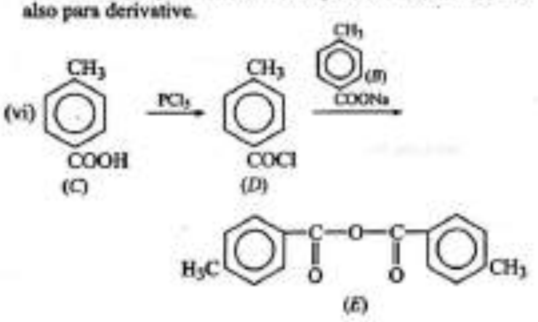
(iv)



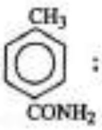
$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CONH_2\end{matrix} \xrightarrow{NaOH} C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COONa\end{matrix} \xrightarrow{HOH} C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COOH\end{matrix}$

(v) Electrophilic substitution on (*C*) gives only one product and thus, (*C*) is para derivative and therefore (*A*) and (*B*) are also para derivative.

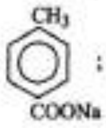
(vi)



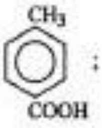
Thus, (*A*) :



; (*B*) :

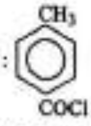


; (*C*) :

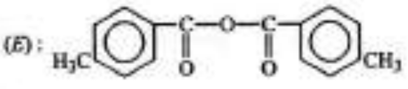


;

(*D*) :

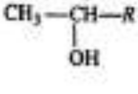


; (*E*) :



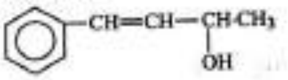
226. (i) Compound (*A*) has —OH gp. along with unsaturation as it reacts with Na and decolourises Br_2/CCl_4.

(ii) (*A*) gives iodoform test and thus, it should have

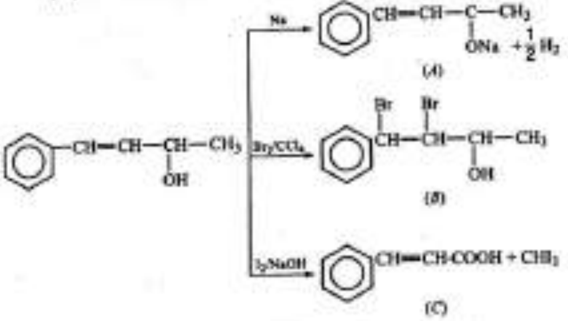


$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—R$ structure.

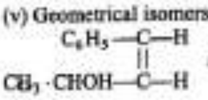
(iii) Thus, (*A*) may be



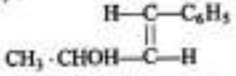
(iv) The reactions :



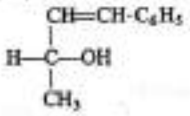
(v) Geometrical isomers of (*A*) :



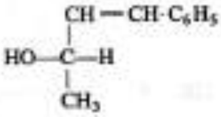
and



(vi) Optical isomers of (*A*) :



and



227. (1) For empirical formula of (*A*)

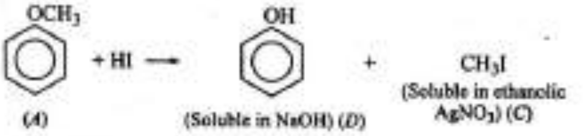
Element	**%**	**Relative No. of atoms**	**Simplest ratio**
C	$\frac{12}{44}\times\frac{0.308}{0.108}\times100=77.77$	6.46	7
H	$\frac{2}{18}\times\frac{0.072}{0.108}\times100=7.40$	7.40	8
O	$100-(77.77)+7.40=14.83$	0.93	1

∴ Empirical formula of (*A*) = $\mathbf{C_7H_8O}$

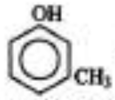
(2) Since, (*B*) gives $C_7H_5OBr_3$ and (*B*) is isomer to (*A*). Thus, molecular formula of (*A*) and (*B*) is C_7H_8O.

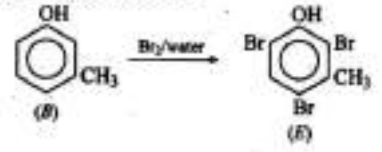
(3) (*A*) is insoluble in NaOH and $NaHCO_3$ so (*A*) is

(4) (*A*) is also confirmed by action with HI

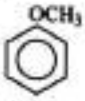


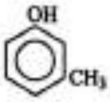
(5) (*B*) is soluble in NaOH and gives (*E*) $C_7H_5OBr_3$ with Br_2 water and so (*B*) is


i.e., *m*-cresol since only meta position can provide tribromo derivative.



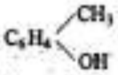
Thus,

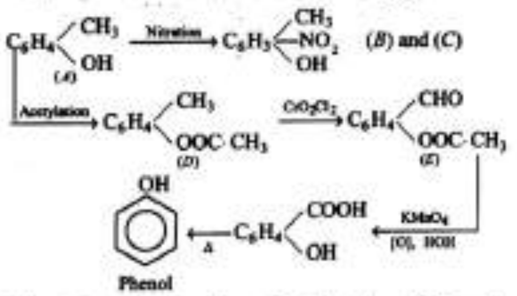
(A) 
Anisole

(B) 
m-Cresol

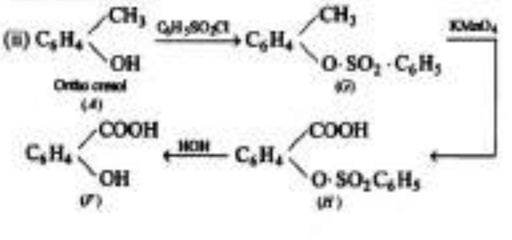
(C) CH_3I (Methyl iodide) (D) 
Phenol

(E)  (2,4,6-Tribromo *m*-cresol)

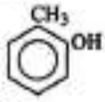
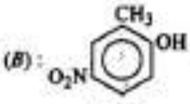
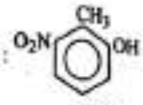
228. (i) The reactions suggest that (A) is 
$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown OH\end{matrix}$

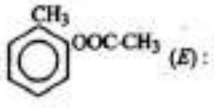
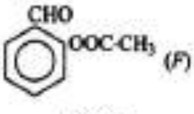
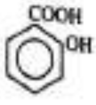


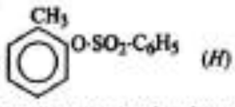
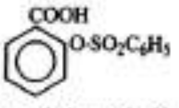
Since, (F) on heating gives phenol and thus (F) is ortho derivative, *i.e.*, salicylic acid. Thus, (A), (D) and (E) are also ortho derivative.

(ii) 

Thus,

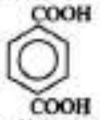
(A) : 
(B) : 
(C) : 

(D) : 
(E) : 
(F) : 

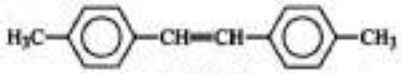
(G) : 
(H) : 

229. (i) (A) decolourises bromine solution and adds up one H_2 molecule and thus, (A) has one double bond.

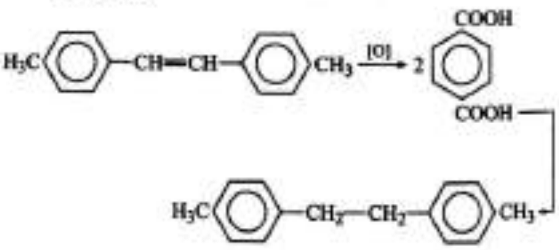
(ii) Oxidation of (A) gives (B) which forms only one mono substitution product. The molecular formula of (B) $C_6H_4(COOH)_2$ suggests that (B) is,

 (*P*-isomer)

(iii) Keeping in view of the above facts (A) seems to be


1,2-Ditolyl ethene

Reactions:

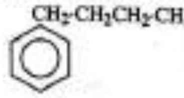


230. (1) (A) has mono substituted alkyl group and thus, molecular formula suggests that (A) is  where, *R* is $—C_4H_9$.

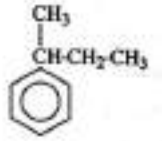
(2) The alkyl group attached on benzene ring is oxidised only if it has at least one benzylic hydrogen atom. Since, the alkyl group shows resistance to oxidation and thus, it should not have benzylic carbon atom, *i.e.*, *R* is $—C(CH_3)_3$.

(3) Thus, (A) is 

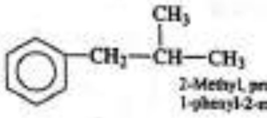
(4) Other (mono substituted) isomers of (*A*) are



n-Butylbenzene or 1-phenylbutane

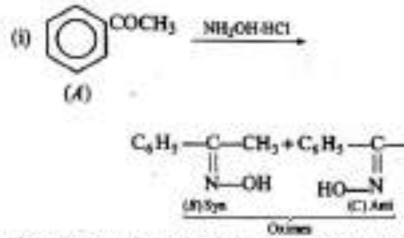


sec. Butylbenzene or 1-methyl-1-phenylpropane

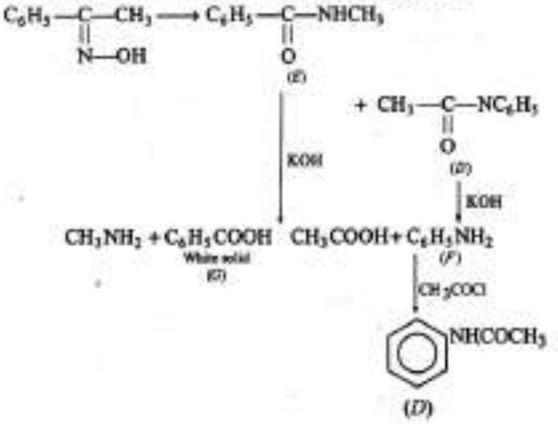


2-Methyl, propylbenzene or 1-phenyl-2-methyl propane

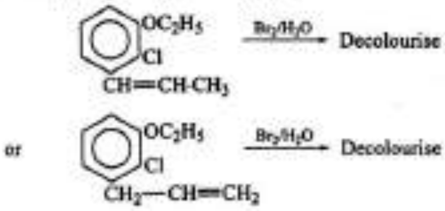
231.



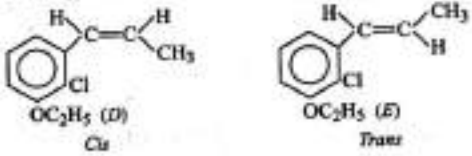
(ii) Oximes undergo Beckmann rearrangement as:

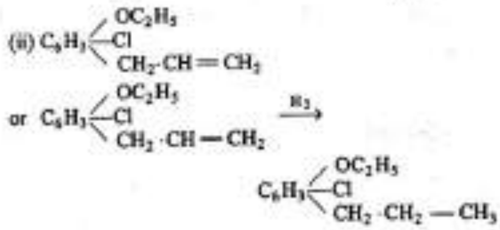


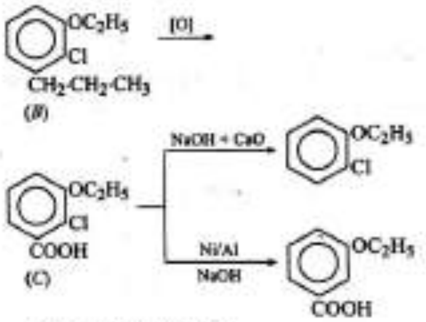
232. The properties suggests that (*A*) is,



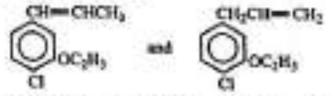
(i) Shows geometrical isomerism while (ii) does not,



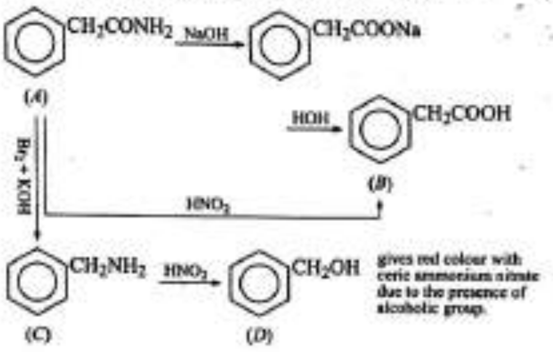




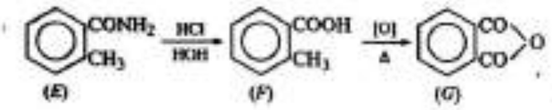
Note : (*A*) may also be

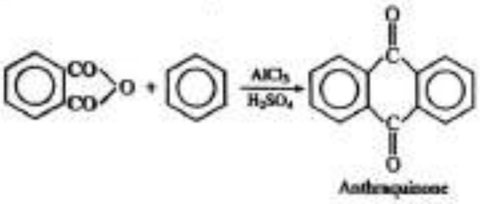


233. The statements provided suggest (*A*) to be $C_6H_5CH_2CONH_2$ having molar mass = 135 g mol⁻¹.



The reaction are





Anthraquinone

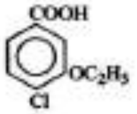
An isomer (E) of (A) is

234. (i) (A) and (B) ($C_{11}H_{13}OCl$) both are isomers and unsaturated.

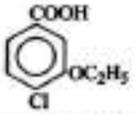
(ii) $(A) \xrightarrow{H_2} (C)$

$(B) \xrightarrow{H_2} (C)$

(iii) (A) $\xrightarrow[KMnO_4]{\text{Oxidation}}$

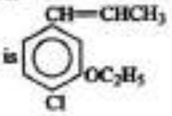


(B) $\xrightarrow[KMnO_4]{\text{Oxidation}}$

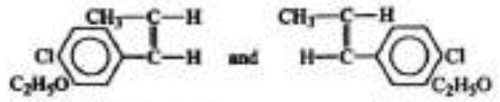


(iv) The side chain at I carbon of ring is oxidised to —COOH

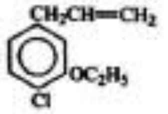
∴ (A) is



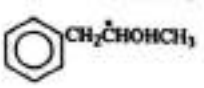
with two geometrical isomers



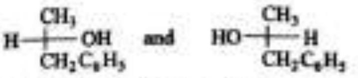
(B) is



235. The statements given from (i) to (iv) suggest (A) to be:

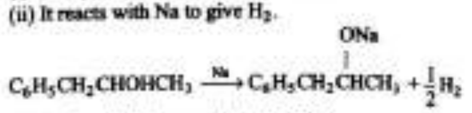


or



(i) It is optically active has C* centre.

(ii) It reacts with Na to give H_2.



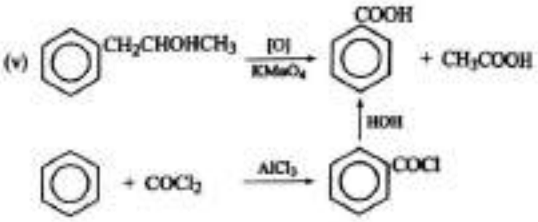
$$C_6H_5CH_2CHOHCH_3 \xrightarrow{Na} C_6H_5CH_2\overset{ONa}{\overset{|}{C}}HCH_3 + \frac{1}{2}H_2$$

(iii) It gives iodoform with I_2 + NaOH.

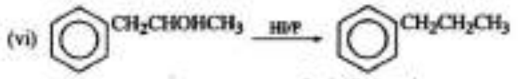
$$C_6H_5CH_2CHOHCH_3 \xrightarrow{I_2 + NaOH} C_6H_5CH_2COONa + \underset{\text{Yellow}}{CHI_3}$$

(iv) It does not react with Br_2 + CCl_4.

(v)



(vi)



Optically inactive
(1-phenyl propane)

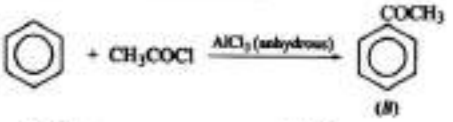
(vii) Being secondary alcohol, it gives test with Lucas reagent in about 5 minute.

236. (i) The molecular formula suggests that (A) is

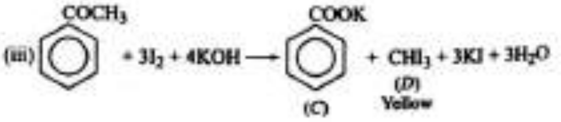
(ii)

Acetophenone

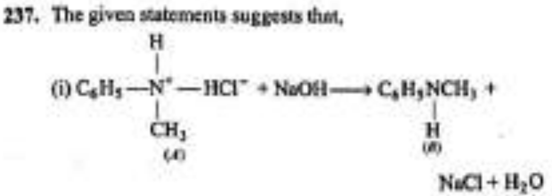
(B) can also be obtained as,



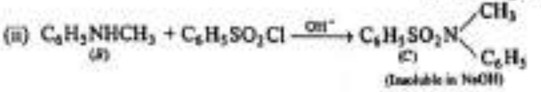
(iii)



237. The given statements suggests that,

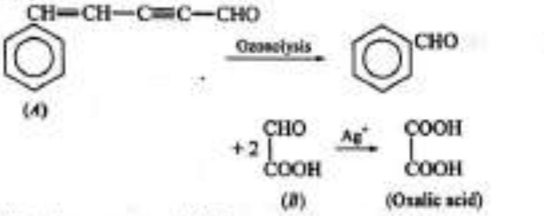


$$\text{(i)}\ \underset{(A)}{C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-HCl^-} + NaOH \longrightarrow \underset{(B)}{C_6H_5\underset{\underset{H}{|}}{N}CH_3} + NaCl + H_2O$$

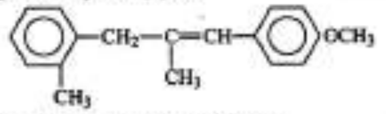


$$\text{(ii)}\ \underset{(B)}{C_6H_5NHCH_3} + C_6H_5SO_2Cl \xrightarrow{OH^-} \underset{\substack{(C)\\ \text{(Insoluble in NaOH)}}}{C_6H_5SO_2N\begin{smallmatrix}CH_3\\ C_6H_5\end{smallmatrix}}$$

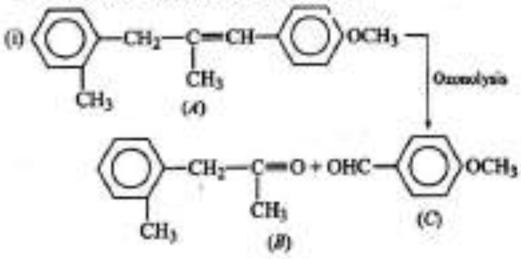
238. The statement provides that the compound (*A*), $C_{11}H_8O$ may be



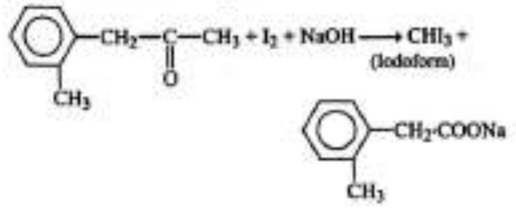
239. The given compound (*A*) is,

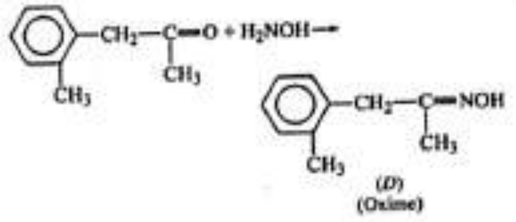


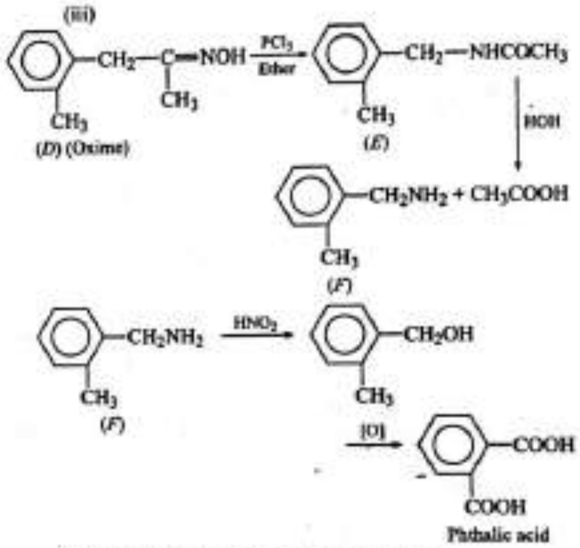
This is proved by following ahead steps.



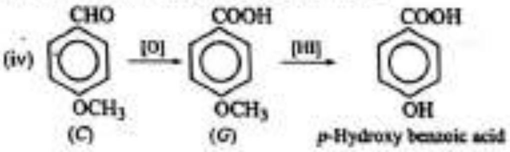
(ii) (*B*) gives iodoform test as it has $CH_3-\underset{\underset{O}{\|}}{C}-$ unit and produces oxime with NH_2OH.



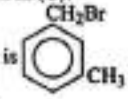


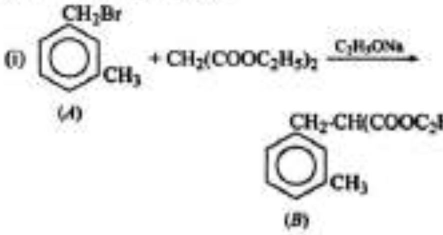


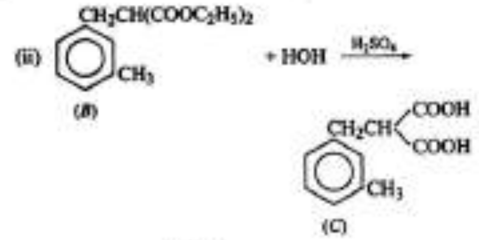
This confirms ortho position of CH_3 in ring.

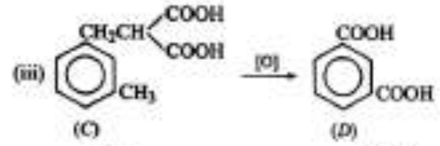


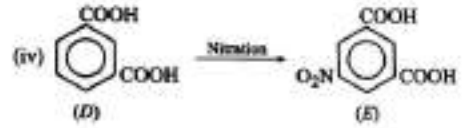
Formation of *p*-hydroxy benzoic acid confirms that two groups are at para position in (*C*).

240. The given compound (*A*) is  . This is confirmed by the following findings.



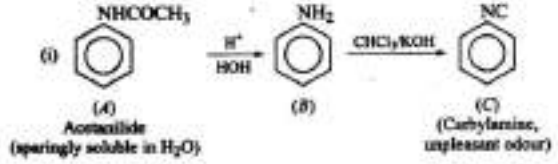


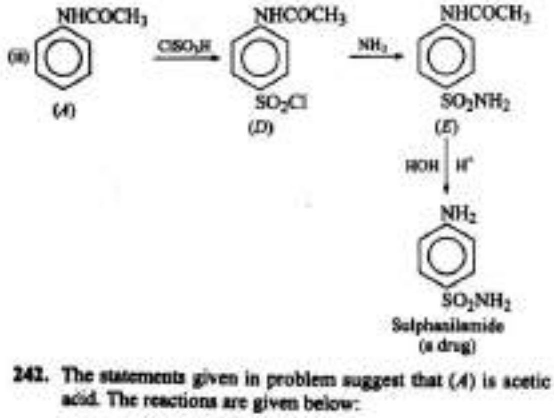




The compound (*E*) a mononitro derivative in which each group is at same distance in benzene nucleus means that it is symmetrical trisubstituted (1,3,5) product and thus, two groups in (*A*), (*B*), (*C*) and (*D*) are at meta positions.

241. The statements given in the problem suggest the following compounds.



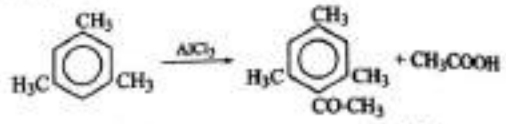


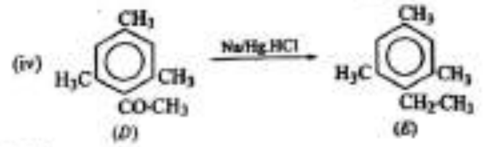
242. The statements given in problem suggest that (*A*) is acetic acid. The reactions are given below:

(i) $\underset{(A)}{CH_3COOH} \xrightarrow[700°C]{AlPO_4} \underset{(B)\ \text{Ketene}}{CH_2=C=O}$

(ii) $\underset{(B)}{CH_2=C=O} + \underset{(A)}{CH_3COOH} \longrightarrow \underset{(C)}{(CH_3CO)_2O}$

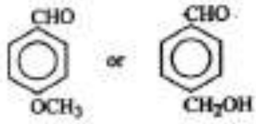
(iii) $(CH_3CO)_2O$ +





243. The isomers are :

(*A*)

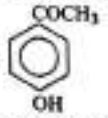


Presence of —CHO group and thus reduces Tollen's reagent.

(*B*)

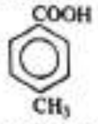
Presence of —CHO group and thus reduces Tollen's reagent. Phenolic group gives positive test with $FeCl_3$(aq.).

(*C*)



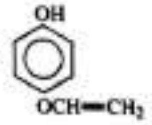
Presence of methyl ketone group and thus gives positive iodoform test.

(*D*)



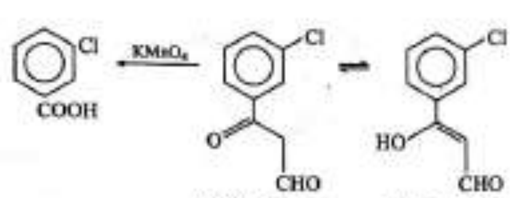
Presence of carboxylic group and thus forms sodium salt of acid.

(*E*)



On acid hydrolysis gives 1,4-dihydroxy benzene.

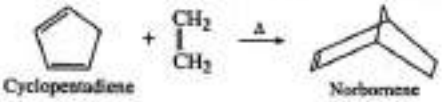
244.



(*A*) Keto form (*B*) Enol form

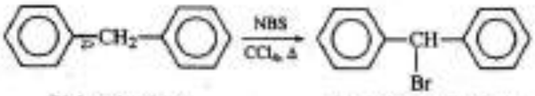
245.

(i)



Cyclopentadiene Norbornene

(ii)



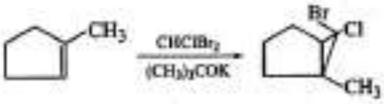
Diphenylmethane Bromodiphenylmethane

246. (a) $CH_3CH_2CHClCOOH \xrightarrow{KOH\ (alc.)} CH_3CH{=}CHCOOH$

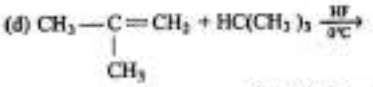
$\xrightarrow{H^+} CH_3CH^+CH_2COOH \xrightarrow{Cl^-} P$

(b) $(CH_3)_3CH \xrightarrow[h\nu]{Br_2} (CH_3)_3C{\cdot}Br \xrightarrow[2.\ D_2O]{1.\ Mg/ether} (CH_3)_3C{\cdot}D$

(c)



(d)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + HC(CH_3)_3 \xrightarrow[0^\circ C]{HF}$$

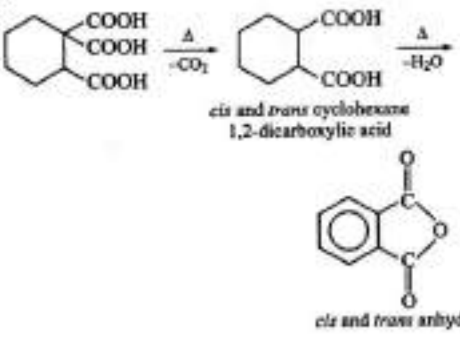
$$(CH_3)_2CH-CH_2{\cdot}C(CH_3)_3$$

(e) $RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2CHO$

(f) $CH_3COCH_3 \xrightarrow{700^\circ C} CH_2{=}C{=}O + CH_4$

(g) $CH_3COOH \xrightarrow{\Delta} CH_2{=}C{=}O + H_2$

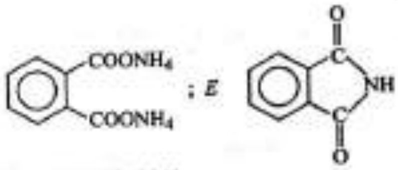
247. (a)



cis and *trans* cyclobexane 1,2-dicarboxylic acid

cis and *trans* anhydrides

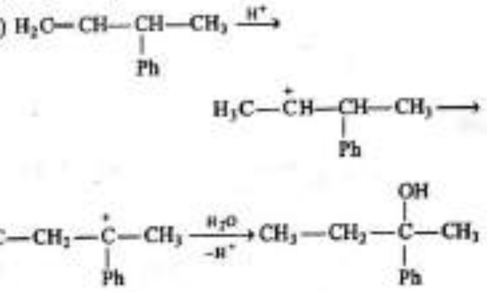
(b) *D* : ; *E*



(c) *A*: $H_2C{=}CH{\cdot}CH_2COPh$

(d) $CH_2{=}CH_2$; Less substituted alkene is formed.

(e)



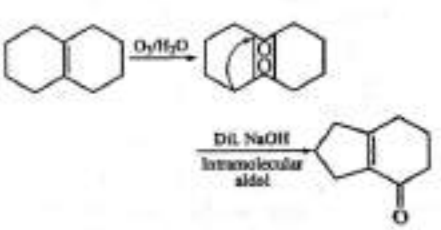
$$H_2C{=}CH-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_3 \xrightarrow{H^+}$$

$$H_3C-\overset{+}{C}H-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_3 \longrightarrow$$

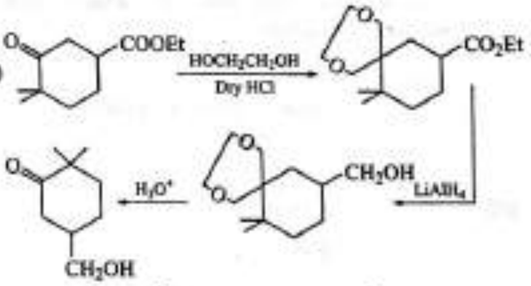
$$H_3C-CH_2-\underset{\displaystyle Ph}{\underset{|}{\overset{+}{C}}}-CH_3 \xrightarrow[-H^+]{H_2O} CH_3-CH_2-\underset{\displaystyle Ph}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_3$$

248.

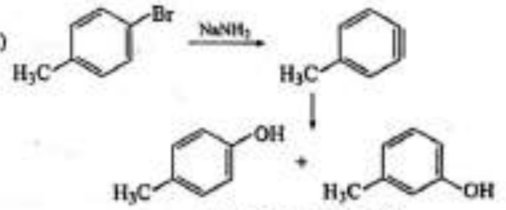
(a)



(b)

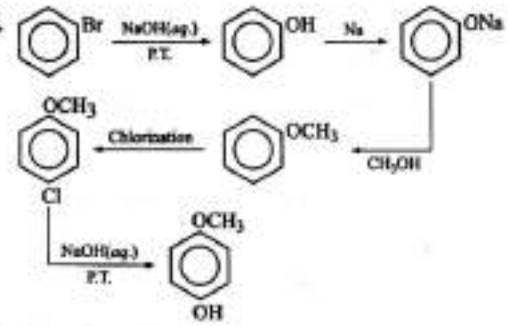


(c)

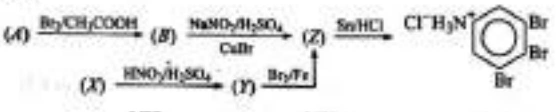


(This is cine substitution)

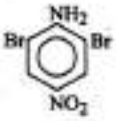
249.

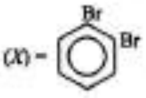


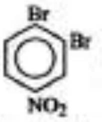
250.

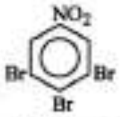


(A) =


(B) =


(X) =


(Y) =


(Z) =


251. *p*-Amino benzoic acid—soluble in acidic medium

p-Hydroxy benzoic acid—insoluble in acidic medium.

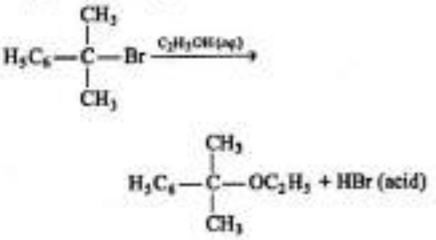
Functional group tests:

(i) —COOH group with $NaHCO_3$ solution gives effervescences of CO_2.

(ii) —OH group gives enolic test with $FeCl_3$.

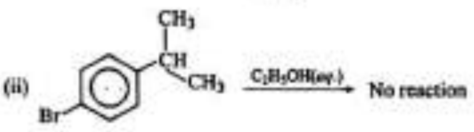
(iii) —NH_2 group gives dye test.

252. (a) (i)

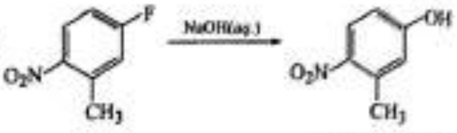


$$H_5C_6-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xrightarrow{C_2H_5OH(aq)} H_5C_6-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OC_2H_5 + HBr\ (acid)$$

(ii)



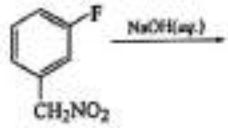
(b) (i)



+ F^- is liberated

This is a bimolecular reaction. Rate of this reaction is being enhanced by presence of electron withdrawing groups at ortho and para positions.

(ii)



F is not liberated.

Bimolecular mechanism is not possible in this case.

(c) (i) Due to presence of lone pair on nitrogen atom NO group is electron donating and ortho, para directing.

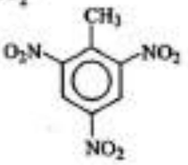
(ii) NO_2 group is electron withdrawing and meta directing.

(d) Due to reduction of central ring, three four membered antiaromatic rings become stable while on reduction of terminal ring only one antiaromatic ring can be stabilized.

253. (*A*) H_2SO_4

(*B*) Br_2

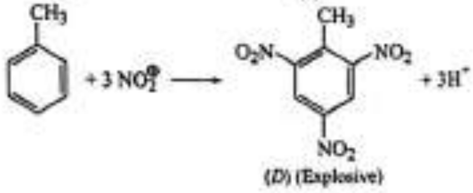
(*C*) $NO_2^{\oplus}$

(D)


Reactions involved are:

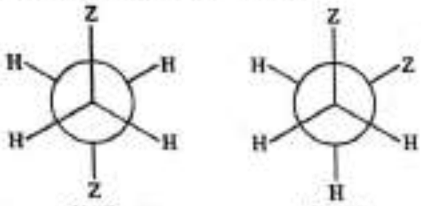
$$\underset{(A)}{2H_2SO_4} + 2NaBr + MnO_2 \longrightarrow \underset{(B)\ (\text{Brown fumes})}{Br_2} + Na_2SO_4 + MnSO_4 + 2H_2O$$

$$\underset{(A)}{H_2SO_4} + HNO_3 \longrightarrow HSO_4^- + \underset{(C)}{\overset{\oplus}{NO_2}} + H_2O$$



(*D*) (Explosive)

254. (a)



(Anti) (Gauche)

Mole fraction of anti form = 0.82

Mole fraction of Gauche form = 0.18

$$\mu_{obs} = 1$$

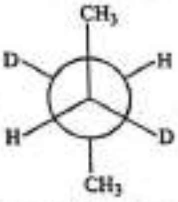
$$1 = \mu_{(anti)} \times 0.82 + \mu_{(Gauche)} \times 0.18$$

$$\mu_{(anti)} = 0$$

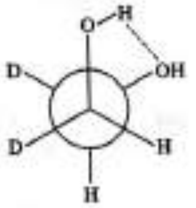
$$\therefore \quad 1 = \mu_{(Gauche)} \times 0.18$$

$$\mu_{Gauche} = \frac{1}{0.18} = 5.55\,D$$

(b) (i)

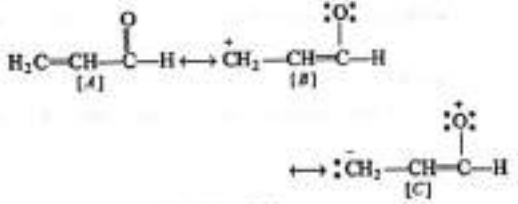


(ii)



255. 1.93, 1.97 and 2.0 respectively.

256.



$$H_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{\overset{\displaystyle :\overset{..}{\underset{..}{O}}:^{-}}{|}}{C}{-}H \longleftrightarrow :\overset{-}{C}H_2{-}CH{=}\overset{\overset{\displaystyle :\overset{+}{O}:}{|}}{C}{-}H$$

[A] [B] [C]

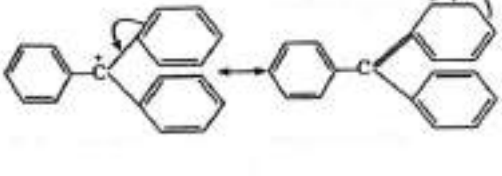
Stability order : $[A] > [B] > [C]$

$[A]$ is more stable as it has no formal charge and have more covalent bonds with complete octet. $[B]$ has negative charge on more electronegative atom 'O' whereas $[C]$ has negative charge on less electronegative atom 'C' thus $[C]$ is less stable than $[B]$.

257. Stability order $\underset{9\,\alpha\text{-H atom}}{(CH_3)_3C^+} > \underset{3\,\alpha\text{-H atoms}}{CH_3\overset{+}{C}H_2} > \underset{\text{no }\alpha\text{-H atom}}{\overset{+}{C}H_3}$

The stability can be explained in terms of hypercojugation of carbocations. More is the number of α-H atoms in molecule showing hyperconjugation, more is its stability.

258.

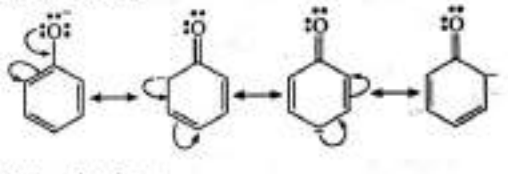


⟷ so on

Due to the presence of three benzene rings, triphenyl methyl cation forms nine canonical structures showing exhaustive resonance stabilization.

259. $:\overset{-}{C}{\equiv}N$ and $:\overset{-}{N}{\equiv}C$ are two tautomeric forms of cyanide ion $:\overset{-}{C}N$ is less stable than $\overset{-}{N}C$ because negative charge is present on less electronegative atoms.

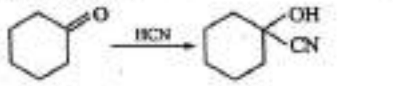
260. **Phenoxide ion :**

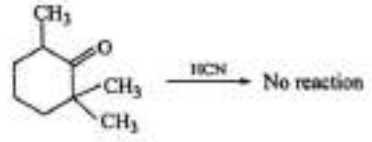


Carboxylate ion :

Carboxylate ion is more stabilized due to the presence of negative charge on more electronegative atom in both the canonical forms, whereas in phénoxide ion, negative charge also exist in less electronegative atom in all but except one canonical form.

261.





due to steric hindrance of three methyl gps at α-carbon of $\rangle C{=}O$ gp

262.

$$H_2\overset{..}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{..}{N}H{-}\overset{..}{N}H_2 \longleftrightarrow H_2\overset{+}{N}{=}\overset{\overset{\displaystyle O^-}{|}}{C}{-}\overset{..}{N}H\overset{..}{N}H_2$$

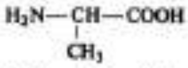
As a result of resonance in semicarbazide only NH_2 gp directly attached to CO gp shows a decrease in electron density (see N acquires + ve charge) and thus does not act as nucleophile. The other NH_2 gp is not involved and retains its nucleophile nature.

263. (4)

Tetrapeptide contains 3 peptide linkage and gives 4 amino acid on hydrolysis

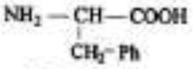
Glycine (Gly) $H_2N{-}CH_2{-}COOH$

Alanine (Ala)



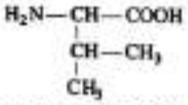
$H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH$

Phenyl alanine (Phe)



$NH_2-\underset{CH_2-Ph}{\underset{|}{CH}}-COOH$

Valine (Val)



$H_2N-\underset{\underset{CH_3}{\underset{|}{CH-CH_3}}}{\underset{|}{CH}}-COOH$

Since tetrapeptide contains free COOH at alanine so that alanine is last unit of tetrapeptide. Glycine does not contain chiral carbon so that Glycine cannot be at first position in tetrapeptide. Hence possible structure of this tetrapeptide will be 4

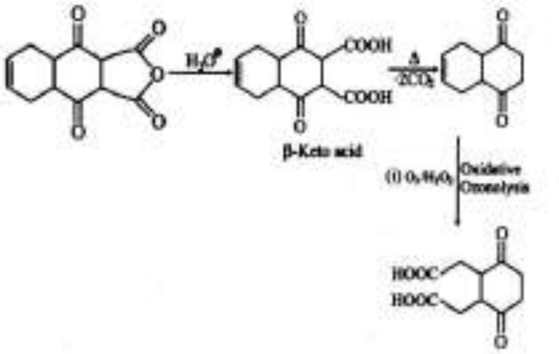
PVGA VGPA
PGVA VPGA

264. (6)

Melamine is

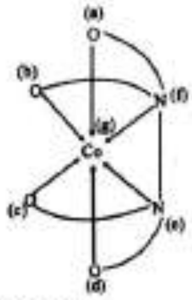
Number of lone pairs on melamine = 6

265. (2)



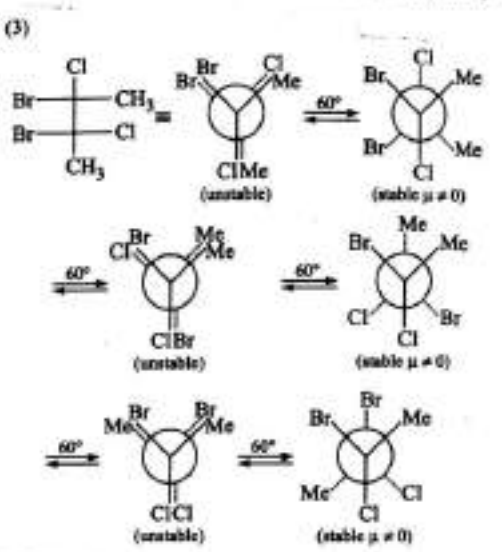
266. (8)

EDTA is



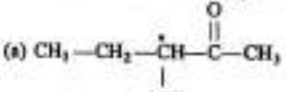
N—Co—O bond angles are
agf, bgf, egf, dgf, age, bge, cge, dge

267. (3)



268. (5) Stereoisomers also react separately with $NaBH_4$. The total number of ketones that give a racemic product(s) are :

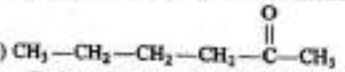
(a)



$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-\overset{O}{\overset{||}{C}}-CH_3$

will not give a racemic mixture on reduction with $NaBH_4$

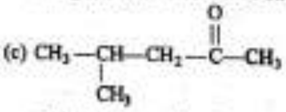
(b)



$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

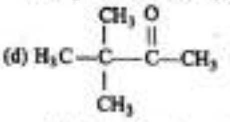
(c)



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

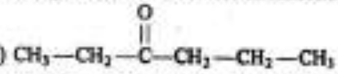
(d)



$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{||}{C}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

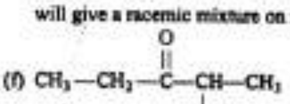
(e)



$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_2-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

(f)

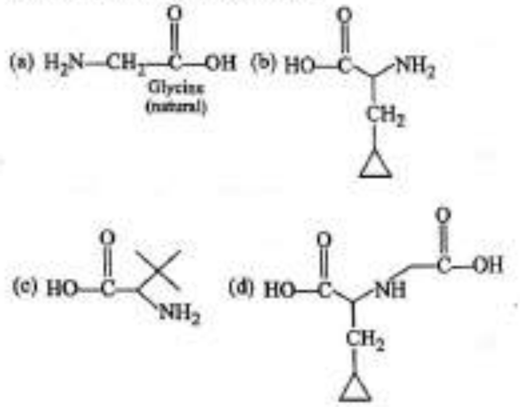


$CH_3-CH_2-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

will give a racemic mixture on reduction with $NaBH_4$

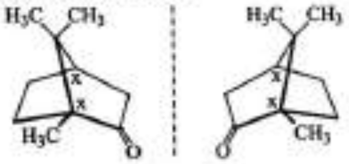
269. (1)

This peptide on complete hydrolysis produced 4 distinct amino acids which are given below :



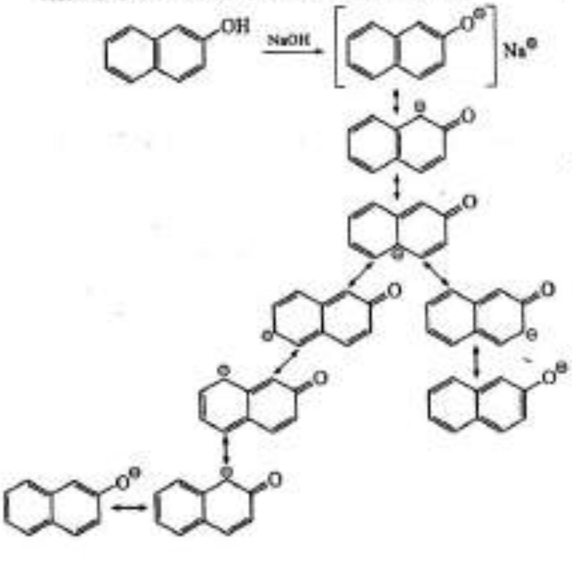
Only glycine is naturally occurring amino acid

270. (2) *M* is an organic compound known as camphor. It contains two **rigid** chiral centre so it can exist only in **two** enantiomeric forms.

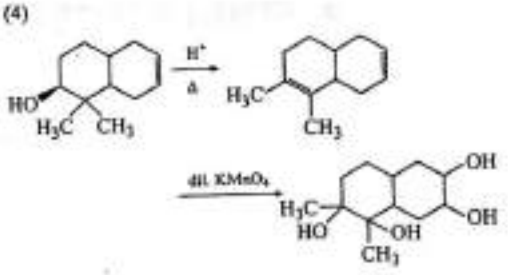


271. (9)

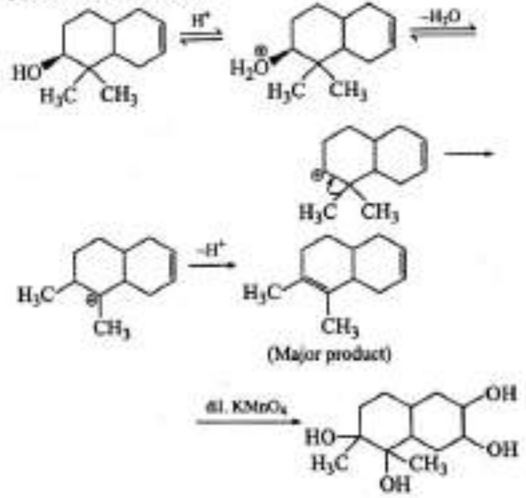
Reaction of β-naphthol gives sodium salt. Given below are resonance structure of anion of sodium salt formed.



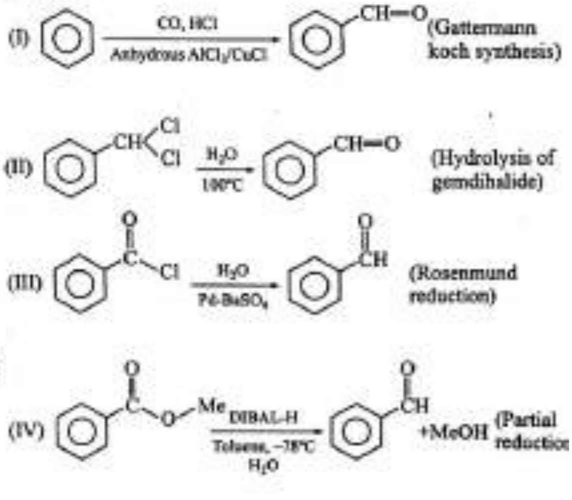
272. (4)



Mechanism of reaction



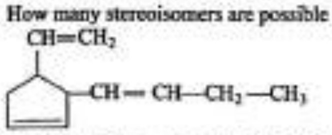
273. (4)



• SINGLE INTEGER ANSWER PROBLEMS •

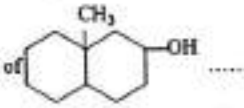
1. Volume ratio of gases evolved (at NTP) at cathode and anode during the electrolysis of $HCOONa_{(aq)}$ is ....
2. Volume ratio of gases evolved (at same P and T) at cathode and anode during the electrolysis of $CH_3COONa_{(aq)}$.
3. Mole ratio of gases evolved at cathode and anode during the electrolysis of $CH_3(CH_2)_2COONa_{(aq)}$:
4. The number of α-H atoms in 2-methyl but-2-ene is ......
5. The maximum number of tautomers of a compound can be ......
6. The compound shows metamerism. It must possess a functional group which has valence equal to or greater than ......
7. A molecule having formula C_7H_8O can show maximum number of aromatic isomers :
8. The number of α-H atoms in but-2-ene is ......
9. Number of acidic hydrogen, in the molecule $CH_3CO\text{-}CHI\text{-}CO\text{-}CH_3$:
10. The number of possible structural and stereo isomers that can be produced during monochlorination of 2-methyl butane are ......
11. The degree of unsaturation in cyclobutanone is ......
12. The degree of unsaturation in benzene is ......
13. The maximum number of acidic hydrogen in a molecule of C_6H_{10} is :
14. The number of C—O bonds in Ninhydrin is :
15. The number optical isomers of cyclic alcohol having molecular formula C_4H_7OH.
16. Alkaline solution of glucose shows an equilibrium. The number of molecules involved in equilibrium are ......
17. A polyene has four double bonds. Maximum no. of products that can be formed on ozonolysis are :
18. Number of π-bonds in allyl cyanide is ......
19. Number of H-atoms in glycine is ......
20. Number of pairs of *cis-trans* isomers for the compound having molecular formula $C_2IBrClF$:
21. Number of enantiomeric pairs obtained on monochlorination of 2-methyl butane :
22. Total number of molecules having disubstitution nature for the molecular formula C_6H_{14} :
23. The number of enantiomeric pairs formed on monochlorination of 2-methyl butane :
24. The number of 2° carbon atoms in 2,2,4-trimethyl hexane are ......
25. The number of diastereoisomeric pair of the compound $CH_3CHOH\cdot CHBr\cdot CH_3$ are ......
26. Total enantiomeric pairs of compound sorbitol $CH_2OH(CHOH)_4CH_2OH$ are ......
27. Total number of meso isomers of sorbitol are ......
28. Number of p-orbitals left unused in sp-hybridized carbon atom ......
29. Number of asymmetric carbon atoms in glucose is ......
30. Number of 4° carbon atoms in 2,2,4,4-tetramethyl pentane is ......
31. An alkane forms monosubstitution products. The minimum number of carbon atoms in it should be ......
32. The ratio of asymmetric carbon atoms and number of enantiomeric pairs of butan-2,3-diol is ......
33. Number of π-bonds in tetra cyanomethane is ......
34. *d*-2-iodobutane on treatment with NaI in acetone produces how much optically active forms ......
35. 0.22 g of organic compound C_xH_yO occupied 112 mL at NTP and on combustion gave 0.44 g CO_2. The ratio of $y:x$ is ......
36. Possible number of alkanes with molecular formula C_7H_{16} are ......
37. Which ratio of CH_4 and O_2 on heating in presence of Cu or Fe at high pressure yields CH_3OH?
38. The molar mass of an organic compound is 64 g mol^{-1}. If it is assumed that vapour density of CH_4 is one, the vapour density of compound will be ......
39. Number of molecules of alkene required for the reaction of one molecules of B_2H_6 to carry out hydroboration ......
40. 11.43 g of Br_2 reacts with how much pent-1-ene?
41. 1.60 g Br_2 reacts with 1.12 g alkene. The number of carbon atoms in alkene is ......
42. The silver salt of an unknown alkyne contains 67.08% Ag. Assuming no other functional gp, the number of carbon atoms in alkyne is ......
43. Number of ethyl alcohol molecules absorbed by one molecule of $MgCl_2$:
44. One mole of glycerol is completely acylated. The number of moles of acetyl chloride needed are ......
45. The ratio of number of carbon atom to number of oxygen atoms in [18]-crown-6-molecules are ......
46. 0.037 g of an alcohol R—OH on treatment with CH_3MgI gives 11.2 cm^3 gas at STP. The number of carbon atoms in alcohol are ......
47. A straight chain organic compound $C_3H_8O_3$ yields $C_9H_{14}O_6$ on complete acetylation. The number of hydroxyl groups in $C_3H_8O_3$ are ......
48. A polyhydric alcohol having molecular formula $C_5H_{12}O_4$ is changed to $C_{13}H_{20}O_8$ on treatment with acetic anhydride. No. of OH gp in alcohol is ......
49. Benzil (PhCOCOPh) is completely reduced by $LiAlH_4$. Number of possible stereomers of molecule obtained after reduction is ......
50. The ratio of carbon and oxygen atoms in 2-methyl benzoic acid is ......
51. Maximum number of stereo isomers of the compound 2,3,5,6-tetrachloroheptane are ......
52. How many isomers are possible for

53. How many stereoisomers are possible for



54. How many isomers are possible for C_3H_6DCl?

55. Number of basic nitrogen atoms in purine is ......

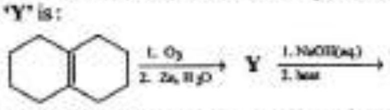
56. The number of stereo isomers of  ......

57. How many structural isomers are possible when one of the hydrogen in diphenyl methane is replaced by a halogen.

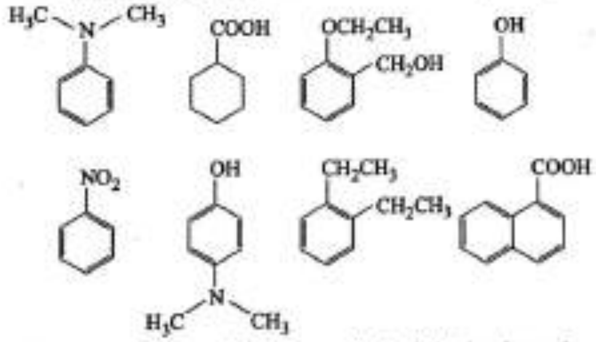
58. The number to chiral centres present in 3,4-dibromo-2-pentanol is ......

59. The total number of cyclic as well as stereoisomers possible for a compound with the molecular formula C_5H_{10} is : (IIT 2009)

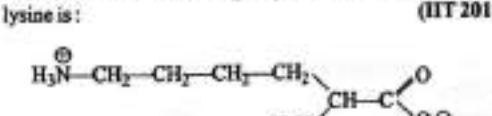
60. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is : (IIT 2010)



61. Amongst the following, the total number of compounds soluble in aqueous NaOH is : (IIT 2010)



62. The total number of basic groups in the following form of lysine is : (IIT 2010)

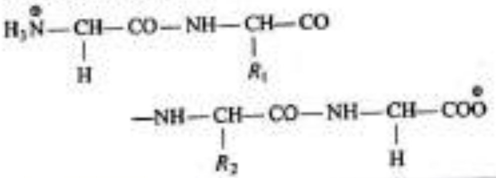


63. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is : (IIT 2010)

64. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclo pentyl hexane using alcoholic KOH is : (IIT 2011)

65. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the compound $CH_3CH_2CH(CH_3)CH_2CH_3$: (IIT 2011)

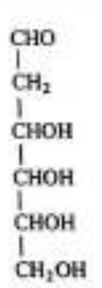
66. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0? (IIT 2012)



$$\overset{\oplus}{H_3N}-\underset{\displaystyle H}{\underset{|}{CH}}-CO-NH-\underset{\displaystyle R_1}{\underset{|}{CH}}-CO-NH-\underset{\displaystyle R_2}{\underset{|}{CH}}-CO-NH-\underset{\displaystyle H}{\underset{|}{CH}}-\overset{\ominus}{COO}$$

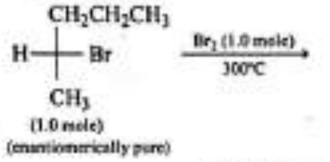
Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

67. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is: (IIT 2012)



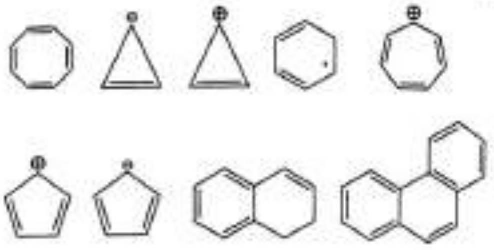
$$\begin{array}{c} CHO \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

68. In the following monobromination reaction, the number of possible chiral products is :



[JEE (Advanced) I 2016]

69. Among the following, the number of aromatic compound(s) is : **[JEE (Advanced) I 2017]**

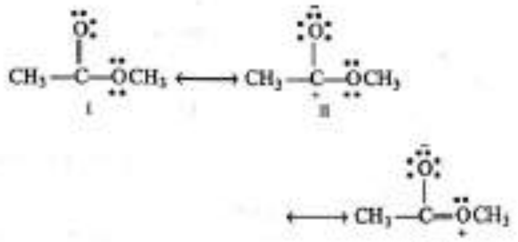


ANSWERS

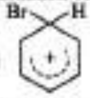
1. Three **2.** Three **3.** Two **4.** Nine **5.** Two **6.** Two **7.** Five **8.** Six **9.** One **10.** Six **11.** Two **12.** Four
13. One **14.** Three **15.** Two **16.** Three **17.** Five **18.** Three **19.** Five **20.** Three **21.** Two **22.** Two **23.** Two **24.** Two
25. Four **26.** Four **27.** Two **28.** Two **29.** Four **30.** Two **31.** Three **32.** Two **33.** Eight **34.** Two **35.** Two **36.** Nine
37. Nine **38.** Four **39.** Six **40.** Five **41.** Eight **42.** Four **43.** Six **44.** Three **45.** Three **46.** Four **47.** Three **48.** Four
49. Three **50.** Four **51.** Eight **52.** Four **53.** Eight **54.** Eight **55.** Three **56.** Eight **57.** Four **58.** Three **59.** Seven **60.** One
61. Four **62.** Two **63.** Six (4+2) **64.** Five **65.** Eight **66.** Eight **67.** Eight **68.** Five **69.** Five

OBJECTIVE PROBLEMS (One Answer Correct)

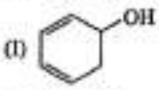
1. Which are ambiphiles or ambidents?
   (a) CH_3CN (b) HCHO
   (c) HF (d) All of these
2. Which of the following canonical structure is more contributor to real structure?

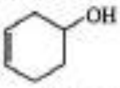


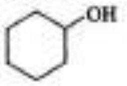
   (a) I (b) II
   (c) III (d) All of these
3. The intermediate formed in bromination of benzene is :
   (a) Br^+ (b)



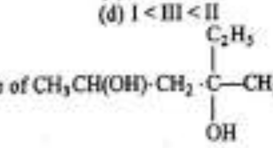
   (c) Br^- (d) $C_6H_5Br^-$
4. The order of ease of dehydration for given alcohols :

(I)


(II)


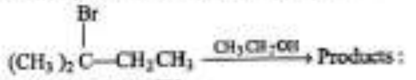
(III)


   (a) III < II < I (b) I < II < III
   (c) II < I < III (d) I < III < II
5. The IUPAC name of



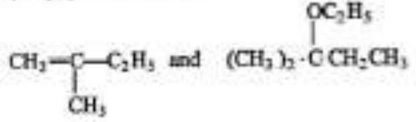
$CH_3CH(OH)\cdot CH_2\cdot \overset{\overset{C_2H_5}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$ is :

   (a) 2-methyl-2,4-pentanediol
   (b) 4-methyl-2,4-hexanediol
   (c) 3-methyl-3,5-hexanediol
   (d) none of the above
6. The Hitler army sign, *i.e.*, reverse of 'Swastik' represents which compound :
   (a) 2,2-dimethyl butane (b) 3,3-dimethyl hexane
   (c) 2,3-dimethyl pentane (d) 3,3-diethyl pentane
7. Which of the following is correct about ionisation energy and electron affinity of methyl free radical $(\dot{C}H_3)$?
   (a) $IE = EA$ (b) $IE > EA$
   (c) $IE < EA$ (d) Nothing can be said
8. The correct decreasing order of nucleophilicity of the following is :
   (a) $RCOO^- > HO^- > RO^-$ (b) $RO^- > OH^- > RCOO^-$
   (c) $RO^- > RCOO^- > OH^-$ (d) $H^-O > RO^- > RCOO^-$
9. Which of the following shows heterovalent resonance ?
   (a) CO_3^{2-} (b) C_6H_6
   (c) CO_2 (d) $CH_2=CH-CH=CH_2$
10. Which of the following hydrate will be more stable ?
   (a) $Br_2CHCH(OH)_2$ (b) $Br_2CH\cdot CH_2CH(OH)_2$
   (c) $CH_3CH(OH)_2$ (d) $BrCH_2CH(OH)_2$
11. Which of the following carbonyl compound will show addition of HCN?
   (a) $(CH_3)_2CH\cdot COCH(CH_3)_2$
   (b) $C_6H_5CO\cdot C_6H_5$
   (c) CH_3COCH_3
   (d) All of the above
12. Predict the products formed in the reaction



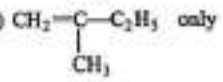
$(CH_3)_2\overset{\overset{Br}{|}}{C}-CH_2CH_3 \xrightarrow{CH_3CH_2OH}$ Products :

   (a) $(CH_3)_2C=CH\cdot CH_3$
   (b) $(CH_3)_2C=CH\cdot CH_3$,



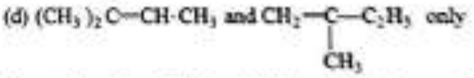
$CH_2=\underset{\underset{CH_3}{|}}{C}-C_2H_5$ and $(CH_3)_2\cdot\overset{\overset{OC_2H_5}{|}}{C}CH_2CH_3$

   (c)



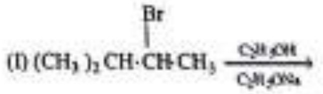
$CH_2=\underset{\underset{CH_3}{|}}{C}-C_2H_5$ only

   (d)



$(CH_3)_2C=CH\cdot CH_3$ and $CH_2=\underset{\underset{CH_3}{|}}{C}-C_2H_5$ only

13. The product formed during β-elimination in the reaction is :



(I) $(CH_3)_2CH\cdot\overset{\overset{Br}{|}}{C}H\cdot CH_3 \xrightarrow[C_2H_5ONa]{C_2H_5OH}$

(II) $(CH_3)_2CH\cdot CH_2\cdot CH_2Br \xrightarrow[C_2H_5ONa]{C_2H_5OH}$

   (a) only 2-methyl but-2-ene in I and II
   (b) 3-methyl but-1-ene in II and 2-methyl but-2-ene and 3-methyl but-1-ene in I
   (c) 2-methyl but-2-ene and 3-methyl but-1-ene in II and 2-methyl but-2-ene in I
   (d) all the three enes in I and II
14. S_N1 reactions take place fastest in the medium :
   (a) H_2O (b) CH_3OH
   (c) C_6H_6 (d) acetone
15. 1-bromo-3-chloropropane on treating with aq. NaCN gives :
   (a) $Cl\cdot CH_2CH_2CN$ (b) $Br\cdot CH_2\cdot CH_2CN$
   (c) $Cl\cdot CH_2\cdot CH_2CH_2CN$ (d) $Br\cdot CH_2\cdot CH_2\cdot CH_2CN$
16. An optically active compound is 50% optically pure then for 100 g sample of this means :
   (a) one enantiomer is 50% and the other enantiomer is absent

(b) one enantiomer is 50% and the other enantiomer is also 50%
(c) one enantiomer is 75% and the other enantiomer is 25%
(d) the compound has no optical activity

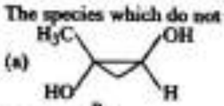
17. The simplest chiral alkanes have molar mass ...... and the number is ......
(a) 100, 2 (b) 86, 1
(c) 100, 1 (d) 114, 1

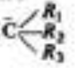
18. The molecule $CH_3CH{=}CH \cdot CH(CH_3)OH$ can show :
(a) Geometrical isomerism only
(b) Optical isomerism only
(c) Structural isomerism only
(d) Structural and stereoisomerism including geometrical and optical both

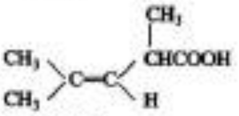
19. 2-methyl-1-chloro butane an optically active alkane on subjecting for Wurtz reaction gives :
(a) Optically inactive 3,6-dimethyl octane
(b) Optically active 2,6-dimethyl octane
(c) Optically active 3,6-dimethyl octane
(d) Optically inactive 2,6-dimethyl octane

20. Select the correct statement :
(a) $R_1C^{\oplus}$ in a carbocation is chiral carbon
(b) $R_2C^{\cdot}$ in a free radical is chiral carbon
(c) R_3C^{-} in a carbanion is a chiral carbon
(d) sp^2 carbon in oximes and imines are chiral

21. The species which do not possess chirality :

(a)


(b)


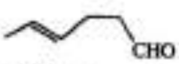
(c)


(d) CH_3CDHCl

22. The correct structure of *trans*-2-hexenal is :

(a)

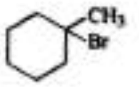

(b)

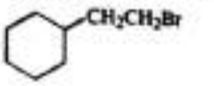

(c)


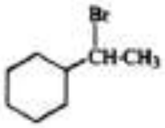
(d)


23. One of the chain termination step in the halogenation of alkanes other than methane is :
(a) Addition reaction
(b) Neutralisation reaction
(c) Elimination reaction
(d) Disproportionation reaction

24. The correct decreasing order for dehydrohalogenation for the given halides is :

(I)


(II)


(III)


(a) I > III > II (b) I > II > III
(c) III > I > II (d) II > I > III

25. Which one is not correctly matched ?
(a) Adkin's catalyst ($CuO \cdot Cr_2O_4$)
(b) Adam's catalyst (PtO_2)
(c) Lindlar's catalyst Pd on $CaCO_3$ + $(CH_3COO)_2Pb$ and quinolene
(d) Wilkinson catalyst $P(Ph_3)_2Cl_3$

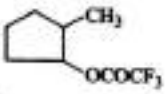
26. Which of the reactant does not form the product according to peroxide effect on 2-methyl propene ?
(a) CH_3SH (b) $CBrCl_3$
(c) $CHCl_3$ (d) None of these

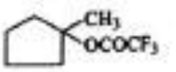
27. Which of the following can be used for hydroxylation of alkene ?
(a) OsO_4/pyridine followed by hydrolysis by $Na_2SO_3 + NaHSO_3$
(b) Baeyer's reagent at room temperature
(c) HCOOH followed by hydrolysis
(d) All of the above

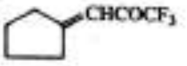
28. The degree or element of unsaturation (DU) is given by the formula $DU = \frac{2n_1 + 2 - n_2}{2}$; where n_1 and n_2 are number of C and H or Cl-atoms respectively. Which can be said about degree of unsaturation :
(a) DU = 1 mean on olefinic bond or one ring
(b) DU = 2 means two olefinic bond or one triple (C≡C) bond, two C=C or two rings or one ring with C=O bond
(c) DU = 0 mean no unsaturation
(d) All of the above

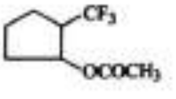
29. The number of optical isomers of alkyne C_6H_{10} are :
(a) 2 (b) 4
(c) 6 (d) 8

30. Which one represents the product of the reaction given below ?

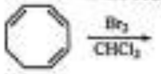
(a)


(b)


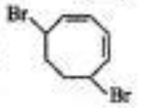
(c)


(d)


31. The product formed in the reaction is :

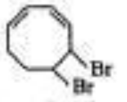


(a)



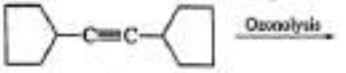
(b) $C_8H_{10}Br_6$

(c)

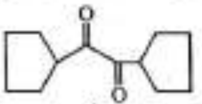


(d) none of these

32. The product formed in the reaction given is :

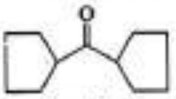


(a)

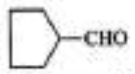


(b)

(c)



(d)



33. Which of the following does not react with propynide ion ?

(a) H_2O (b) CH_3OH

(c) $NH_3(l)$ (d) 1-hexene

34. Which of the following is not dissolved in conc. H_2SO_4 :

(a) Acetylene (b) Ethane

(c) But-2-yne (d) Propene

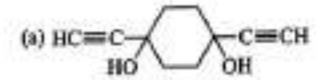
35. How many terminal alkynes isomers are possible for the formula C_6H_{10} :

(a) 2 (b) 3

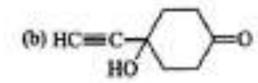
(c) 4 (d) 5

36. The product of the reaction of cyclohexa-1,4-dione with acetylene in acidic medium is :

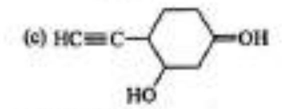
(a)



(b)



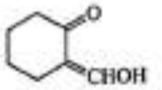
(c)



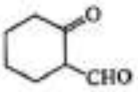
(d) No reaction

37. The major reaction product of combination of cyclohexanone with ethyl formate in presence of C_2H_5ONa is :

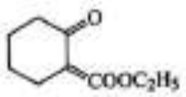
(a)



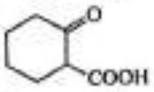
(b)



(c)

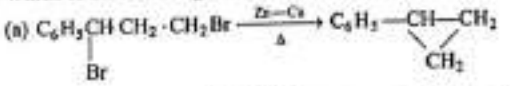


(d)



38. Which of the following reaction is not correct ?

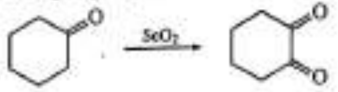
(a)



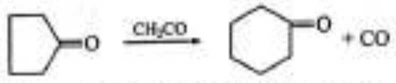
$C_6H_5\underset{\underset{Br}{|}}{C}H\,CH_2\cdot CH_2Br \xrightarrow[\Delta]{Zn-Cu} C_6H_5-CH \overset{}{-} CH_2$ (with CH_2 bridging below)

(b) $ClCH_2CH_2CH_2CN \xrightarrow{Conc.NaOH} HO\cdot CH_2\cdot CH_2\cdot CH_2CN$

(c)



(d)



39. 1,2-dibromo cyclohexane on treatment with base yields 1,3-cyclohexadiene and not cyclohexyne. The reason is :

(a) H-atoms are not available at 1,2-positions

(b) elimination of HBr takes place

(c) a triple bond in a small ring is not favourable

(d) all of the above

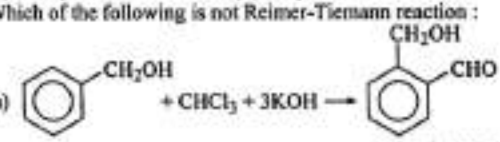
40. Carbocations do not gain stability by :

(a) Hydride shift (b) Methyl shift

(c) Phenyl shift (d) Ethyl shift

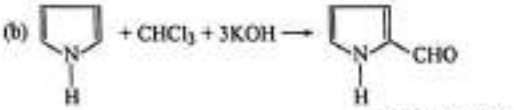
41. Which of the following is not Reimer-Tiemann reaction :

(a)



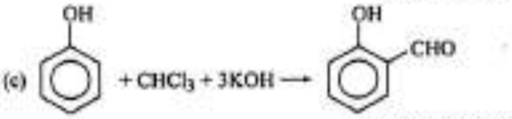
$+ 3KCl + 2H_2O$

(b)



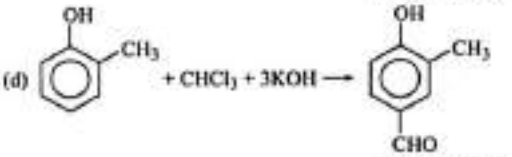
$+ 3KCl + 2H_2O$

(c)



$+ 3KCl + 2H_2O$

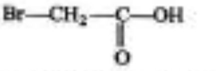
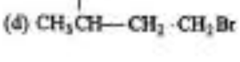
(d)



$+ 3KCl + 2H_2O$

42. Which of the following statement is wrong ?
    (a) H_2O is a poor nucleophile and good leaving group
    (b) OH^- is a good nucleophile and good leaving group
    (c) F^- is a good nucleophile but poor leaving group
    (d) I^- is a poor nucleophile but good leaving group

43. Select the wrong statement :
    (a) Nucleophilicity of nucleophile is its ability to donate electron pair to metal ion
    (b) Basic nature of a base is its ability to donate electron pair to a proton
    (c) Nucleophilicity of a nucleophile is its ability to donate electron pair to a carbocation (or an electrophile)
    (d) Nucleophiles may or may not carry –ve charge

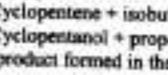
44. Which of the following compound on reacting with Mg will give Grignard reagent ?
    (a) $HOCH_2CH_2CH_2Br$
    (b) $CH_3C{\equiv}CCH_2CH_2I$
    (c) 
    $Br{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$
    (d) 
    $CH_3\overset{\overset{NH_2}{|}}{C}H{-}CH_2\cdot CH_2Br$

45. Select the wrong statement :
    (a) Al isopropoxide is a specific reducing agent for aldehydes and ketones having some other reducible groups like $>C{=}C<$, $-C{\equiv}C-$, $-NO_2$, etc.
    (b) Al terbutoxide oxidises 1° and 2° alcohols into aldehydes and ketones respectively
    (c) Nucleophilicity is increased with the number of electron repelling group R irrespective of the nature of R
    (d) $CH_2 \cdot CH_2Cl$ is a weaker base than $CH_3CH_2O^-$

46. Which of the following will not give iodoform test?
    (a) Pyruvic acid
    (b) Benzophenone
    (c) Lactic acid
    (d) Acetophenone

47. Which fact does not support about the use of $ZnCl_2$ with HCl in Lucas reagent test for the test of alcohols ?
    (a) $ZnCl_2$ is a Lewis acid
    (b) It forms H_2ZnCl_4 with HCl which is stronger acid than HCl
    (c) H_2ZnCl_4 reacts with alcohols to form $R^{\oplus}$ readily
    (d) $ZnCl_2$ reacts with alcohol to form R^+ readily

48. Ethoxy ethanol and methyl isopropyl ether can be distinguished by :
    (a) conc. HI
    (b) iodoform test
    (c) Amm. $AgNO_3$
    (d) $ZnCl_2$

49. In,  $\xrightarrow{\text{dil. } H_2SO_4}$; the products are :
    (a) Pentanol + isobutene
    (b) Cyclopentanol + isobutene
    (c) Cyclopentene + isobutanol
    (d) Cyclopentanol + propene

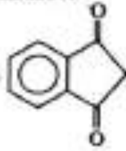
50. The product formed in the reaction :

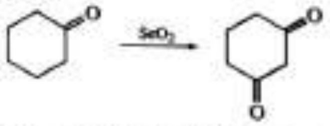
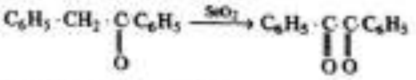
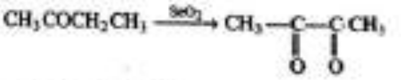
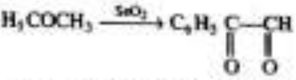
$$Ph \cdot CH_2CH_2COCl + H_2 \xrightarrow[\text{S or quinoline}]{Pd/C} \text{is :}$$

    (a) $Ph \cdot CH_2CHO$
    (b) $PhCH_2CH_2CH_2OH$
    (c) $Ph \cdot CH_2 \cdot CH_2CHO$
    (d) $PhCH_2CH_2CH_3$

51. Which of the following statement about carbonyl compounds is correct ?
    (a) α-H atom is acidic
    (b) The anion left after removal of H^+ is stabilised enolate anion
    (c) The base, catalysed aldol condensation is due to the acidic nature of α-H-atom
    (d) All of the above

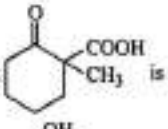
52. Conversion of carbonyl group of a molecule to methylene group cannot be done successfully if substrate :
    (a) contains alkali sensitive group, in case of Wolff Kishner reduction
    (b) contains acid sensitive group, in case of Clemmensen reduction
    (c) is sterically hindered ketone, in case of Clemmensen reduction or Wolff Kishner reduction
    (d) all of the above

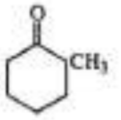
53. Ninhydrin  exists as a hydrate. Which C=O is hydrated :
    (a) Top one
    (b) Middle one
    (c) Bottom one
    (d) All of these

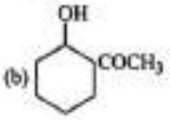
54. Which one does not correctly represents the oxidation by SeO_2?
    (a) 
    (b) 
    $C_6H_5 \cdot CH_2 \cdot \underset{\underset{O}{\|}}{C}C_6H_5 \xrightarrow{SeO_2} C_6H_5 \cdot \underset{\underset{O}{\|}}{C}\underset{\underset{O}{\|}}{C}C_6H_5$
    (c) 
    $CH_3COCH_2CH_3 \xrightarrow{SeO_2} CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}CH_3$
    (d) 
    $C_6H_5COCH_3 \xrightarrow{SeO_2} C_6H_5\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}H$

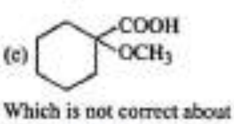
55. Benzaldehyde do not respond test for –CHO group by Fehling's solution or Benedicts solution because :
    (a) it does not contain α-H-atom
    (b) it is aromatic aldehyde
    (c) it undergoes Cannizzaro reaction due to alkaline nature of these reagent
    (d) all of the above

56. $C_nH_{2n}O_2$, a saturated monocarboxylic acid formula does not represent its isomerism with :
(a) esters
(b) hydroxy carbonyl compounds
(c) hydroxy oxiranes
(d) anhydrides

57. The product formed on heating  is :

(a) 

(b) 

(c) 

(d) $C_6H_{11}OCH_3$

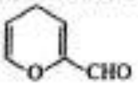
58. Which is not correct about fumaric and maleic acid?
(a) K_2 of fumaric acid is more than maleic acid
(b) Maleiate ion shows H-bonding
(c) Fumarate ion shows H-bonding
(d) Maleiate ion is less stable than fumarate ion

59. The correct order for increasing stability is :
(a) $C_6H_{11}\overset{+}{C}H_2 < C_6\overset{+}{H}_{11} < C_6H_{11}\overset{+}{C}(CH_3)_3$
(b) $C_6\overset{+}{H}_{11} < C_6H_{11}\overset{+}{C}H_2 < C_6H_{11}\overset{+}{C}(CH_3)_3$
(c) $C_6H_{11}\overset{+}{C}(CH_3)_3 < C_6H_{11}\overset{+}{C}H_2 < C_6\overset{+}{H}_{11}$
(d) $C_6H_{11}\overset{+}{C}H_2 < C_6H_{11}\overset{+}{C}(CH_3)_3 < C_6\overset{+}{H}_{11}$

60. Which type of nitroalkanes do not show tautomerism ?
(a) *p*-nitro alkanes (b) *s*-nitro alkanes
(c) *t*-nitro alkanes (d) None of these

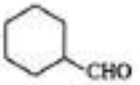
61. Which alkyl halide cannot be used for alkylation of amines ?
(a) 3° halide (b) Allyl and vinyl halide
(c) β-alkyl halide (d) All of these

62. Which will not show Cannizzaro reaction ?

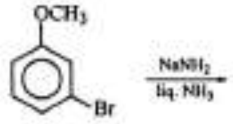
(a) 

(b) $C_6H_5COCHCl_2$

(c) $(CH_3)_3CCHO$

(d) 

63. The product formed in the reaction are :



(a) *o*-anisidine (b) *m*-anisidine
(c) *p*-anisidine (d) all of these

64. Total structural isomers of C_4H_8 are :
(a) 2 (b) 3
(c) 4 (d) 5

65. Cyclic isomers of C_5H_{10} are :
(a) 1 (b) 3
(c) 4 (d) 5

66. Which cycloalkane does not exhibit geometrical isomerism?
(a) 1,2-dimethyl cyclo propane
(b) 1,1,2-trimethyl cyclo propane
(c) 1,3,5-trimethyl cyclo hexane
(d) 1,2-dimethyl cyclo butane

67. *Cis*-but-2-ene on heating with I_2 gives :
(a) *trans*-but-2-ene (b) 1,2-di iodo butane
(c) 1,1-di iodo butane (d) no reaction

68. How many isomers of C_6H_{12} can be hydrogenated to give 2-methyl pent-1-ene?
(a) 2 (b) 3
(c) 4 (d) 5

69. Which represents the increasing stability order at room temperature for :
(I) *n*-pentane; (II) iso pentane; (III) neo pentane?
(a) I < II < III (b) III < II < I
(c) II < III < I (d) I < III < II

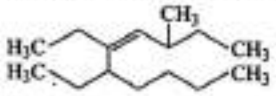
70. The total cyclic alcoholic isomers of C_4H_7OH and the number of chiral molecules respectively are :
(a) 5, 2 (b) 5, 3
(c) 4, 2 (d) 4, 3

71. Which one is not correctly matched ?
(a) Carbocation-sp^2-trigonal planar
(b) Carbanion-sp^3-pyramidal
(c) Me^+-sp^2-trigonal planar
(d) Singlet carbene-sp^2-coplanar

72. Which is not a characteristic of triplet carbene ?
(a) *sp*-linear
(b) Two bond pair of electron and no lone pair of electron
(c) Two electrons with same spin in different orbitals
(d) Two electrons with opposite spin in one orbital

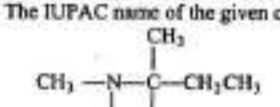
73. Which of the following nitroalkanes is insoluble in alkalies :
(a) *p*- (b) *s*-
(c) *t*- (d) all of these

74. The IUPAC name of the following compound is :



(a) 5,6-diethyl-3-methyl dec-4-ene
(b) 7-methyl-2,4,6-trien
(c) 6-methyl heptene
(d) 3,3-diethyl-5-ethyl-4-decane

75. The IUPAC name of the given compound is :



$CH_3-\underset{CH_3}{N}-\overset{CH_3}{\underset{C_2H_5}{C}}-CH_2CH_3$

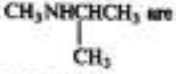
(a) 3-methyl-3-*N*,*N*-dimethyl pentane

(b) 3-ethyl-3-*N*,*N*-dimethyl pentane
(c) 3-methyl-3-*N*,*N*-dimethyl butane
(d) none of these

76. Which of the following reaction is not reversible ?
(a) Esterification
(b) Hydrolysis of ester by acids
(c) Hydrolysis of ester by alkalies
(d) None of the above

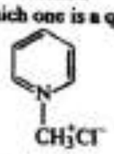
77. Which of the following has shorter $\rangle$C=O bond?
(a) $(RCO)_2O$ (b) $RCOOR'$
(c) $RCOCl$ (d) $RCONH_2$

78. $CH_3NHCH_2 \cdot CH_2 \cdot CH_3$ and $CH_3NH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ are :

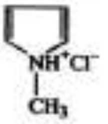


(a) Chain isomers (b) Position isomers
(c) Metamers (d) Functional isomers

79. Which one is a quaternary salt?

(a)


(b) $(CH_3)_3\overset{+}{N}HCl^-$

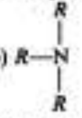
(c)


(d) $(CH_3)_4N^+Cl^-$

80. Of the following amine the lowest b.pt. amine is :
(a) *n*-butyl amine (b) *n*-pentyl amine
(c) *N*,*N*'-dimethyl ethanamine
(d) *N*-methyl propanamine

81. Which type of amines are obtained by Ritter reaction ?

(a) R_3CNH_2

(b)


$$R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{N}}}}$$

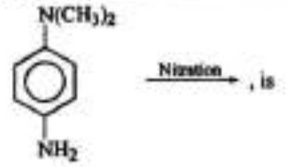
(c) R_2—NH (d) R—NH_2

82. Glucose reacts wtih phenyl hydrazine to yield an glucosazone. Which is not correct about this reaction :
(a) In all three molecule of phenyl hydrazine are used for one molecule of glucose
(b) Phenyl hydrazine acts as reducing agent as well as condensating agent
(c) Fructose also gives same osazone
(d) Only one molecule is used as condensating agent

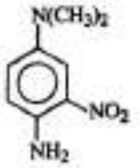
83. Fructose or glucose or mannose with dil. NaOH solution gives an equilibrium mixture of ...... sugars :
(a) 2 (b) 3
(c) 4 (d) 5

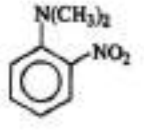
84. Halogen atoms although *o*- and *p*- directing group but it deactivates rings for further S_E reactions. The deactivating effect is due to :
(a) + *E* effect (b) + *M* (or + *T* effect)
(c) − *I* effect (d) + *I* effect

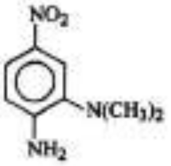
85. The product obtained in the reaction :



, is

(a)


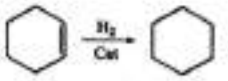
(b)


(c)


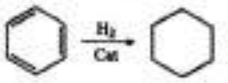
(d) Nitration is not possible

86. The correct order for increasing rate of nitration is :
(a) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 < C_6D_6$
(b) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 = C_6D_6$
(c) $C_6H_5NO_2 < C_6H_6 < C_6H_5Cl < C_6D_6$
(d) $C_6H_5Cl < C_6H_5NO_2 < C_6D_6 < C_6H_6$

87. If



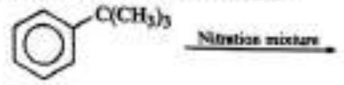
; $\Delta H = -29$ kcal mol^{-1} and

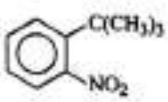


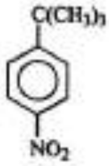
; $\Delta H = -51$ kcal mol^{-1}

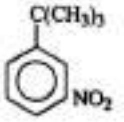
The resonance energy of C_6H_6 is :
(a) − 36 kcal mol^{-1} (b) + 36 kcal mol^{-1}
(c) − 22 kcal mol^{-1} (d) + 22 kcal mol^{-1}

88. The product obtained in the reaction is :



(a)


(b)


(c)


(d) All of these

89. $C_6H_5CH_2CH_3$ and $C_6H_5CHClCH_3$ can be distinguished by :
(a) Alcoholic KOH (b) Alcoholic $AgNO_3$
(c) Acidified $KMnO_4$ (d) None of these

90. Toluene reacts with Br_2/Fe gives *p*-bromo toluene as major product because —CH_3 group :
(a) activates the ring by hyperconjugation
(b) causes steric hindrance
(c) deactivates the ring
(d) only *p*-directing

91. Tetraphenyl methane can be obtained by the reaction of :

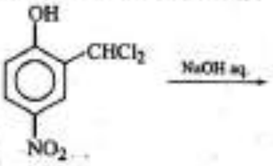
(a) $C_6H_6 + CCl_4 \xrightarrow{AlCl_3}$

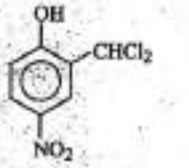
(b) $C_6H_5Cl + (C_6H_5)_3\overset{-\,+}{CK} \xrightarrow[\text{liq. }NH_3]{KNH_2}$

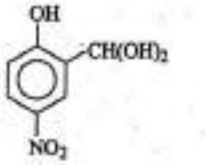
(c) $C_6H_6 + CHCl_3 \xrightarrow{AlCl_3}$

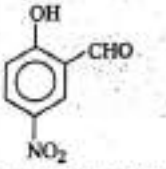
(d) $C_6H_5Cl + CH_4 \xrightarrow{AlCl_3}$

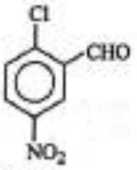
92. The product formed in the reaction is :



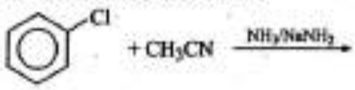
(a)


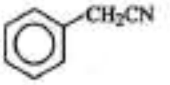
(b)


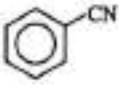
(c)


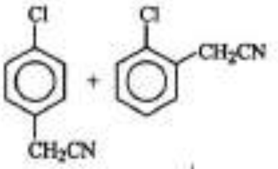
(d)


93. The product formed in the reaction is :



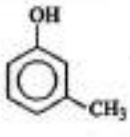
(a)


(b)


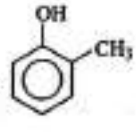
(c)


(d)


94. Which of the following cresols can produce tribromo derivative on dissolution in Br_2 water ?

(a)


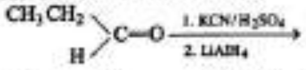
(b)

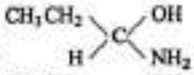

(c)


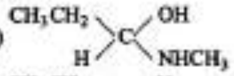
(d) All of these

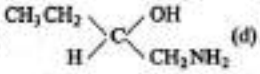
95. *p*-aminobenzoic acid and *p*-hydroxy benzoic acid in a solution can be separated by :
(a) acids (b) alkalies
(c) ether (d) alcohol

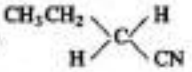
96. The product formed in the reaction is :



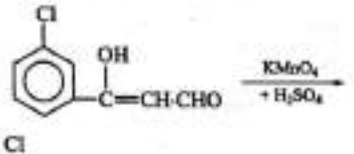
(a)


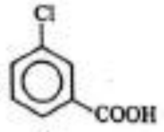
(b)


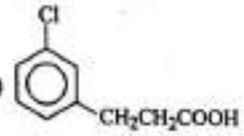
(c)


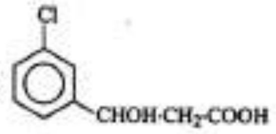
(d)


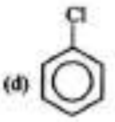
97. The product formed in the reaction is :



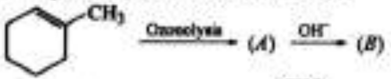
(a)


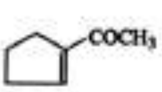
(b)


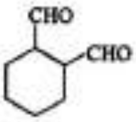
(c)


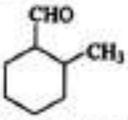
(d)


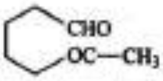
98. The final product (*B*) formed in the reaction :



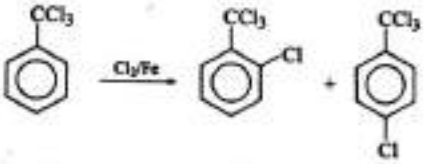
(a) 

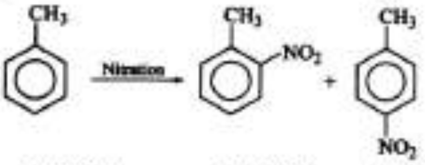
(b) 

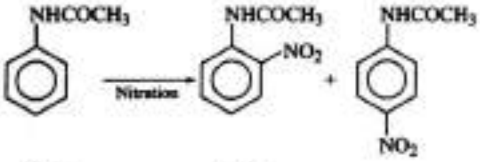
(c) 

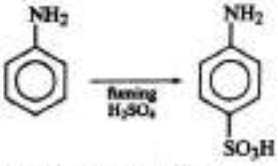
(d) 

99. The product formed in the reaction is not correctly given in :

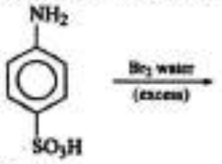
(a) 

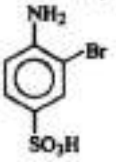
(b) 

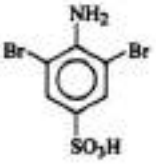
(c) 

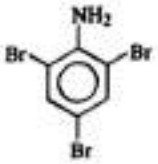
(d) 

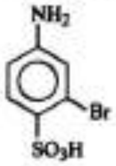
100. The product formed in the reaction :



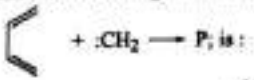
(a) 

(b) 

(c) 

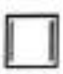
(d) 

101. The product formed during the reaction :



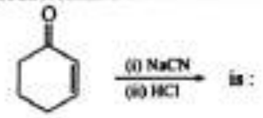
(a) 

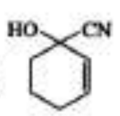
(b) 

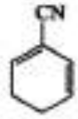
(c) 

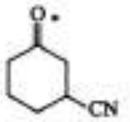
(d) none of these

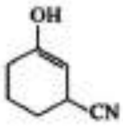
102. The product formed in the reaction



(a) 

(b) 

(c) 

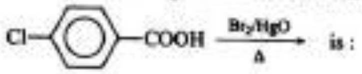
(d) 

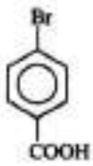
103. The product formed in  is :

(a) $CHO\cdot(CH_2)_4\cdot CHO$ (b) $CHO(CH)_4COOH$
(c) $CHO(CH)_4\cdot CHO$ (d) $COOH(CH)_4COOH$

104. The number of products of ozonolysis of polyenes (if *n* is number of double bonds) are :
(a) *n* (b) $n+1$
(c) $n+2$ (d) $n+3$

105. Which of the following is obtained in the reaction :



(a) 

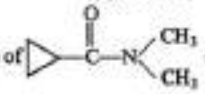
(b) 

(c)

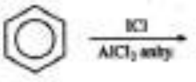

(d)


106. Dihydroxy acetone on treatment with HIO_4 gives :
(a) HCOOH (b) HCHO
(c) HCHO and HCOOH (d) HCHO and CO_2

107. Which of the following is not reducing sugar :
(a) Fructose (b) Glucose
(c) Lactose (d) Sucrose

108. The IUPAC name of

$\triangleright\!-\overset{\overset{O}{\|}}{C}-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
is:
(a) *N,N*-dimethyl cyclopropanone
(b) *N,N*-dimethyl cyclopropanamine
(c) *N,N*-dimethyl cyclopropanamide
(d) cyclopropanone dimethyl amine

109. Urea has :
(a) Chain isomer (b) Position isomer
(c) Geometrical isomer (d) Tautomer

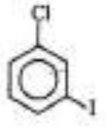
110. The product formed in the reaction :


is :

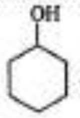
(a)


(b)

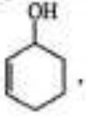

(c)


(d)


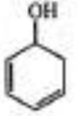
111. The correct order for dehydration for the following is :

(I)


,

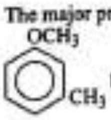
(II)


,

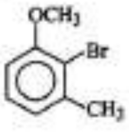
(III)


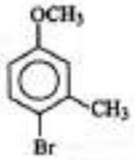
(a) I > II > III (b) III > II > I
(c) I > III > II (d) II > III > I

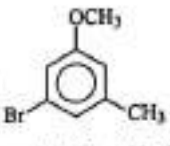
112. The decreasing order of the stability of carbocations is :
$CH_3\cdot\overset{+}{C}H\cdot CH_3$; $CH_3\cdot\overset{+}{C}H\cdot OCH_3$; $CH_3\cdot\overset{+}{C}H\cdot COCH_3$
(I) (II) (III)
(a) I > II > III (b) III > II > I
(c) III > I > II (d) II > I > III

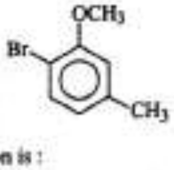
113. The major product formed on monobromination of


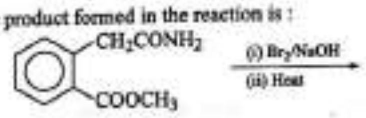
by $FeBr_3/Br_2$:

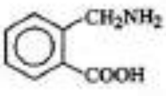
(a)


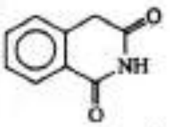
(b)


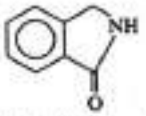
(c)


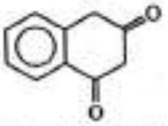
(d)


114. The product formed in the reaction is :


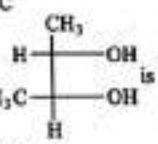
(a)


(b)


(c)


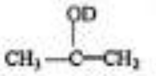
(d)


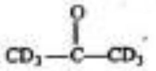
115. Which of the following is not an intermediate in Hofmann bromamide reaction ?
(a) *R*NCO (b) *R*CON
(c) *R*CONHBr (d) *R*NC

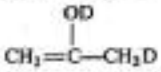
116. Correct configuration of molecule


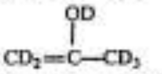
is :
(a) 1*S*, 2*S* (b) 1*S*, 2*R*
(c) 1*R*, 2*S* (d) 1*R*, 2*R*

117. The enol form of acetone after treatment with D_2O gives :

(a)

$CH_3-\overset{\overset{OD}{|}}{C}-CH_3$

(b)

$CD_3-\overset{\overset{O}{\|}}{C}-CD_3$

(c)

$CH_2=\overset{\overset{OD}{|}}{C}-CH_2D$

(d)

$CD_2=\overset{\overset{OD}{|}}{C}-CD_3$

118. In the compound $CH_2=CH-CH_2-CH_2-C\equiv CH$, the C_2-C_3 bond is of the type :

(a) $sp-sp^2$ (b) sp^3-sp^3

(c) $sp-sp^3$ (d) sp^2-sp^3

119. Hybridization of carbon in singlet carbene is :

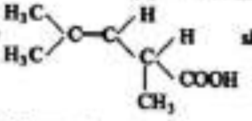
(a) sp (b) sp^2

(c) sp^3 (d) none of these

120. Hybridization of carbon in triplet carbene is :

(a) sp (b) sp^2

(c) sp^3 (d) none of these

121. The structure  shows :

(a) geometrical isomerism

(b) optical isomerism

(c) geometrical and optical isomerisms

(d) tautomerism

122. Allyl isocyanide has :

(a) 9σ and 4π bonds

(b) 8σ and 5π bonds

(c) 9σ, 3π and 3 non-bonded electrons

(d) 8σ, 3π and 4 non-bonded electrons

123. Which is not correct about the stability of carbocation :

(a) Presence of electron attracting gp shows destabilization

(b) Presences of electron repelling gp shows stabilization

(c) Presence of Resonance shows stabilization

(d) Presence of Resonance shows destabilization

124. In the following groups,

$$\underset{\text{I}}{—\text{OAc}} \quad \underset{\text{II}}{—\text{OMe}} \quad \underset{\text{III}}{—\text{OSO}_2\text{Me}} \quad \underset{\text{IV}}{—\text{OSO}_2\text{CF}_3}$$

the order of leaving group ability is :

(a) I > II > III > IV (b) IV > III > I > II

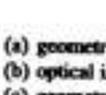
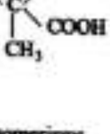
(c) III > II > I > IV (d) II > III > IV > I

125. Which of the following always stabilizes both carbocation and carbanion if present :

(a) Electron attracting gp (b) Electron repelling gp

(c) Resonance (d) All of these

126. In the following compounds,

(I)  (II)  (III)  (IV) 

the order of basic nature is :

(a) IV > I > III > II (b) III > I > IV > II

(c) II > I > III > IV (d) I > III > II > IV

127. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is :

(a) 2 (b) 3

(c) 4 (d) 1

128. Which of the following is/are correct :

(a) Quartz is an optically active substance

(b) Benzil shows optical activity

(c) Optically in active substance always yields optically inactive substance

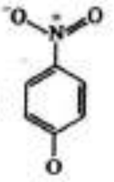
(d) All of these

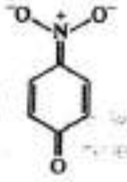
129. The intermediate during the addition of HCl to propene in the presence of peroxide is :

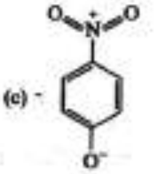
(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_2\overset{\bullet}{C}HCH_3$

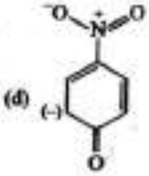
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\dot{C}H_2$

130. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is :

(a) 

(b) 

(c) 

(d) 

131. The correct basic character of methyl amines in gaseous phase is :

(a) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(c) $(CH_3)NH_2 > (CH_3)_2NH > (CH_3)_3N > NH_3$

(d) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$

132. IUPAC name of :

$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(CH_3)CH_2{\cdot}CH_2CH_2CH_2CH(CH_3)CH_3$

(a) 3, 4, 9-trimethyl decane

(b) 2, 7, 8-trimethyl decane

(c) Isopropyl heptane

(d) 2, 4, 9-trimethyl decane

133. The most reactive cycloalkane is :

(a) Cyclopropane (b) Cyclobutane

(c) Cyclopentane (d) Cycloheptane

134. $(CH_3)_3C{-}MgCl$ on reaction with D_2O gives :

(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$

(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$

135. The strongest acid among the following is :

(a) $CH \equiv CH$ (b) C_6H_6

(c) C_2H_6 (d) CH_3OH

136. Buna-N rubber is a copolymer of :

(a) Propadiene + Vinyl chloride

(b) Butadiene + Vinyl cyanide

(c) Propadiene + Butadiene

(d) None of the above

137. Which of the following will not decolorize Baeyer's reagent:
   (a) 1, 1, 2-trimethyl ethene
   (b) 1, 1-dimethyl ethene
   (c) 1, 2-dimethyl ethene
   (d) 1, 1, 2, 2-tetramethyl ethene

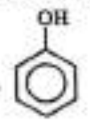
138. Which of the following gives iodoform test :
   (a) *m*-and *p*-hydroxy phenol
   (b) Ethyl acetoacetate
   (c) Pentan-3-one
   (d) diethyl malonate

139. Electrolysis of 2% NaCl solution with C_2H_5OH gives :
   (a) CH_3CHO (b) $CHCl_3$
   (c) CH_3COCH_3 (d) CCl_4

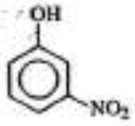
140. $CHCl_3$ and CCl_4 can be identified by :
   (a) Iodoform test (b) Wurtz reaction
   (c) Carbylamine reaction (d) Wolf-Kishner reaction

141. Select the correct statement
   (a) S_N1 reactions are sterospecific and stereo selective
   (b) S_N2 reaction are stereospecific but not stereoselective
   (c) S_N2 reactions are stereo selective but not stereospecific
   (d) S_N2 reactions are stereoselective as well as stereospecific

142. In the following compounds,

(I)


(II)

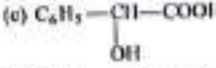

(III)


(IV)

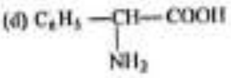

the order of acidic nature is :
   (a) III > IV > I > II (b) I > IV > III > II
   (c) II > I > III > IV (d) IV > III > I > II

143. $CH_3CHO + H_2NOH \longrightarrow CH_3—CH{=}N—OH$
   The above reaction occurs at :
   (a) pH = 1 (b) pH = 3.5
   (c) any value of pH (d) pH = 12

144. $CH_3CH_2COOH \xrightarrow[\text{Red P}]{Br_2} A \xrightarrow{NH_3\ alc.} B$, *B* in the reaction is :
   (a) Lactic acid (b) Ethyl amine
   (c) Propyl amine (d) Alanine

145. Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly.
   (a) $C_6H_5—CO—CH_2—COOH$
   (b) $C_6H_5—CO—COOH$
   (c)


$C_6H_5—\underset{OH}{\underset{|}{CH}}—COOH$

   (d)


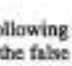
$C_6H_5—\underset{NH_2}{\underset{|}{CH}}—COOH$

146. The acid *D* obtained through the following sequence of reactions is :

$$C_2H_5Br \xrightarrow{Alc.\ KOH} A \xrightarrow[CCl_4]{Br_2} B \xrightarrow[(excess)]{KCN} C \xrightarrow{H_3O^+} D$$

   (a) Succinic acid (b) Malonic acid
   (c) Maleic acid (d) Oxalic acid

147. Which of the following acids on heating loses a molecule of H_2O to form an α, β-unsaturated acid?
   (a) $CH_3CHOHCOOH$ (b) $HOCH_2COOH$
   (c) $CH_3CHOHCH_2COOH$ (d) $HOCH_2CH_2CH_2COOH$

148. The molecule  does not contain :
   (a) Allylic H-atom
   (b) Vinylic H-atom
   (c) H-atom attached on *sp*-hybridized carbon
   (d) H-atom attached on sp^3-hybridized carbon

149. Presence of which increases the solubility of alkenes in water :
   (a) Ag^+ (b) Ag
   (c) Cl_2 (d) Br_2

150. Among the following statements on the nitration of aromatic compounds, the false one is :
   (a) The rate of nitration of benzene is almost the same as that of hexadeuterobenzene
   (b) The rate of nitration of toluene is greater than that of benzene
   (c) The rate of nitration of benzene is greater than that of hexadeuterobenzene
   (d) Nitration is an electrophilic substitution reaction

151. Which of the following decolorizes few drops of dilute $KMnO_4$ and gives brown mass :
   (a) *n*-butanol (b) *s*-butanol
   (c) *t*-butanol (d) none of these

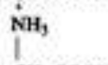
152. Which aldehyde gives positive test with Tollens reagent but not with Benedicts solution :
   (a) HCHO (b) C_6H_5CHO
   (c) CH_3CHO (d) $CH_2{=}CH{\cdot}CHO$

153. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with :
   (a) SO_2Cl_2 (b) $SOCl_2$
   (c) Cl_2 (d) NaOCl

154. The bond order of individual C—C bond in benzene is :
   (a) one (b) two
   (c) between one and two (d) one and two alternately

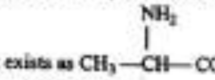
155. Molecule in which the distance between the two adjacent carbon atoms is largest in :
(a) Ethane (b) Ethene
(c) Ethyne (d) Benzene

156. Which of the following is correct about alanine ?
(a) It is α-amino propanoic acid



$CH_3-\underset{}{\overset{\overset{+}{N}H_3}{\overset{|}{C}H}}-COOH$

(b) It exists as $CH_3\,CH\cdot COOH$ in solution of pH = 2



$CH_3-\overset{\overset{NH_2}{|}}{C}H-COO^-$

(c) It exists as $CH_3-CH-COO^-$ in solution of pH = 10
(d) All of the above

157. Among the following the compound that can be most readily sulphonated is :
(a) Benzene (b) Nitrobenzene
(c) Toluene (d) Chlorobenzene

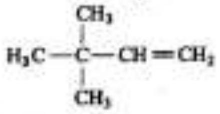
158. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is :
(a) 2 (b) 3
(c) 4 (d) 5

159. The compound with no dipole moment is :
(a) Methylchoride (b) Carbon tetrachloride
(c) Methylene chloride (d) Chloroform

160. The compound 1, 2-butadiene has :
(a) Only *sp* hybridized carbon atoms
(b) Only sp^2 hybridized carbon atoms
(c) Only *sp* and sp^2 hybridized carbon atoms
(d) *sp*, sp^2 and sp^3 hybridized carbon atoms

161. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism ?
(a) 2-butene (b) 2-butyne
(c) 2-butanol (d) butanal

162. The IUPAC name of the compound having the formula is :

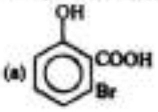


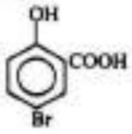
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$$

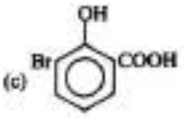
(a) 3, 3, 3-trimethyl-1-propene
(b) 1, 1, 1-trimethyl-2-propene
(c) 3, 3-dimethyl-1-butene
(d) 2, 2-dimethyl-3-butene

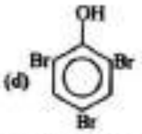
163. The compound that is most reactive towards electrophilic nitration is :
(a) toluene (b) benzene
(c) benzoic acid (d) nitrobenzene

164. Salicylic acid on bromination gives

(a) 

(b) 

(c) 

(d) 

165. The bond between carbon atom (1) and carbon atom (2) in compound $N\equiv\underset{1}{C}-\underset{2}{C}H=CH_2$ involves the hybridization as :
(a) sp^2 and sp^2 (b) sp^3 and *sp*
(c) *sp* and sp^2 (d) *sp* and *sp*

166. The IUPAC name of the compound $CH_2=CH-CH(CH_3)_2$ is :
(a) 1, 1-dimethyl-2-propene (b) 3-methyl-1-butene
(c) 2-vinyl propane (d) none of these

167. Which of the following will have least hindered rotation about carbon-carbon bond ?
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane

168. If two compounds have the same empirical formula but different molecular formulae, they must have :
(a) different percentage composition
(b) different molecular weight
(c) same velocity
(d) same vapour density

169. The number of isomers of C_6H_{14} is :
(a) 4 (b) 5
(c) 6 (d) 7

170. Out of the following compounds which will have a zero dipole moment ?
(a) 1,1-dichloro ethylene
(b) *cis*-1, 2-dichloro ethylene
(c) *trans*-1, 2-dichloroethylene
(d) None of these compounds

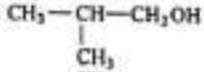
171. Polarisation of electrons in acrolein may be written as :
(a) $\overset{-\delta}{C}H_2=CH-\overset{+\delta}{C}=O$
(b) $\overset{-\delta}{C}H_2=CH-CH=\overset{+\delta}{O}$
(c) $\overset{-\delta}{C}H_2=\overset{+\delta}{C}H_2-CH=O$
(d) $\overset{+\delta}{C}H_2=CH-CH=\overset{-\delta}{O}$

172. What is the decreasing order of strength of the bases OH^-, NH_2^-, $HC\equiv C^-$ and $CH_3CH_2^-$?
(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

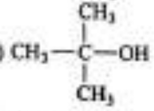
173. The Cl—C—Cl in 1, 1, 2, 2, tetrachloroethene and tetrachloromethane respectively will be about :
(a) 120° and 109° 5' (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

174. In CH_3CH_2OH the bond that undergoes heterolytic cleavage most readily is :
(a) C—C (b) C—O
(c) C—H (d) O—H

175. The compound which gives the most stable carbenium ion on dehydration is :

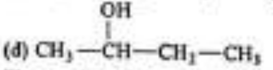
(a) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(b) 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

(c) $CH_3-CH_2-CH_2-CH_2OH$

(d) 

$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3$

176. The number of sigma and pi bonds in 1-butene 3-yne are :
(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi (d) 6 sigma and 4 pi

177. The compound which has one isopropyl group is :
(a) 2, 2, 3, 3-tetramethyl pentane
(b) 2, 2-dimethyl pentane
(c) 2, 2, 3-trimethyl pentane
(d) 2-methyl pentane

178. The C—H bond distance is the longest in :
(a) C_2H_2 (b) C_2H_4
(c) C_2H_6 (d) $C_2H_2Br_2$

179. Amongst the following, the most basic compound is :
(a) benzylamine (b) aniline
(c) acetanilide (d) *p*-nitroaniline

180. The formation of cyanohydrin from ketone is an example of :
(a) electrophilic addition (b) nucleophilic addition
(c) nucleophilic substitution (d) electrophilic substitution

181. The enolic form of acetone contains :
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(c) 10 sigma bonds, 1 pi bond and 1 lone pair
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair

182. The hybridisation of carbon atoms in C—C single bond of $H-C\equiv C-CH=CH_2$.
(a) sp^3-sp^3 (b) sp^2-sp^3
(c) $sp-sp^2$ (d) sp^3-sp

183. Isomers which can be interconverted through rotation around a single bond are :
(a) conformers (b) diastereomers
(c) enantiomers (d) positional isomers

184. Which statement is not correct ?
(a) Phenoxide ion has more number of canonical forms than benzoate ion
(b) Only one canonical form of phenoxide ion has –ve charge on more electronegative O-atom
(c) Phenoxide ion is more stable than benzoate ion
(d) Two canonical form of benzoate ion have –ve charge an more electronegative O-atom

185. Which of the following are oxidised by Fehling solution :
(a) Glucose (b) Phenyl hydrazine
(c) HCOOH (d) C_6H_5CHO

186. Arrange in order of decreasing trend towords S_E reactions :
(I) Chlorobenzene, (II) benzene
(III) Anilinium chloride, (IV) Toluene
(a) II > I > III > IV (b) III > I > II > IV
(c) IV > II > I > III (d) I > II > III > IV

187. Malonic acid and succinic acid can be identified by :
(a) Heating followed with addition of $NaHCO_3$
(b) Fehling solution
(c) Iodoform test
(d) Litmus

188. Arrange the following compounds in order of increasing dipole moment :
(I) Toluene (II) *m*-dichlorobenzene
(III) *o*-dichlorobenzene (IV) *p*-dichlorobenzene
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III

189. Ammonium formate on heating gives :
(a) HCOOH (b) NH_3
(c) $HCONH_2$ (d) N_2H_4

190. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is :
(a) MeCOCl (b) MeCHO
(c) MeCOOMe (d) MeCOOCOMe

191. How many optically active stereoisomers are possible for butane-2, 3-diol ?
(a) 1 (b) 2
(c) 3 (d) 4

192. The optically active tartaric acid is named as D (+) tartaric acid because it has a positive :
(a) Optical rotation and is derived from D glucose
(b) pH in organic solvent
(c) Optical rotation and is derived from D (+) glyceraldehyde
(d) Optical rotation when substituted by deuterium

193. The conversion of 3,3-dimethyl but-1-ene into 3,3-dimethyl butanol can be made by :
(a) acid catalysed hydration
(b) oxymercuration-demercuration
(c) hydroboration-oxidation
(d) acidified $KMnO_4$ oxidation

194. Marsh gas mainly contains :
(a) C_2H_2 (b) CH_4
(c) H_2S (d) CO

195. Which of the following decolourises alkaline $KMnO_4$ solution :
(a) C_3H_8 (b) C_2H_4
(c) CH_4 (d) CCl_4

196. The compound with the highest boiling point is :
(a) *n* - hexane (b) *n* - pentane
(c) 2, 2 - dimethylpropane (d) 2 - methylbutane

197. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$ the major product is :
(a) propanal (b) propyl hydrogen sulphate
(c) acetone (d) propanol

198. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warning ?
(a) ethylene (b) benzene
(c) hexane (d) aniline

199. Baeyer's reagent is :
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution

200. Acidic hydrogen in present in :
(a) ethyne (b) ethane
(c) benzene (d) ethene

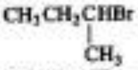
201. Anti-Markovnikoff addition of HBr is not observed in :
(a) Propene (b) but-1-ene
(c) but-2-ene (d) pent-2-ene

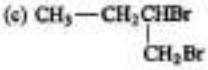
202. The highest boiling point is expected for :
(a) iso-octane
(b) *n* - octane
(c) 2, 2, 3, 3-tetramethyl butane
(d) *n* - butane

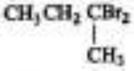
203. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are :
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

204. In the addition of HBr to propene in the absence of peroxides the first step involves the addition of :
(a) H^+ (b) Br^-
(c) $H^•$ (d) Br

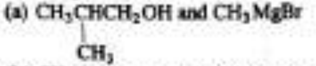
205. The chief reaction product of reaction between *n* - butane and bromine at 130° C is :
(a) $CH_3CH_2CH_2CH_2Br$

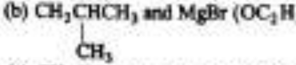
(b) 
$CH_3CH_2\underset{|}{C}HBr(CH_3)$

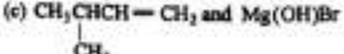
(c) 
$CH_3—CH_2CHBr(CH_2Br)$

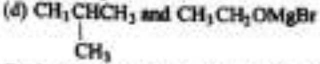
(d) 
$CH_3CH_2CBr_2(CH_3)$

206. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :

(a) 
$CH_3CH(CH_3)CH_2OH$ and CH_3MgBr

(b) 
$CH_3CH(CH_3)CH_3$ and $MgBr(OC_2H_5)$

(c) 
$CH_3C(CH_3)HCH=CH_2$ and $Mg(OH)Br$

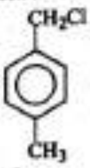
(d) 
$CH_3CH(CH_3)CH_3$ and CH_3CH_2OMgBr

207. During debromination of *meso*-2, 3 dibromobutane, the major compound formed is :
(a) *n* - butane (b) 1-butene
(c) *cis* - 2 - butene (d) *trans* - 2 - butene

208. When cyclohexane is poured on water, it floats, because :
(a) Cyclohexane is in boat form
(b) Cyclohexane is in chair form
(c) Cyclohexane is in crown from
(d) Cyclohexane is less dense than water

209. Which is not correct for aspirin ?
(a) It contains acetyl gp
(b) It contains hydroxy gp
(c) It contains carboxylic gp
(d) It is acetylation product of *o*-hydroxy benzoic acid

210. Which of the following is most reactive for S_N2 reaction ?

(a) 

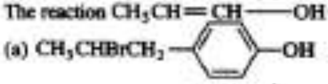
(b) 

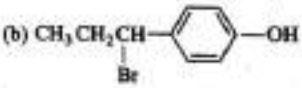
(c) 

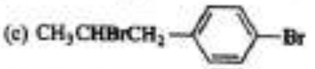
(d) 

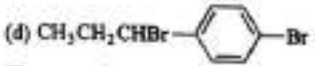
211. Bakelite is a condensation polymer of phenol and :
(a) HCOOH (b) HCHO
(c) $HCOOCH_3$ (d) But-1-ene

212. The reaction $CH_3CH=CH$—OH with HBr gives :

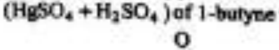
(a) 

(b) 

(c) 

(d) 

213. The product (s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be :

(a) 
$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

(b) $CH_3—CH_2—CH_2—CHO$
(c) $CH_3—CH_2—CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$

214. CCl_4, has no net dipole moment because of :
(a) Its planar structure
(b) Its regular tetrahedral structure
(c) Similar sizes of C and Cl atom
(d) Similar electron affinities of C and Cl atom

215. Chlorobenzene can be prepared by reacting aniline with :
(a) Hydrochloric acid ;
(b) Cuprous chloride
(c) Chlorine in presence of anhydrous a aluminium chloirde
(d) Nitrous acid followed by heating with cuprous chloride

216. HBr reacts fastest with :
(a) 2-methyl propan-2-ol (b) Propan-1-ol
(c) Propan-2-ol (d) 2-methyl propan-1-ol

217. The reaction conditions leading to the best yield of C_2H_5Cl are :
(a) $C_2H_6\text{(excess)} + Cl_2 \xrightarrow{\text{light}}$
(b) $C_2H_6 + Cl_2\text{(excess)} \xrightarrow[\text{room temp.}]{\text{dark}}$
(c) $C_2H_6 + Cl_2\text{(excess)} \xrightarrow{\text{UV light}}$
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

218. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly :
(a) Benzoyl chloride (b) *m*-chloro toluene
(c) Benzyl chloride (d) *o* and *p*-chloro toluene

219. *n*-propylbromide on treatment with ethanolic potassium hydroxide produces :
(a) Propane (b) Propene
(c) Propyne (d) Propanol

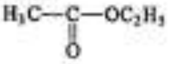
220. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :
(a) *o*-cresol (b) *p*-cresol
(c) 2, 4-dihydroxy toluene (d) benzyl alcohol

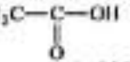
221. 1-chlorobutane on reaction with alcoholic potash gives :
(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

222. In the reaction of *p*-chlorotoluene with KNH_2 in liq. NH_3 the major product is :
(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloro aniline

223. Benzyl chloride can be prepared from toluene by chlorination with :
(a) SO_2Cl_2 (b) $SOCl_2$
(c) Cl_2 (d) NaOCl

224. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of :
(a) Carbanion (b) Carbene
(c) Free radical (d) Carbocation

225. Ethyl alcohol is heated with conc. H_2SO_4 the product formed is :
(a) 
$H_3C-\underset{\underset{O}{\|}}{C}-OC_2H_5$
(b) C_2H_6
(c) C_2H_4 (d) C_2H_2

226. Which of the following is basic ?
(a) CH_3-CH_2-OH
(b) $OH-CH_2-CH_2-OH$
(c) $H-O-O-H$
(d) 
$H_3C-\underset{\underset{O}{\|}}{C}-OH$

227. The compound which is not isomeric with diethyl ether is :
(a) *n*-propyl methyl ether (b) butan-1-ol
(c) 2-methyl propan-2-ol (d) butanone

228. The compound which reacts fastest with Lucas reagent at room temperature is :
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-1-ol (d) 2-methylpropan-2-ol

229. Diethyl ether on heating with conc. HI gives two moles of :
(a) ethanol (b) iodoform
(c) ethyl iodide (d) methyl iodide

230. An industrial method of preparation of methanol is :
(a) catalytic reduction of carbon monoxide in presence of $ZnO-Cr_2O_3$
(b) by reacting methane with steam at 900°C with a nickel catalyst
(c) by reducing formaldehyde with $LiAlH_4$
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

231. When phenol is treated with excess bromine water, it gives :
(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol

232. The compound that will not give iodoform on treatment with alkali and iodine is :
(a) acetone (b) ethanol
(c) diethyl ketone (d) isopropyl alcohol

233. Which of the following is *o*-, *p*-directing gp :
(a) $-CH=CH_2$ (b) $-CCl_3$
(c) $-NH_3^+$ (d) COCl

234. Which of the following compounds is oxidised to prepare methyl ethyl ketone ?
(a) 2-propanol (b) 1-Butanol
(c) 2-Butanol (d) *t*-Butyl alcohol

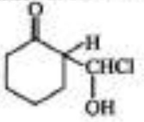
235. Hydrogen bonding is maximum in :
(a) ethanol (b) diethyl ether
(c) ethyl chloride (d) triethyl amine

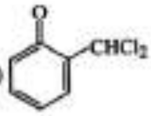
236. Phenol reacts with bromine in carbon disulphide at low temperature to give :
(a) *m*-bromophenol (b) *o*-and *p*-bromophenol
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

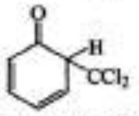
237. The products of combination of an aliphatic thiol (RSH) at 298 K are :
(a) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$
(b) $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$
(c) $CO_2(l)$, $H_2O(l)$ and $SO_2(l)$
(d) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$

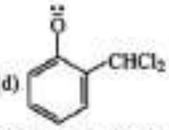
238. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ is :
(a) $C_6H_5OH + CH_3I$ (b) $C_6H_5I + CH_3OH$
(c) $C_6H_5CH_3 + HIO$ (d) $C_6H_6 + CH_3OI$

239. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate ?

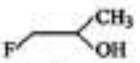
(a) 

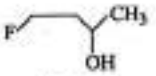
(b) 

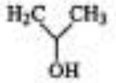
(c) 

(d) 

240. The order of reactivity of the following alcohols towards conc. HCl is :


I


II


III


IV

(a) I > II > III > IV (b) I > III > II > IV
(c) IV > III > II > I (d) IV > III > I > II

241. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives :
(a) diphenyl ether (b) *p*-hydroxy azobenzene
(c) chlorobenzene (d) benzene

242. Among the following compounds, the strongest acid is :
(a) HC ≡ CH (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

243. The reagent with which both acetaldehyde and acetone react easily is :
(a) Fehling's reagent (b) Grignard reagent
(c) Schiff's ragent (d) Tollen's reagent

244. A compound that gives a positive iodoform test is :
(a) 1-pentanol (b) 2-pentanone
(c) 3-pentanone (d) pentanal

245. When acetaldehyde is heated with Fehling's solution it gives a precipitate of :
(a) Cu (b) CuO
(c) Cu_2O (d) $Cu + Cu_2O + CuO$

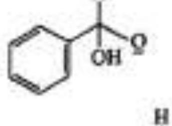
246. The Cannizzaro reaction is not given by :
(a) trimethylacetaldehyde (b) acetaldehyde
(c) benzaldehyde (d) formaldehyde

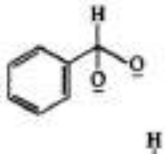
247. *m*-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives :
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol

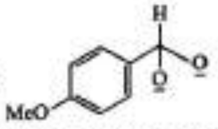
248. In the Cannizzaro reaction given below,

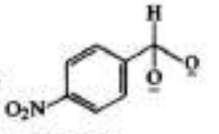
$2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCO_2^-$ the slowest step is :
(a) the attack of ^-OH at the carbonyl group,
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of $PhCH_2OH$

249. In a Cannizzaro reaction, the intermediate that will be the best hydride donor is :

(a) 

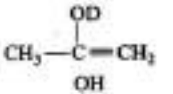
(b) 

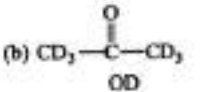
(c) 

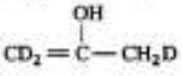
(d) 

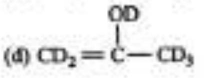
250. Which of the following will react with water :
(a) $CHCl_3$ (b) $Cl_3C{\cdot}CHO$
(c) CCl_4 (d) $ClCH_4{\cdot}CH_2Cl$

251. The enol form of acetone after treatment with D_2O, gives :

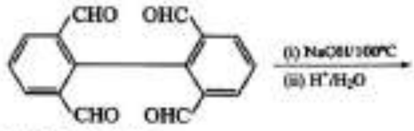
(a) 
$CH_3-\overset{\overset{\large OD}{|}}{C}=CH_2$

(b) 
$CD_3-\overset{\overset{\large O}{\|}}{C}-CD_3$

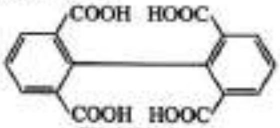
(c) 
$CD_2=\overset{\overset{\large OH}{|}}{C}-CH_2D$

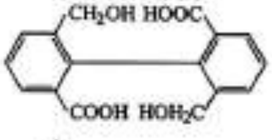
(d) 
$CD_2=\overset{\overset{\large OD}{|}}{C}-CD_3$

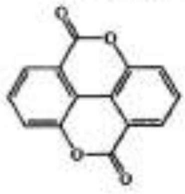
252.

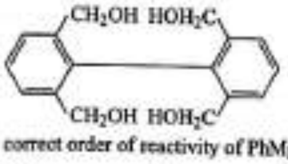


Major product is :

(a) 

(b) 

(c) 

(d) 

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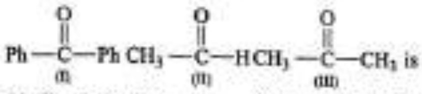
253. The correct order of reactivity of PhMgBr with



$$\underset{(I)}{Ph-\overset{O}{\overset{\|}{C}}-Ph} \quad \underset{(II)}{CH_3-\overset{O}{\overset{\|}{C}}-H} \quad \underset{(III)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \text{ is :}$$

(a) (I) > (II) > (III)
(b) (III) > (II) > (I)
(c) (II) > (III) > (I)
(d) (I) > (III) > (II)

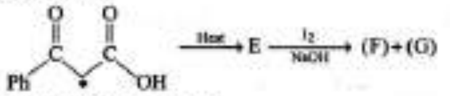
254. How will you convert butan-2-one to propanoic acid ?
(a) Tollen's reagent
(b) Fehling's solution
(c) $NaOH/I_2/H^+$
(d) $NaOH/NaI/H^-$

255. $C_6H_5CHO + (X)$

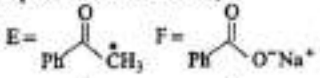
$$\xrightarrow[H_3O^+]{CH_3COONa} C_6H_5CH{=}CHCOOH + Y$$

The compound (X) is :
(a) CH_3COOH
(b) $BrCH_2-COOH$
(c) $(CH_3CO)_2O$
(d) $CHO-COOH$

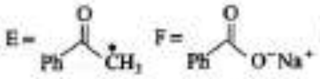
256. In the following reaction sequence, the correct structures of E, F and G are :



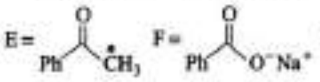
(* implies C labelled carbon)

(a) 

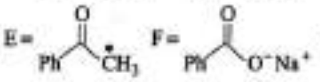
$G = \overset{*}{C}H_3I^-$

(b) 

$G = CHI_3$

(c) 

$G = \overset{*}{C}HI_3$

(d) 

$G = \overset{*}{C}H_3I$

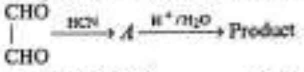
257. Acetamide is treated separately with the following reagents. Which one of the these would give methyl amine ?
(a) PCl_5
(b) $KOH + Br_2$
(c) Sodalime
(d) Hot conc. H_2SO_4

258. Hydrogenation of benzyl chloride in the presence of Pd on $BaSO_4$ gives :
(a) Benzylalcohol
(b) Benzaldehyde
(c) Benzoic acid
(d) Phenol

259. The organic product formed in the reaction $C_6H_5COOH \xrightarrow[H_3O^+]{LiAlH_4}$

(a) $C_6H_5CH_2OH$
(b) $C_6H_5COOH + CH_4$
(c) $C_6H_5CH_3 + CH_3OH$
(d) $C_6H_5CH_3 + CH_4$

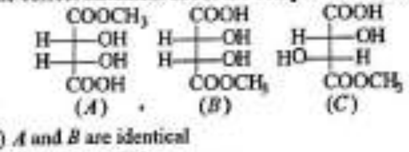
260. The products formed in the reaction :



$$\begin{array}{c}CHO\\ |\\ CHO\end{array} \xrightarrow{HCN} A \xrightarrow{H^+/H_2O} \text{Product}$$

(a) *d*-tartaric acid
(b) *l*-tartaric acid
(c) *meso* tartaric acid
(d) *d*, *l*-and mesotartaric acid

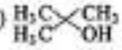
261. The correct statement about the compounds *A*, *B* and *C* is :

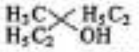


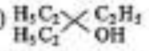
(a) *A* and *B* are identical
(b) *A* and *B* are diastereomers
(c) *A* and *C* are enantiomers
(d) *A* and *B* are enantiomers

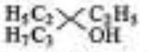
262. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from.
(a) methyl group
(b) carboxylic acid group
(c) methylene group
(d) bicarbonate

263. Ethyl ester $\xrightarrow[\text{(excess)}]{CH_3MgBr} P$, The product '*P*' will be :

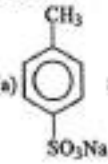
(a) 

(b) 

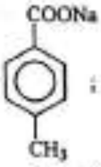
(c) 

(d) 

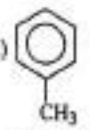
264. 4-Methylbenzenesulphonic acid reacts with sodium acetate to give :

(a) 

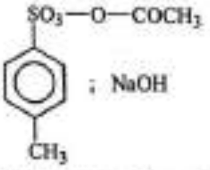
; CH_3COOH

(b) 

; SO_3

(c) 

; SO_3

(d) 

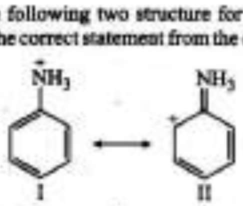
; NaOH

265. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine is :
(a) methylamine
(b) ethylamine
(c) diethylamine
(d) triethylamine

266. Carbylamine test is performed in alcoholic KOH by heating a mixture of :
(a) chloroform and silver powder
(b) trihalogenated methane and primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine

267. Butanenitrile may be prepared by heating :
(a) Propyl alcohol with KCN
(b) Butyl alcohol with KCN
(c) Butyl chloride with KCN
(d) Propyl chloride with KCN

268. Examine the following two structure for the anilinium ion and choose the correct statement from the ones given below :



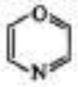
(a) It is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
(b) It is not an acceptable canonical structure because it is not-aromatic
(c) It is not an acceptable canonical structure because the nitrogen has 10 valence electrons.
(d) It is an acceptable canonical structure.

269. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a :

(a) base	(b) acid
(c) reducing agent	(d) catalyst

270. In the following compounds :


I


II


III

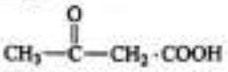

IV

the order of basic nature is :

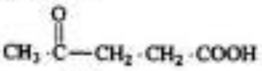
(a) IV > I > III > II	(b) III > I > IV > II
(c) II > I > III > IV	(d) I > III > II > IV

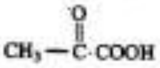
271. Among the following statements on the nitration of aromatic compounds, the false one is :
(a) that rate of nitration of benzene is almost the same as that of hexadeutereobenzene.
(b) the rate of nitration of toluene is greater than that of benzene
(c) the rate of nitration of benzene is greater than that of hexadeutereobenzene
(d) nitration is an electrophilic substitution reaction.

272. Which of the following undergoes decarboxylation on heating :

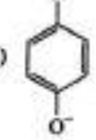
(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2\cdot COOH$

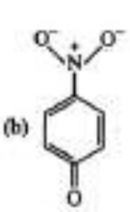
(b) CH_3COOH

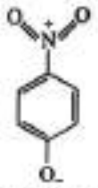
(c) 
$CH_3\cdot\overset{\overset{O}{\|}}{C}-CH_2\cdot CH_2\cdot COOH$

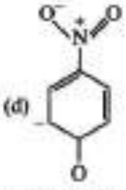
(d) 
$CH_3-\overset{\overset{O}{\|}}{C}\cdot COOH$

273. The most unlikely representation of resonance structures of p-nitrophenoxide ion is :

(a) 

(b) 

(c) 

(d) 

274. The pair of compounds in which both the compounds give positive test with Tollen's reagent is :
(a) Glucose and Sucrose
(b) Fructose and Sucrose
(c) Acetophenone and Hexanal
(d) Glucose and Fructose

275. The two forms of *D*-glucopyranose obtained from the solution of *D*-glucose are called :

(a) Isomers	(b) Anomers
(c) Epimers	(d) Enantiomers

276. Identify the correct order of boiling points of the following compounds :

$$\underset{(1)}{CH_3CH_2CH_2CH_2OH}, \qquad \underset{(2)}{CH_3CH_2CH_2CHO},$$
$$\underset{(3)}{CH_3CH_2CH_2COOH}$$

(a) 1 > 2 > 3	(b) 3 > 1 > 2
(c) 1 > 3 > 2	(d) 3 > 2 > 1

277. The product of acid catalysed hydration of 2-phenylpropene is :

(a) 3-phenyl-2-propanol	(b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol	(d) 2-phenyl-1-propanol

278. The best method to prepare cyclohexene from cyclohexanol is by using :

(a) Conc. $HCl + ZnCl_2$	(b) Conc. H_3PO_4
(c) HBr	(d) Conc. HCl

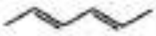
279. In the reaction :

$$C_6H_5COOH + NaH\overset{14}{C}O_3 \rightarrow C_6H_5COONa + CO_2 + H_2O;$$

C^{14} appears in :

(a) CO_2	(b) C_6H_5COONa
(c) In both	(d) All are correct

280. The correct order of stability of the following is :


(I)


(II)

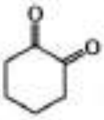

(III)

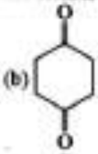

(IV)

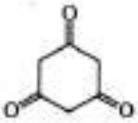
(a) I > II > III > IV (b) I > IV > III > II
(c) II > III > I > IV (d) IV > III > II > I

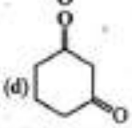
281. Which of the following has non polar nature :
(a) *p*-dicyanobenzene (b) *p*-dimethoxy benzene
(c) *p*-dihydroxy benzene (d) *p*-dimercapto benzene

282. In which of the following enolic form is more :

(a) 

(b) 

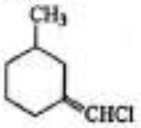
(c) 

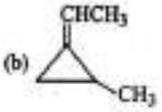
(d) 

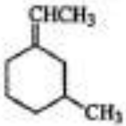
283. Which of the following is optically active :
(a) 1, 1-dibromo-1-chloropropane
(b) 1 , 3-dibromo-1-chloropropane
(c) 1, 1-dibromo-3-chloropropane
(d) 1, 3-dibromo-2-chloropropane

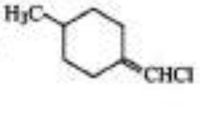
284. Which of the following pair belong to metamers :
(a) 3-methyl butan-2 one and pentane-2-one
(b) Pentane-2-one and Pentane-3-one
(c) *o*-and *m*-methoxytoluene
(d) all of the above

285. Which of the following will not show geometrical isomerism :

(a) 

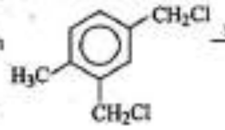
(b) 

(c) 

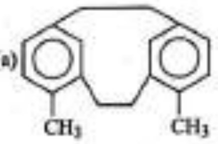
(d) 

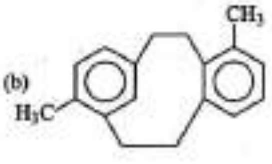
286. Compound  gives identification test with :
(a) $NaHSO_3$ (b) Br_2 water
(c) Fehling solution (d) $FeCl_3$ (*aq.*)

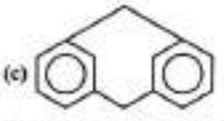
287. Calcium carbide on reacting with heavy water will give :
(a) $Ca(OD)_2 + C_2H_2$ (b) $Ca(OD)_2 + C_2D_2$
(c) $CaD_2 + C_2D_2$ (d) $Ca(OD)_2 + CD_4$

288. In the reaction  $\xrightarrow{Na + ether}$ Product ;

Product is :

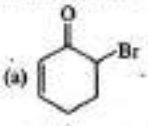
(a) 

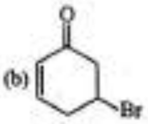
(b) 

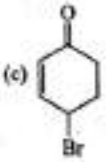
(c) 

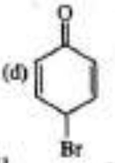
(d) Both (a) and (b)

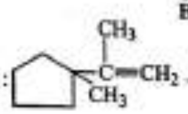
289. Which of the following will not give phenol on treatment with alc. KOH :

(a) 

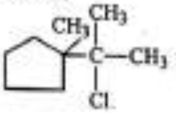
(b) 

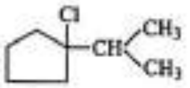
(c) 

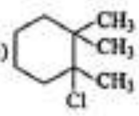
(d) 

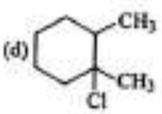
290. In the reaction :  $\xrightarrow{HCl}$ Product ;

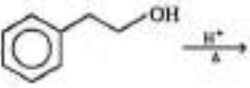
Product is :

(a) 

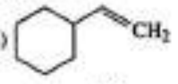
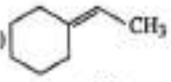
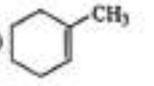
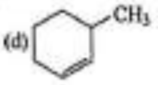
(b) 

(c) 

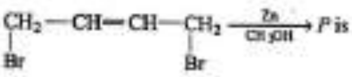
(d) 

291. In the reaction  Major product

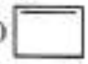
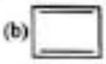
(*A*) ; Thus *A* is :

(a) 
(b) 
(c) 
(d) 

292. Predominating product of the reaction :

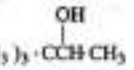


$$\underset{\text{Br}}{\text{CH}_2}-\text{CH}=\text{CH}-\underset{\text{Br}}{\text{CH}_2}\xrightarrow[\text{CH}_3\text{OH}]{\text{Zn}} P \text{ is :}$$

(a) 
(b) 

(c) $CH_2=C=C=CH_2$ (d) $CH_2=CH-CH=CH_2$

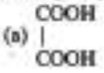
293. Clemmensen reduction of the compound $(CH_3)_3C \cdot COCH_3$ gives main product as :

(a) $(CH_3)_2CH \cdot CH(CH_3)_2$ (b) 

$(CH_3)_3 \cdot \overset{\text{OH}}{\overset{|}{\text{C}}}\text{H}\,CH_3$

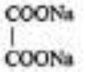
(c) $(CH_3)_3C \cdot CH_2 \cdot CH_3$ (d) None of these

294. Carbon mono oxide is passed over heated sodium hydroxide till complete conversion of NaOH to product. The product obtained is dissolved in water and the solution reduces Tollen's reagent as well as reduces mercuric chloride to black precipitate. The product was :

(a) 

$\begin{array}{c}\text{COOH}\\|\\\text{COOH}\end{array}$

(b) HCOOH

(c) HCOONa (d) 

$\begin{array}{c}\text{COONa}\\|\\\text{COONa}\end{array}$

295. Which of the following does not posses acidic hydrogen :

(a) Pentan-2, 4-diane (b) 2, 4, 6-trinitrophenol
(c) DMF (d) Hexane-2, 4-diane

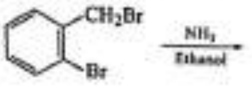
296. Dehydrochlorination allyl chloride gives :

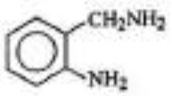
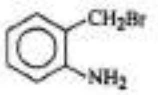
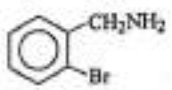
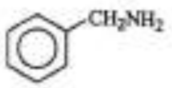
(a) Propadiene (b) Allyl alcohol
(c) Acetone (d) Propene

297. Iodoform test is given by :

(a) Pyruvic acid (b) Methyl acetate
(c) Methyl benzoate (d) Phenyl acetate

298. The major product obtained in the reaction :



(a) 
(b) 
(c) 
(d) 

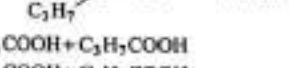
299. Select the wrong statement :

(a) S_N2 reactions are stereospecific as well as stereo selective
(b) S_N1 reactions are neither stereospecific nor stereo selective
(c) Free radicals posses less tendency for rearrangement than carbocation
(d) Nucleophilicity of RS^- is lesser than RO^-

300. Select the wrong statement :

(a) $LiAlH_4$ is stronger reducing agent than $NaBH_4$
(b) $LiAlH_4$ acts as reducing agent in ether medium but $NaBH_4$ in presence of protic solvent.
(c) Carboxylic gp is reduced to 1° alcohol by $LiAlH_4$ in ether or B_2H_6 in THF or H_2 / Pd
(d) Unsaturated carbonyls on reduction with $LiAlH_4$ in ether gives saturated alcohols.

301. The products formed on the reaction :

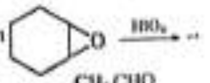


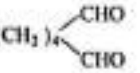
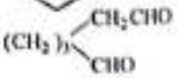
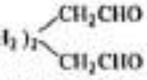
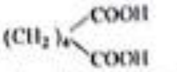
$$\begin{array}{l}\text{CH}_3\\\text{C}_3\text{H}_7\end{array}\!\!>\text{C}=\text{O}\xrightarrow{[O]} \text{.... are}$$

(a) $CH_3COOH + C_3H_7COOH$
(b) $CH_3COOH + C_2H_5COOH$
(c) $C_3H_7COOH + HCOOH$
(d) $CH_3COCH_3 + CH_3COOH$

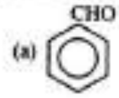
302. Which of the following reaction is wrongly reported :

(a) $RONa + R'Cl \longrightarrow ROR + NaCl$
(b) $RONa + (CH_3)_3 \cdot C \cdot Cl \longrightarrow (CH_3)_3 \cdot C \cdot O \cdot R + NaCl$
(c) $RONa + (CH_3)_3 \cdot C \cdot Cl \longrightarrow R_2C = CH_2 + HCl$
(d) $(CH_3)_3CONa + CH_3Cl \longrightarrow (CH_3)_3C \cdot OCH_3 + NaCl$

303. The product formed in the reaction 

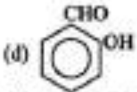
(a) 
(b) 
(c) 
(d) 

304. Which of the following does not gives Schiff's reagent test at all :

(a) 

(b) CH_3CHO

(c) CH_3COCH_3

(d) 

305. The molecules that will have dipole moment are :
(a) 2, 2-dimethyl propane
(b) *trans* 2-pentene
(c) *cis* 3-hexene
(d) 2, 2, 3, 3-tetramethyl butane

306. The product formed in the reaction :

$ClCH_2 \cdot CHCl_2 \xrightarrow{OH^-}$ is :

(a) $CHCl = CHCl$	(b) $CH_2 = CCl_2$
(c) $CH_2OH—CHO$	(d) $CH_2Cl—CHO$

307. Correct increasing acidic nature of the given alcohols is :

C_2H_5OH	CF_3CH_2OH	CCl_3CH_2OH
I	II	III

(a) I < III < II	(b) III < II < I
(c) I < II < III	(d) II < III < I

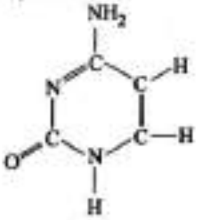
308. Hydroxylation of ethylene can not be made by :

(a) cold alk. $KMnO_4$	(b) OsO_4 in pyridine
(c) Peroxy formic acid	(d) $H_2O + O_2$

309. During free radical substitution of hydrocarbons, the abstraction of which hydrogen atom is easiest.

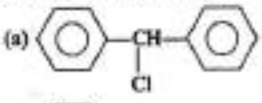
(a) Allylic	(b) Vinylic
(c) CH_4	(d) 3°

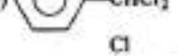
310. Which atom in the following compound shows more than one kind of hybridisation :

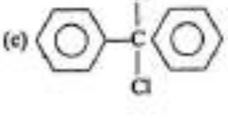


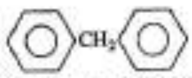
(a) C	(b) N
(c) O	(d) H

311. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhy. $AlCl_3$?

(a) 

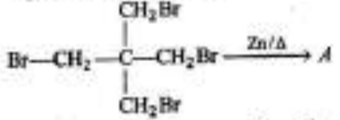
(b) 

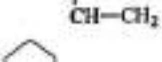
(c) 

(d) 

312. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory :
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

313. Identify '*A*' in the reaction :



(a) 

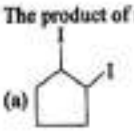
(b) 

(c) 

(d) $CH_3C \equiv C—CH=CH_2$

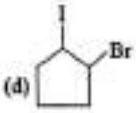
314. 

The product of reaction is :

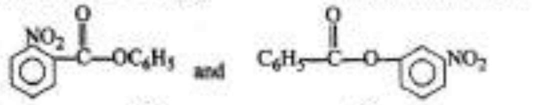
(a) 

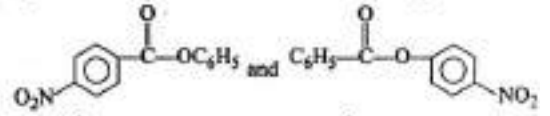
(b) 

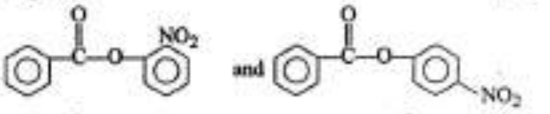
(c) 

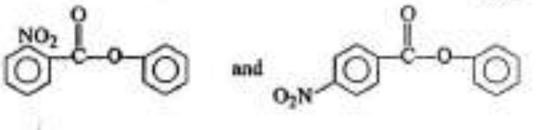
(d) 

315. 
$C_6H_5—\overset{O}{\overset{\|}{C}}—OC_6H_5 \xrightarrow{\text{mononitration}}$ Products formed are :

(a) 

(b) 

(c) 

(d) 

316. An example of a sigma bonded organometallic compound is :

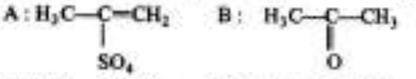
(a) ruthenocene (b) Grignard's reagent
(c) ferrocene (d) cobaltocene

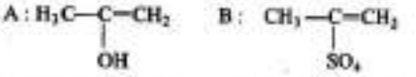
317. Mixture of chloroxylenol and terpineol acts as :

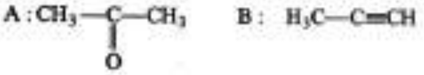
(a) analgesic (b) antiseptic
(c) antipyretic (d) antibiotic

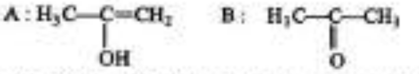
318. Predict the correct intermediate and product in the following reaction :

$$H_3C{-}C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{(A)}{\text{intermediate}} \longrightarrow \underset{(B)}{\text{product}}$$

(a) 
A : $H_3C{-}\underset{SO_4}{\underset{|}{C}}{=}CH_2$ B : $H_3C{-}\underset{O}{\underset{\|}{C}}{-}CH_3$

(b) 
A : $H_3C{-}\underset{OH}{\underset{|}{C}}{=}CH_2$ B : $CH_3{-}\underset{SO_4}{\underset{|}{C}}{=}CH_2$

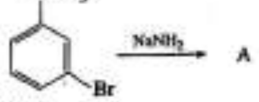
(c) 
A : $CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3$ B : $H_3C{-}C{\equiv}CH$

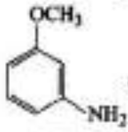
(d) 
A : $H_3C{-}\underset{OH}{\underset{|}{C}}{=}CH_2$ B : $H_3C{-}\underset{O}{\underset{\|}{C}}{-}CH_3$

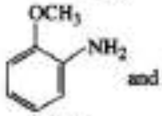
319. Which of the following reactions is appropriate for converting acetamide to methanamine?

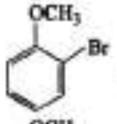
(a) Carbylamine reaction
(b) Hofmann hypobromamide reaction
(c) Stephens reaction
(d) Gabriels phthalimide synthesis

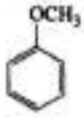
320. Identify A and predict the type of reaction :



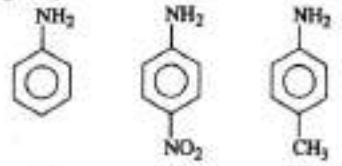
(a)  and substitution reaction

(b)  and elimination addition reaction

(c)  and cine substitution reaction

(d)  and cine substitution reaction

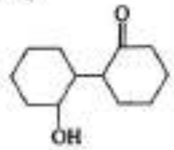
321. The correct increasing order of basic strength for the following compounds is :

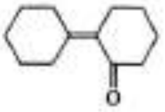


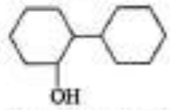
(I) (II) (III)

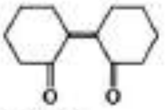
(a) II < III < I (b) III < I < II
(c) III < II < I (d) II < I < III

322. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

(a) 

(b) 

(c) 

(d) 

323. The correct statement regarding electrophile is :

(a) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile
(b) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
(c) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
(d) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile

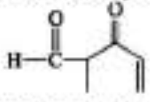
324. The heating of phenyl-methyl ethers with HI produces :

(a) ethyl chlorides (b) iodobenzene
(c) phenol (d) benzene

325. Which of the following statement is not correct?

(a) Insulin maintains sugar level in the blood of a human body
(b) Ovalbumin is a simple food reserve in egg white
(c) Blood proteins thrombin and fibrinogen are involved in blood clotting
(d) Denaturation makes the proteins more active

326. The IUPAC name of the compound is :



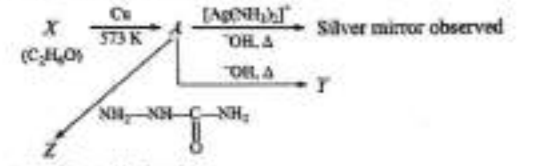
(a) 3-keto-2-methylhex-4-enal
(b) 5-formylhex-2-en-3-one

(c) 5-methyl-4-oxohex-2-en-5-al
(d) 3-keto-2-methylhex-5-enal

327. Which one is the correct order of acidity ?

(a) $CH_2{=}CH_2 > CH_3{-}CH{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$
(b) $CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$
(c) $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH_3{-}CH_3$
(d) $CH_3{-}CH_3 > CH_2{=}CH_2 > CH_3{-}C{\equiv}CH > CH{\equiv}CH$

328. Consider the reaction :



Identify *A*, *X*, *Y* and *Z*.

(a) *A*-methoxymethane, *X*-ethanoic acid, *Y*-acetate ion, *Z*-hydrazine
(b) *A*-methoxymethane, *X*-ethanol, *Y*-ethanoic acid, *Z*-semicarbazide
(c) *A*-ethanal, *X*-ethanol, *Y*-but-2-enal, *Z*-semicarbazone
(d) *A*-ethanol, *X*-acetaldehyde, *Y*-butanone, *Z*-hydrazone

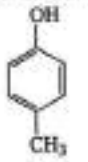
329. The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is :

(a) sublimation
(b) chromatography
(c) crystallisation
(d) steam distillation

330. With respect to the conformers of ethane, which of the following statements is true?

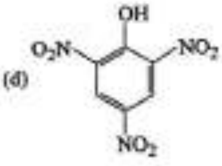
(a) Bond angle remains same but bond length changes
(b) Bond angle changes but bond length remains same
(c) Both bond angle and bond length changes
(d) Both bond angles and bond length remains same

331. Which one is the most acidic compound ?

(a)


(b)


(c)

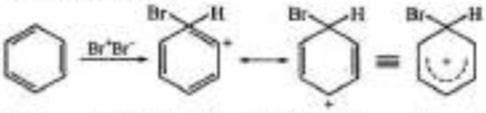

(d)


SOLUTIONS (One Answer Correct)

1. (d) Ambiphiles are nucleophile as well as electrophile.

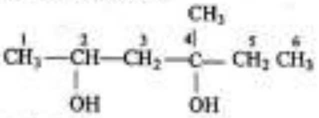
2. (a) I is neither having charge as well as each C and O-atom has complete octet.

3. (b)



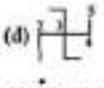
4. (a) The ease of dehydration of alcohols giving conjugated diene in maximum.

5. (b)



$$\overset{1}{C}H_3-\underset{OH}{\overset{2}{C}H}-\overset{3}{C}H_2-\underset{OH}{\overset{CH_3}{\overset{4}{C}}}-\overset{5}{C}H_2\,\overset{6}{C}H_3$$

6. (d)



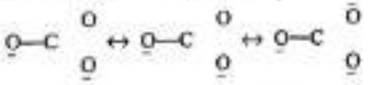
7. (b) $\dot{C}H_3 + e \longrightarrow :\bar{C}H_3; EA$

$\dot{C}H_3 \longrightarrow \overset{+}{C}H_3 + e; IE$

Gaining of electron leads to stable octet of carbanion ion whereas losing an electron leads to unstable carbocation with sextet of electron.

8. (b) The acidic character is $RCOOH > H_2O > ROH$.

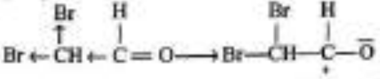
9. (d) Similar number of bonds in different canonical forms leads to isovalent resonance whereas different number of bonds in different canonical forms leads to heterovalent resonance, *e.g.*,



$$\bar{O}-C\begin{matrix}O\\ \\ \bar{O}\end{matrix} \leftrightarrow \bar{O}-C\begin{matrix}O\\ \\ \bar{O}\end{matrix} \leftrightarrow \bar{O}-C\begin{matrix}\bar{O}\\ \\ O\end{matrix}$$

$$H_2C=CH-CH=CH_2 \longleftrightarrow H_2\overset{\ominus}{C}-CH=CH-\overset{\oplus}{C}H_2$$

10. (a) Two Br-atoms are more closer to carbonyl group and thus produces more positive charge on C of carbonyl group.

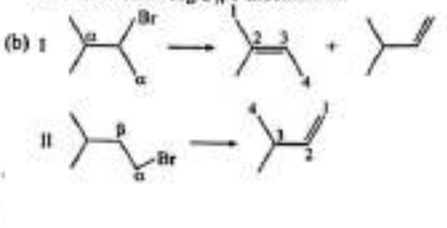


$$Br \leftarrow \overset{\overset{Br}{\uparrow}}{C}H \leftarrow \overset{\overset{H}{|}}{C}=O \longrightarrow Br-\overset{\overset{Br}{|}}{C}H-\underset{+}{\overset{\overset{H}{|}}{C}}-\bar{O}$$

11. (c) 2,4-dimethyl pentan-2-one (a) and Benzophenone (b) will not show reaction due to steric effect of bulky di-isopropyl group and heavier phenyl groups on account of steric effect.

12. (b) 3° alkyl halides shows elimination as well as substitution reactions following S_N1 mechanism.

13. (b)



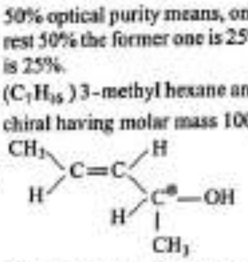
14. (a) Higher is the dielectric constant of medium, more is solvation of intermediate carbocation.

15. (c) Br-atom is replaced by CN^-; C—Cl bond energy > C—Br bond energy.

16. (c) 50% optical purity means, one enantiomer is 50% and in rest 50% the former one is 25% and the other enantiomer is 25%.

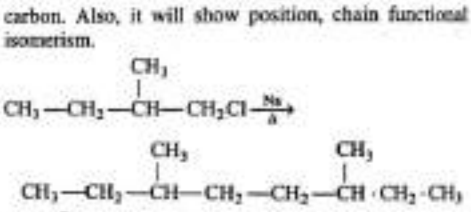
17. (a) (C_7H_{16}) 3-methyl hexane and 2,3-dimethyl pentane are chiral having molar mass 100 g mol^{-1}.

18. (d)



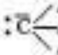
Doubly bonded carbon with $\underset{ab}{C}=\underset{ac}{C}$ and C^* chiral carbon. Also, it will show position, chain functional isomerism.

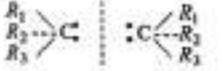
19. (c)



$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2Cl \xrightarrow[\Delta]{Na}$$

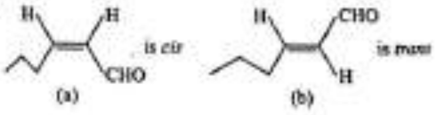
$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H\cdot CH_2\cdot CH_3$$

20. (c)  is chiral but the two isomers cannot be isolated due to umbrella type rapid inversion which leads for racemization.

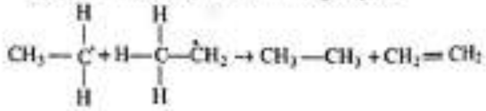


21. (b) It is chiral but do not possess chirality, *i.e.*, the property to rotate the plane of polarised light.

22. (b)



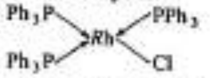
23. (d) Halogenation of alkanes involves free radical mechanism. The chain terminating step is



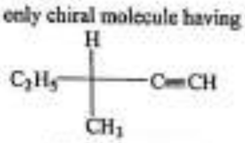
$$CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{\dot{C}}}}}+H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\dot{C}H_2 \rightarrow CH_3-CH_3+CH_2=CH_2$$

24. (a) The ease of dehydrohalogenation is 3° > 2° > 1°.

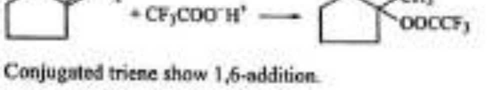
25. (d) Wilkinson's catalyst is



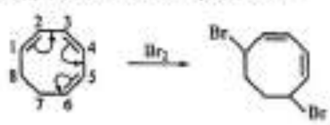
26. (d) All show addition according to peroxide effect.
27. (d) All are used to produce diols from alkenes.
28. (d) All are facts.
29. (a) The only chiral molecule having two enantiomer is



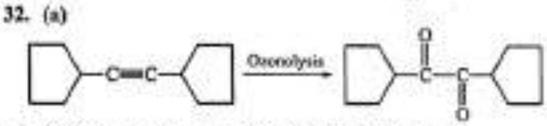
30. (b)



31. (a) Conjugated triene show 1,6-addition.



32. (a)



33. (d) Except hexene-1, all forms alkyne (propyne)

$$CH_3-C\equiv\overset{\ominus}{C}: \xrightarrow[\substack{b.\ H^+\ \text{from}\ CH_3OH\\ c.\ H^+\ \text{from}\ NH_3}]{a.\ H^+\ \text{from}\ H_2O} CH_3-C\equiv CH$$

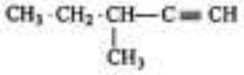
34. (b) Alkenes and alkynes from carbocation and HSO_4^- ions.

In C_2H_2 the carbocation is $[CH_2=\overset{+}{C}]$ and in C_4H_6 it is $[CH_3\overset{+}{C}=CH-CH_3]$ more is the *s* character in the positively charged carbocation, lesser is its stability. However, in $CH_3\overset{+}{C}=CH-CH_3$, presence of electron releasing methyl group provide stability to this cation.

35. (c) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot C\equiv CH$

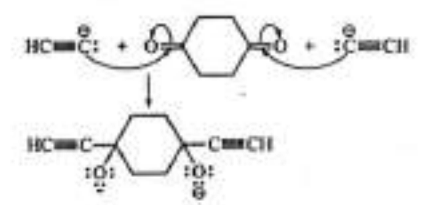
$(CH_3)_2CH\text{-}CH_2\cdot C\equiv CH$

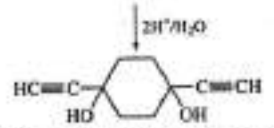
$(CH_3)_3CH_2\cdot C\equiv CH$



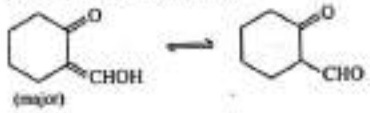
$$\underset{\displaystyle CH_3}{CH_3\cdot CH_2\cdot \underset{|}{CH}-C\equiv CH}$$

36. (a) $CH\equiv CH \longrightarrow CH\equiv\overset{\ominus}{C}: + H^+$

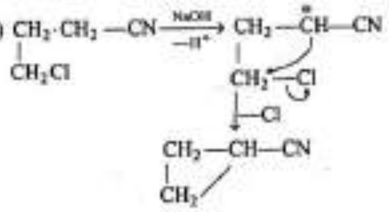




37. (a) This is Claisen condensation and the product is predominantly in enol form.



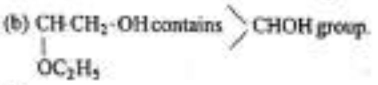
38. (b)



39. (c) The simplest cycloalkyne which is stable is cyclo octyne.
40. (d) Follow hydride shift.
41. (a) —OH group is not in the nucleus.
42. (b) Stronger bases are good nucleophile and poor leaving group.
43. (a) Rest all are facts.
44. (b) Rest all contains acidic H-atom and thus they would destroy Grignard reagent.
45. (c) The effect of increase in nucleophilicity due to increasing number of electron repelling group *R* is counteracted by the shielding of the reactive site by the *R* groups.
46. (b) Benzophenone does not have α-H-atom.
47. (d) $ZnCl_2 + HCl \longrightarrow H_2ZnCl_4$

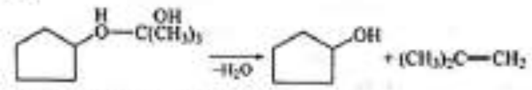
$$H_2ZnCl_4 + ROH \longrightarrow RO\overset{\oplus}{H_2} \xrightarrow[-H_2O]{} R^{\oplus} \xrightarrow[Cl^-]{} RCl$$

48. (b)



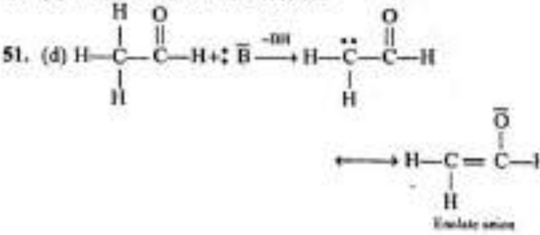
$$\underset{\displaystyle OC_2H_5}{\underset{|}{CH}}\cdot CH_2\cdot OH \text{ contains } \rangle CHOH \text{ group.}$$

49. (b)



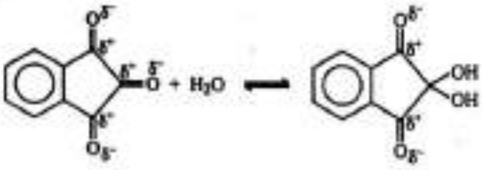
50. (c) This is Rosenmunds reaction.

51. (d)

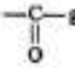


52. (d) These are facts about the respective reactions :
Clemmensen reduction : Zn—Hg + conc. HCl
Wolff Kishner reduction : alk. NH_2NH_2
Sterically hindered ketone are resistant to reduction

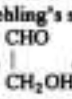
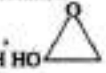
53. (b)



The adjacent δ^+ are separated by the hydration of middle carbonyl group.

54. (a) SeO_2 oxidises α-carbon to  $-\underset{\underset{O}{\|}}{C}-$ group.

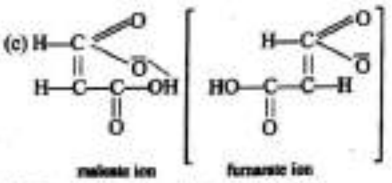
55. (c) It is a fact as it undergoes Cannizzaro reaction giving $C_6H_5CH_2OH$ and C_6H_5COOH. No doubt HCHO also undergoes Cannizzaro reaction but in it HCOOH is formed which give +ve test with Fehling's solution.

56. (d) $C_2H_4O_2$: CH_3COOH; $HCOOCH_3$,  $\begin{array}{l}CHO\\ |\\ CH_2OH\end{array}$, 

Anhydrides have general formula $C_nH_{2n-2}O_{n-1}$.

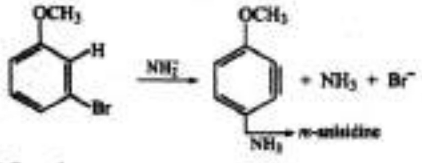
57. (a) β-keto carboxylic acids on heating show decarboxylation.

58. (c)



maleate ion fumarate ion

59. (b) Due to hyperconjugation
60. (c) *t*-nitro alkanes do not have α-H-atom.
61. (d) Alkylation of amine is made by 1° alkyl halides.
62. (d) It has α-H-atom.
63. (b) Due to the formation of benzyne intermediate.



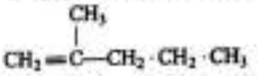
64. (d) Pent-1-ene, pent-2-ene, 2-methyl but-2-ene and two cyclic isomers: cyclobutane and methyl cyclopropane.

65. (b) Methylcyclobutane and cyclopentane; (1,1-dimethyl. cyclopropane; 1,2-dimethyl cyclopropane.)

66. (b) It has two CH_3 groups at one position.

67. (a) Interconversion of *cis* to *trans* and *trans* to *cis* alkenes occurs on heating with I_2.

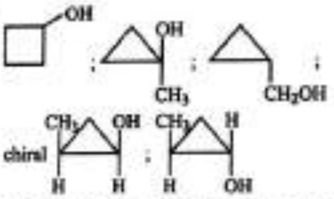
68. (c) $(CH_3)_2CH \cdot CH_2 \cdot CH = CH_2$
$(CH_3)_2CH \cdot CH = CHCH_3$
$(CH_3)_2C = CH \cdot CH_2 \cdot CH_3$



$CH_2 = \overset{\overset{CH_3}{|}}{C} - CH_2 \cdot CH_2 \cdot CH_3$

69. (a) The stability of alkanes increases with increasing branching.

70. (a)

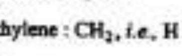


71. (d) Singlet carbene sp^2 has bent shape due to the presence of one lone pair.

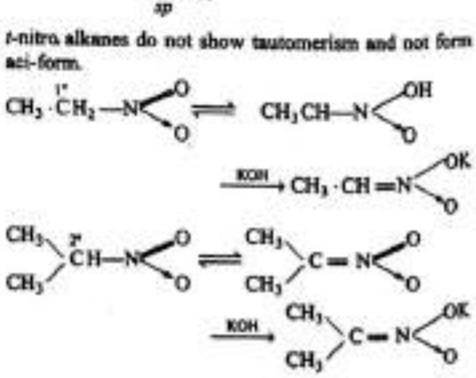
All the electrons are paired.

72. (d) Triplet methylene : CH_2, *i.e.*, H $:\overset{\bullet}{\underset{\bullet}{C}}:$ H

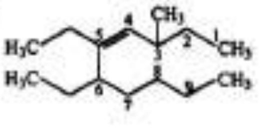
A diradical in which unshared electrons are not paired.



73. (c) *t*-nitro alkanes do not show tautomerism and not form aci-form.



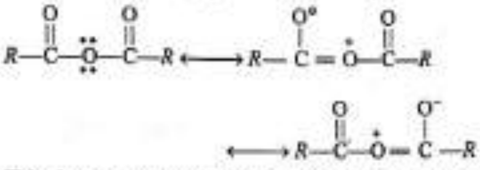
74. (a)



75. (a) Follow IUPAC rules.

76. (c) Ester hydrolysis by alkali is not reversible.

77. (a) A degree of cross conjugation exists in anhydride.



This decreases the delocalisation of electron to each carbonyl oxygen and provides less double bond character to C—O bond of $>C=O$ group.

78. (c) Bivalent or polyvalent functional group compounds show only metamerism.

79. (d) *N* is attached to four carbon atoms.

80. (c) *t*-amines having the same molar mass possess lowest b.pt. as they do not show H-bonding.

81. (a) In Ritter method, tertiary alcohol reacts with HCN to give *p*-amine having tertiary alkyl group.

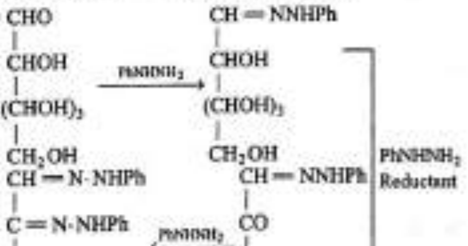
$$R_3COH \xrightarrow{H^{\oplus}} H_2O + \underset{t\text{-carbonium ion}}{R_3\overset{+}{C}}$$

$$R_3\overset{+}{C} \xrightarrow{HCN} R_3C\overset{\oplus}{N}=CH$$

$$R_3C\overset{\oplus}{N}=CH \xrightarrow{H_2O} R_3CNHCHO$$

$$R_3CNHCHO \xrightarrow{OH^-} R_3CNH_2 + HCOO^-$$

82. (d)



83. (b) Either of the three on treating with NaOH gives an equilibrium mixture of all the three sugars. This is known as Lobry-de Bruyn Van Ekenstein rearrangement.

Glucose ⇌ Fructose + Mannose

84. (c) It is $-I$ effect which play main role to deactivate ring. However, S_E reactions proceeds as $+T$ effect ≥ $-I$ effect.

85. (a) $-NH_2$ dominates in directive influence.

86. (b) $C_6H_5NO_2 < C_6H_5Cl < C_6H_6 = C_6D_6$

87. (a) ΔH_{hy} of $3C=C = -29 \times 3 = -87$

$\therefore$ Resonance energy of $C_6H_5 = -87 - (-51)$

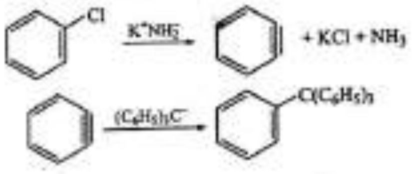
$= -36$ kcal mol^{-1}

88. (b) Due to steric hindrance of *t*-butyl group, *o*-derivative is not formed.

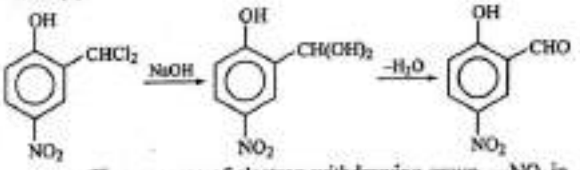
89. (b) $C_6H_5CHClCH_3$ gives white ppt. with $AgNO_3$.

90. (b) Follow mechanism.

91. (b)

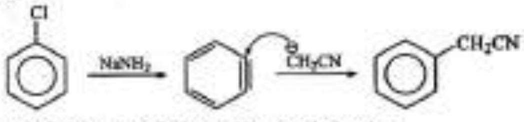


92. (d)



The presence of electron withdrawing group $-NO_2$ in *p*-position stabilizes the intermediate carbocation due to *IE* and *RE*.

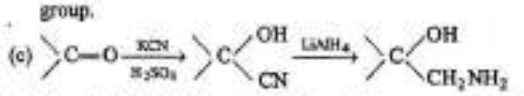
93. (a)



94. (a) Only *m*-cresol gives tri bromo derivative.

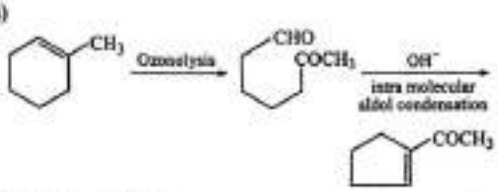
95. (a) *p*-amino benzoic acid is soluble in acid due to $-NH_2$ group.

96. (c)



97. (a) Any side chain in benzene ring is oxidises to $-COOH$ group.

98. (a)



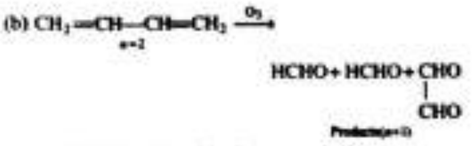
99. (a) CCl_3 is *m*-directing group.

100. (c) It is a fact.

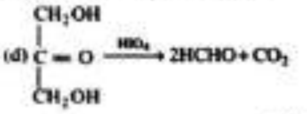
101. (b) Carbenes do not form 1,4-addition with conjugated dienes. They show 1,2-addition.

102. (c) The ease of nucleophilic addition on $C=C$ is greatly enhanced in case of $\alpha-\beta$ unsaturated carbonyl compounds.

103. (c) OsO_4 and $NaIO_4$ oxidises $C=C$ to $-CHO$ groups.

104. (b)

$$CH_2{=}\underset{n=2}{CH}{-}CH{=}CH_2 \xrightarrow{O_3} \underset{\text{Products}(n=0)}{HCHO + HCHO + \begin{matrix} CHO \\ | \\ CHO \end{matrix}}$$

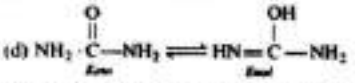
105. (b) —COOH is replaced by Br.

106. (d)

$$\begin{matrix} CH_2OH \\ | \\ C = O \\ | \\ CH_2OH \end{matrix} \xrightarrow{HIO_4} 2HCHO + CO_2$$

(HIO$_4$ breaks C—C bond)

107. (d) Sucrose is non-reducing sugar.

108. (c) Follow IUPAC rules.

109. (d)

$$\underset{\text{Keto}}{NH_2{\cdot}\overset{O}{\overset{\|}{C}}{-}NH_2} \rightleftharpoons \underset{\text{Enol}}{HN{=}\overset{OH}{\overset{|}{C}}{-}NH_2}$$

110. (a) It is electrophilic substitution (I^+Cl^-).

111. (b) III gives aromatic ring, II gives conjugated system on dehydration.

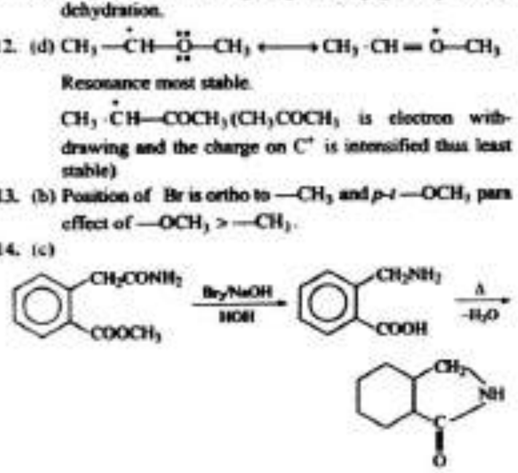
112. (d) $CH_3{-}\overset{+}{C}H{-}\ddot{\underset{..}{O}}{-}CH_3 \longleftrightarrow CH_3{\cdot}CH = \overset{+}{O}{-}CH_3$

Resonance most stable.

$CH_3{\cdot}\overset{+}{C}H{-}COCH_3(CH_3COCH_3$ is electron withdrawing and the charge on C^+ is intensified thus least stable)

113. (b) Position of Br is ortho to —CH$_3$ and p-t —OCH$_3$ para effect of —OCH$_3$ > —CH$_3$.

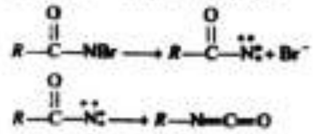
114. (c)



115. (d) $Br_2 + 2KOH \longrightarrow KBr + KBrO + H_2O$

$RCONH_2 + Br_2 \xrightarrow[KOH]{BrO^-} RCONHBr + KBr + H_2O$

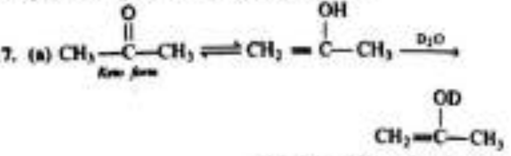
$RCONHBr \xrightarrow{OH^-} RCONBr + H_2O$


$$R{-}\overset{O}{\overset{\|}{C}}{-}NBr \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}\ddot{N}{:} + Br^-$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}\ddot{N}{:} \longrightarrow R{-}N{=}C{=}O$$

$R{-}N{=}C{=}O + 2KOH \longrightarrow RNH_2 + K_2CO_3$

116. (a) Follow priority rule of configuration.

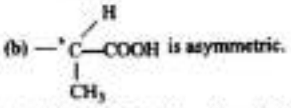
117. (a)

$$\underset{\text{Keto form}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \rightleftharpoons CH_2 = \overset{OH}{\overset{|}{C}}{-}CH_3 \xrightarrow{D_2O} CH_2{=}\overset{OD}{\overset{|}{C}}{-}CH_3$$

(H being acidic replaced by D.)

118. (d) $\overset{1}{C}H_2{=}\overset{2}{C}H{-}\underset{sp^3-sp^3}{\overset{3}{C}H_2{-}\overset{4}{C}H_2}{-}\overset{5}{C}{\equiv}\overset{6}{C}H$

119. (b)C:


120. (a) C:


121. (b)

$$-{}^*\overset{H}{\overset{/}{C}}{-}COOH \;\text{ is asymmetric.}$$
$$\quad\;\; \begin{matrix} | \\ CH_3 \end{matrix}$$

122. (c) $CH_2 = CH{-}CH_2{-}C \equiv N$: 9σ, 3π and 2 non-bonded electrons.

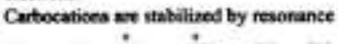
123. (d) Carbocations are stabilized by resonance

$\underset{\text{Allyl carbocation}}{CH_2 = CH{-}\overset{+}{C}H_2} \leftrightarrow \overset{+}{C}H_2{-}CH = CH_2$

124. (b) More basic group has least leaving nature. Conjugate acid order

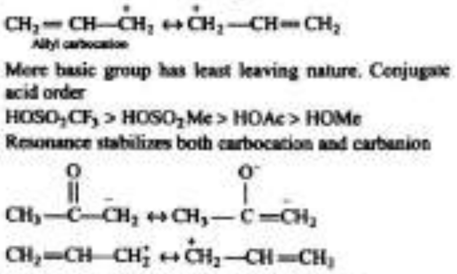
$HOSO_2CF_3 > HOSO_2Me > HOAc > HOMe$

125. (c) Resonance stabilizes both carbocation and carbanion


$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{-}{C}H_2 \leftrightarrow CH_3{-}\overset{O^-}{\overset{|}{C}}{=}CH_2$$

$CH_2{=}CH{-}CH_2^+ \leftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2$

126. (d) Due to aromaticity II and IV are least basic.

127. (a)

$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2{-}CH_3 \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}ClCH_2CH_3$$
$$+ CH_3{-}\underset{(d\text{ and }l)}{\overset{CH_3}{\overset{|}{C}H}{-}\overset{*}{C}HCl{\cdot}CH_3} + CH_3{-}\overset{CH_3}{\overset{|}{C}H}{\cdot}CH_2{\cdot}CH_2Cl$$
$$+ CH_3{-}\underset{(d\text{ and }l)}{{}^*\overset{CH_2Cl}{\overset{|}{C}H}CH_2CH_3}$$

128. (d) All are correct.

129. (b) $CH_3CH = CH_2 \xrightarrow[\text{Peroxide}]{HCl} CH_3\overset{+}{C}H{-}CH_3$ (Addition is electrophilic); HCl addition is not influenced by peroxide.

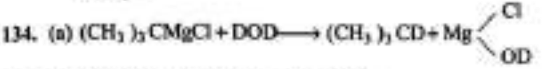
130. (c) N is pentavalent which is not possible.

131. (a) The correct order in vapour phase is (a) whereas in liquid phase is (b).

132. (b) Follow IUPAC rules.

133. (a) Due to maximum strain according to Baeyer's strain theory.

134. (a)



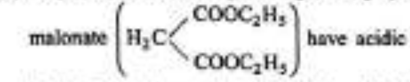
$$(CH_3)_3CMgCl + DOD \longrightarrow (CH_3)_3CD + Mg\begin{cases} Cl \\ OD \end{cases}$$

135. (d) CH_3OH is stronger acid than C_2H_2.

136. (b) It is a fact.

137. (d) It does not have olefinic H-atom.

138. (a) Ethyl aceto acetate $CH_3COCH_2COOC_2H_5$ and diethyl malonate



$$\left(H_2C\begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases}\right)$$

have acidic hydrogen.

Pentan-3-one does not contain $CH_3—CO$ unit.

139. (b) On electrolysis Cl_2 is liberated which reacts with C_2H_5OH and NaOH (formed) to give chloroform.

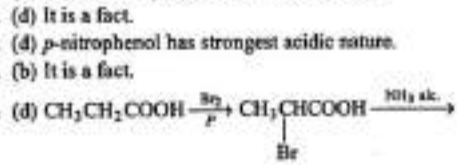
140. (c) Chloroform gives carbylamine reaction.

141. (d) It is a fact.

142. (d) *p*-nitrophenol has strongest acidic nature.

143. (b) It is a fact.

144. (d)

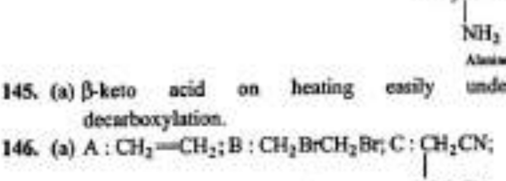


$$CH_3CH_2COOH \xrightarrow[P]{Br_2} CH_3\underset{\underset{Br}{|}}{C}HCOOH \xrightarrow{NH_3\ alc.} CH_3\underset{\underset{NH_2}{|}}{C}H\text{-}COOH$$

Alanine

145. (a) β-keto acid on heating easily undergoes decarboxylation.

146. (a)

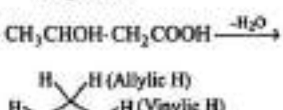


$$A : CH_2{=}CH_2;\ B : CH_2BrCH_2Br;\ C : \begin{matrix} CH_2CN; \\ | \\ CH_2CN \end{matrix}$$

$$D : \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

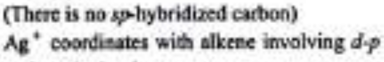
147. (c) $CH_3CHOH\text{-}CH_2COOH \xrightarrow{-H_2O} CH_3\underset{\beta}{CH}{=}\underset{\alpha}{CH}COOH$

148. (c)



(There is no *sp*-hybridized carbon)

149. (a) Ag^+ coordinates with alkene involving *d-p* π-bonding and producing ion.



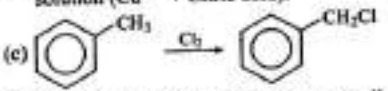
150. (c) Rate of nitration of benzene is same as that of hexadeuterobenzene.

151. (a) $CH_3CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2CHO$

$$\xrightarrow{[O]} CH_3CH_2CH_2COOK + \underset{\text{Brown ppt}}{MnO_2} + KOH$$

152. (b) Aromatic aldehydes are not oxidised by Benedicts solution (Cu^{2+} + Citric acid).

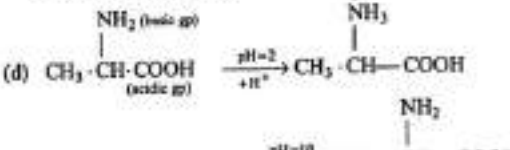
153. (c)



154. (c) Due to delocalisation of π electrons all carbon-carbon bonds become equal. So, the bond order lies between one and two.

155. (a) Single bond length is largest. The bond length is,
$C—C > C{=}C > C{\equiv}C$
(1.5Å)(1.34 Å)(1.20Å)

156. (d)

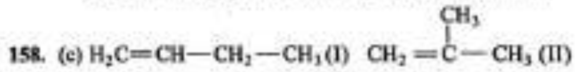


$$CH_3\cdot\overset{\overset{NH_2\ (\text{basic gp})}{|}}{C}H\cdot\underset{(\text{acidic gp})}{COOH} \xrightarrow[+H^+]{pH=2} CH_3\cdot\overset{\overset{\overset{+}{N}H_3}{|}}{C}H—COOH$$

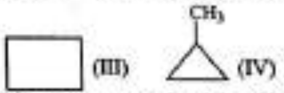
$$\xrightarrow[-H^+]{pH=10} CH_3—\overset{\overset{NH_2}{|}}{C}H—COO^-$$

157. (c) Methyl group is electron donating group, therefore it increases the electron density in benzene ring. Since SO_3 is electrophyle so, toluene is easily sulphonated.

158. (c)



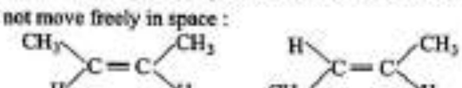
$$H_2C{=}CH—CH_2—CH_3\ (I) \quad CH_2{=}\overset{\overset{CH_3}{|}}{C}—CH_3\ (II)$$



159. (b) In CCl_4 the moment of each bond is cancelled out due to its regular tetrahedron structure.

160. (d) $\underset{sp^2}{H_2C}{=}\underset{sp}{C}{=}\underset{sp^2}{CH}—\underset{sp^3}{CH_3}$

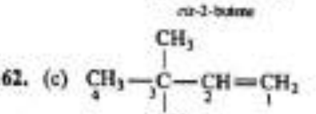
161. (a) Geometrical isomerism arises due to the hindered rotation between >C=C< bond, *i.e.*, atoms or groups do not move freely in space :



cis-2-butene

trans-2-butene

162. (c)



$$\underset{4}{CH_3}—\underset{3}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}}—\underset{2}{CH}{=}\underset{1}{CH_2}$$

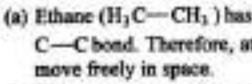
3,3-dimethyl-1-butene

163. (a) $—CH_3$ gp. has + *I* and + *M* effect. It increases the electron density on benzene ring hence toluene is reactive towards electrophilic nitration.

164. (d) It is an experimental fact.

165. (c) $N{\equiv}\underset{1}{\overset{sp}{C}}—\underset{2}{\overset{sp^2}{CH}}{=}\overset{sp^2}{CH_2}$

166. (b)

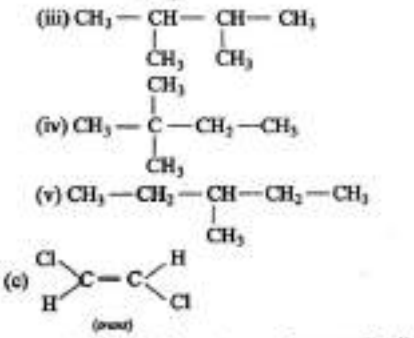


3-methyl 1-butene

167. (a) Ethane ($H_3C—CH_3$) has least hindered rotation about C—C bond. Therefore, atoms or groups attached to it, move freely in space.

168. (b) The two compounds with different molar masses can have the same empirical formula but different molecular formulae.

169. (b)



(i) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

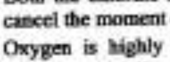
(ii) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_2—CH_3$

(iii) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

(iv) $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—CH_2—CH_3$

(v) $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—CH_3$

170. (c)



(trans)

Both the chlorine atoms are in opposite direction and cancel the moment of each other.

171. (d) Oxygen is highly electronegative than carbon, so it acquires partially negative charge and carbon atom acquires partially positive charge.

172. (a) Stronger is the acid or base, weaker is its conjugate acid or base.

Base strength :

$CH_3—\bar{C}H_2 > \bar{N}H_2 > HC\equiv C^- > OH^-$

Acid strength :

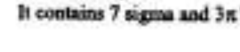
$H—OH > HC\equiv CH > NH_3 > CH_3—CH_3$

173. (a) The former compound has triangular planar structure while later one has tetrahedral structure.

174. (d) The difference of electronegativities between O and H is high, therefore undergo heterolytic cleavage.

175. (b) Tertiary butyl alcohol gives *t*-butyl carbonium ion which is more stable than primary and secondary carbonium ion.

176. (b)

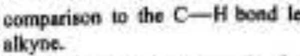


$H\underset{\sigma}{—}\overset{\displaystyle H}{\overset{\sigma|}{C}}\overset{\sigma}{\underset{\pi}{=}}\overset{\displaystyle H}{\overset{|\sigma}{C}}\overset{\sigma}{—}C\overset{\sigma}{\underset{2\pi}{\equiv}}C\overset{\sigma}{—}H$ **σ – bonds = 7**
π – bonds = 3

1-butene-3-yne

It contains 7 sigma and 3π bonds.

177. (d)



$CH_3—CH_2—CH_2—\overset{\displaystyle CH_3}{\overset{|}{CH}}—CH_3$

2-methyl pentane

178. (c) C—H bond length in saturated hydrocarbon is more in comparison to the C—H bond length of alkene and alkyne.

179. (a) In benzyl amine the lone pair of electron on 'N' atom does not come into resonance with ring.

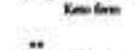
180. (b) $HCN \rightleftharpoons H^+ + \underset{\text{Nucleophile}}{CN^-}$

Ketone　　　Cyanohydrin

It is an example of nucleophilic addition reaction.

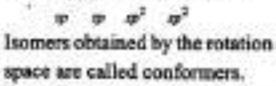
181. (a) Enolic from of acetone contains 9 σ bonds, 1 π bond, 2 lone pair of electrons

$\underset{\text{Enolic form}}{CH_2=\overset{\displaystyle OH}{\overset{|}{C}}—CH_3}$



$\underset{\text{Keto form}}{CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3}$

182. (c)



$H\overset{\sigma}{—}C\overset{\sigma}{\underset{2\pi}{\equiv}}C\overset{\sigma}{—}\overset{\displaystyle H}{\overset{|\sigma}{C}}\underset{\sigma}{=}\overset{\displaystyle H}{\overset{|\sigma}{C}}\underset{\sigma}{—}H$

sp　sp　sp^2　sp^2

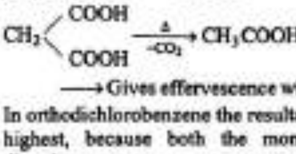
183. (a) Isomers obtained by the rotation of C—C single bond in space are called conformers.

184. (c) Rest all are correct. Point *b* and *d* suggest for more stable nature of benzoate ion.

185. (d) Rest all are oxidised. Benzaldehyde does not contain α-H atom.

186. (c) The electron donating groups facilitate the electrophilic substitution reactions.

187. (a)

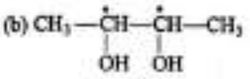


⟶ Gives effervescence with $NaHCO_3$ solution

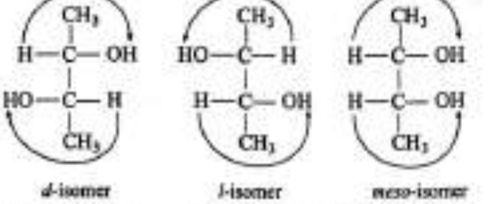
188. (b) In orthodichlorobenzene the resultant dipole moment is highest, because both the moments are in same direction.

189. (c) $HCOONH_4 \xrightarrow{\Delta} HCONH_2 + H_2O$

190. (a) CH_3COCl is most susceptible to nucleophilic attack because Cl atom is also electronegative atom which decreases the electron density on carbonyl carbon making it sensitive towards nucleophilic attack.

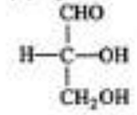
191. (b) 
$CH_3-\overset{*}{C}H(OH)-\overset{*}{C}H(OH)-CH_3$

It has two asymmetric C-atoms therefore optically active isomers $= 2^{n-1} = 2^{2-1} = 2$. It has an optically inactive meso form due to the molecular plane of symmetry. (n = No. of asymmetric carbon atoms)

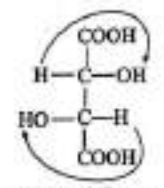


d-isomer (optically active) *l*-isomer (optically active) *meso*-isomer (optically inactive)

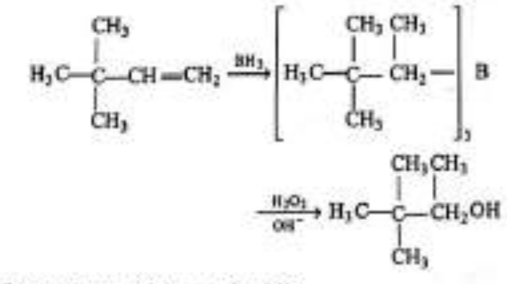
192. (c) D is used to represent the arrangement of —OH group in right side at second last carbon atom as in glyceraldehyde and (+) sign is used to represent the



optical rotation in clockwise direction. Hence (+) tartaric acid is :



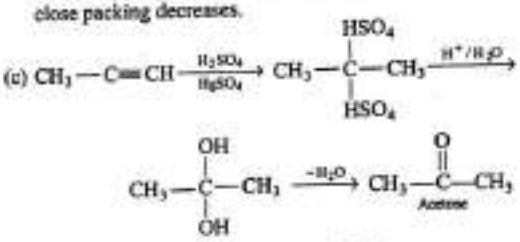
193. (c) Hydroboration – oxidation follows anti Markownikoff addition



194. (b) Marsh gas mainly contains CH_4.

195. (b) The unsaturated compounds (alkenes and alkynes) decolourises alkaline $KMnO_4$ solution. (Test for unsaturation)

196. (a) The straight chain compounds have higher b.pt. than branched compounds. On branching, the tendency of close packing decreases.

197. (c) 

198. (c) Hexane does not dissolve in conc. H_2SO_4.

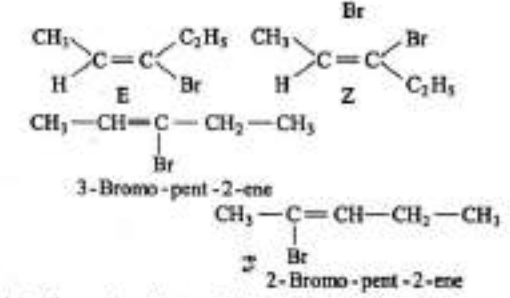
199. (a) Cold dilute alkaline solution of potassium permanganate (1% cold alkaline $KMnO_4$) is known as Baeyer's reagent.

200. (a) Ethyne (terminal alkynes) has acidic H which can be easily replaced by metals.

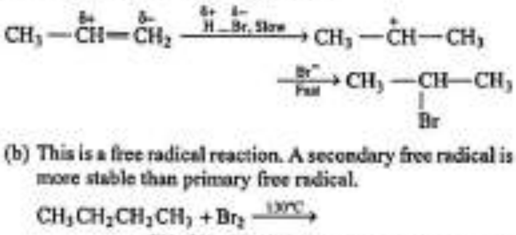
$$HC\equiv CH + Na \xrightarrow[-(1/2)H_2]{180°C} HC\equiv CNa \xrightarrow[-(1/2)H_2]{200°C} \underset{\text{Disodium acetylide}}{NaC\equiv CNa}$$

201. (c) But-2-ene is symmetrical alkene. So it does not show anti Markovnikoff addition.

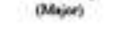
202. (b) Follow answer 196.

203. (b) 

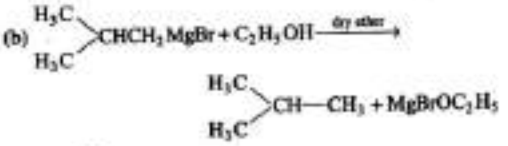
204. (a) Alkens show electrophilic addition.



205. (b) This is a free radical reaction. A secondary free radical is more stable than primary free radical.

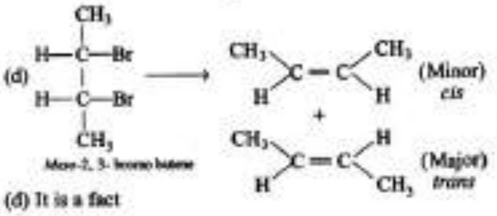


206. (b)



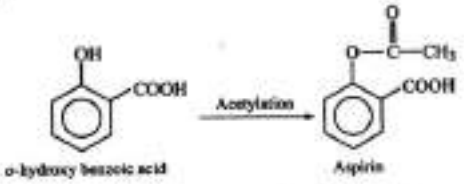
$$(H_3C)_2CHCH_2MgBr + C_2H_5OH \xrightarrow{\text{dry ether}} (H_3C)_2CH{-}CH_3 + MgBrOC_2H_5$$

207. (d)

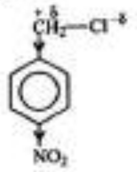


208. (d) It is a fact

209. (b)

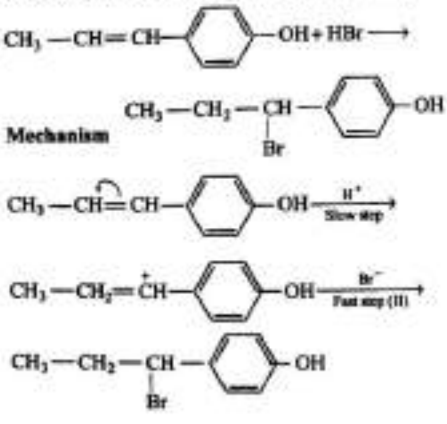


210. (d) Electron withdrawing nature of $—NO_2$ gp increases polarity in CH_2Cl.

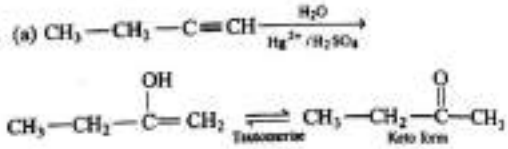


211. (b) Bakelite is condensation polymer of HCHO and phenol.

212. (b)



213. (a)



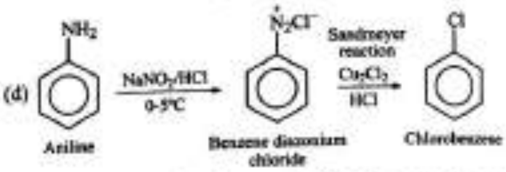
$$CH_3—CH_2—C\equiv CH \xrightarrow[Hg^{2+}/H_2SO_4]{H_2O}$$

$$CH_3—CH_2—\overset{\displaystyle OH}{\overset{|}{C}}=CH_2 \underset{\text{Tautomerise}}{\rightleftharpoons} \underset{\text{Keto form}}{CH_3—CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3}$$

The mechanism involves tautomerism.

214. (b) CCl_4 has a regular symmetrical structure therefore each bond moment is cancelled out from each other.

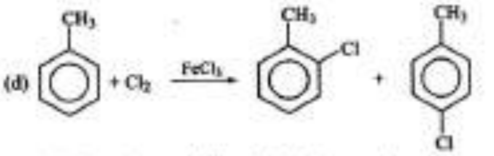
215. (d)



216. (a) Tert. carbonium ion is more stable than secondary or primary carbonium ion.

217. (a) $C_2H_6(\text{excess}) + Cl_2 \xrightarrow{\text{UV light}} C_2H_5Cl + HCl$

218. (d)

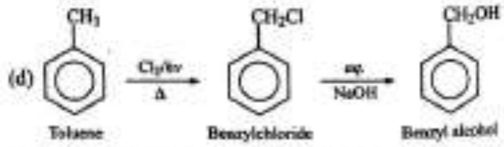


This is an electrophilic substitution reaction.

219. (b) Alc. KOH is a dehydrohalogenating agent.

$$\underset{\text{n-propyl bromide}}{CH_3—CH_2CH_2Br} \xrightarrow{\text{ethanolic KOH}} \underset{\text{propene}}{CH_3—CH=CH_2} + KBr + H_2O$$

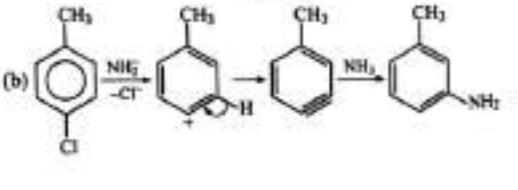
220. (d)



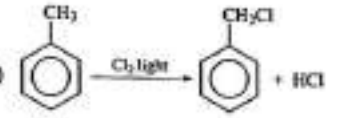
221. (a) $\underset{\text{1-chlorobutane}}{CH_3—CH_2—CH_2—CH_2—Cl} + KOH(\text{alc.}) \longrightarrow$

$$\underset{\text{1-butene}}{CH_3—CH_2—CH=CH_2} + KCl + H_2O$$

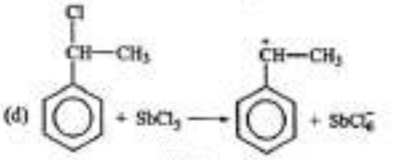
222. (b)



223. (c)



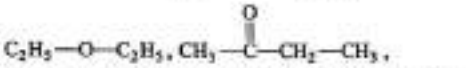
224. (d)



225. (c) $C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} H_2C{=}CH_2 + H_2O$

226. (a) $\overset{\text{C-Base}}{CH_3ONa} \xleftarrow{NaH} \underset{\text{Base}}{\overset{\text{Acid}}{CH_3OH}} \xrightarrow{H_2SO_4} \underset{\text{C-Acid}}{CH_3OH_2^+}$

227. (d)



$C_2H_5{-}O{-}C_2H_5,\ CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3,$

Both the compounds have different molecular formula.

228. (d) The test with Lucas reagent (conc. HCl + Anhyd. $ZnCl_2$) is based on the reactivity order of alcohols to replace —OH gp. by halogen atom, *i.e.*, *tert*-alcohol > sec-alcohol > *p*-alcohol.

$$R{-}OH \xrightarrow{HCl + ZnCl_2} R{-}Cl$$

Primary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ No cloudiness at room temp., it appears only on heating

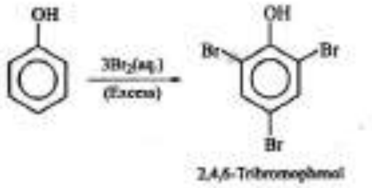
Secondary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ Cloudiness appears within 5 minutes

Tertiary alcohol $\xrightarrow[\text{room temp.}]{\text{Lucas reagent}}$ Cloudiness appears immediately

229. (c) $C_2H_5OC_2H_5 + 2HI \xrightarrow{\Delta} 2C_2H_5I + H_2O$

230. (a) $\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_3-ZnO} \underset{\text{Methanol}}{CH_3OH}$

231. (d)



2,4,6-Tribromophenol

The —OHgp is an electron donating gp. and it activates the benzene ring for electrophilic substitution.

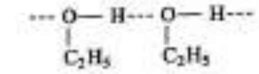
232. (c) Iodoform test is given by compounds having methyl ketones, sec. alcohol and ethyl alcohol (only *p*-alcohol).

233. (a) It is an experimental fact. Follow directive influence of gps.

234. (c) Secondary alcohols are oxidised by $K_2Cr_2O_7 + H_2SO_4$ to produce ketone.

$$\underset{\text{2-Butanol}}{CH_3CHOHCH_2CH_3} \xrightarrow{(O)} \underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$$

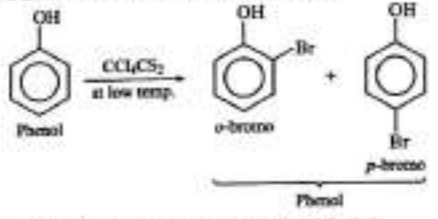
235. (a)



$$\cdots\underset{\underset{\displaystyle C_2H_5}{|}}{O}{-}H\cdots\underset{\underset{\displaystyle C_2H_5}{|}}{O}{-}H\cdots$$

Hydrogen bonding is maximum in ethanol because it forms intermolecular H-bonding.

236. (b) This is controlled bromination reaction.



237. (b) $RSH + O_3 \longrightarrow CO_2(g) + H_2O(l) + SO_2(g)$.

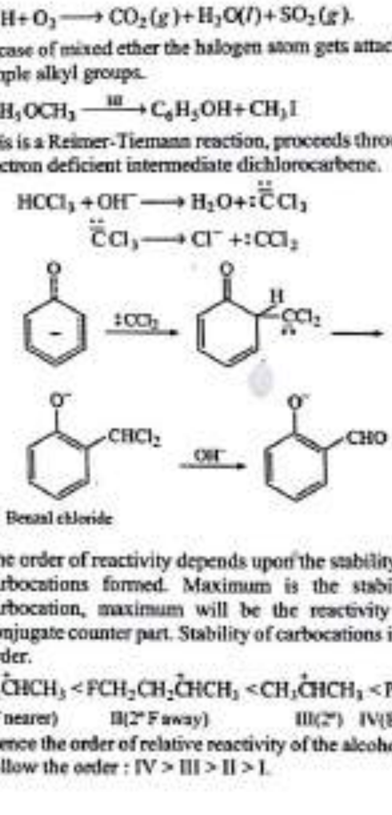
238. (a) In case of mixed ether the halogen atom gets attached to simple alkyl groups.

$$C_6H_5OCH_3 \xrightarrow{HI} C_6H_5OH + CH_3I$$

239. (d) This is a Reimer-Tiemann reaction, proceeds through an electron deficient intermediate dichlorocarbene.

$$HCCl_3 + OH^- \longrightarrow H_2O + :\overset{..}{C}Cl_3$$

$$\overset{..}{C}Cl_3 \longrightarrow Cl^- + :CCl_2$$



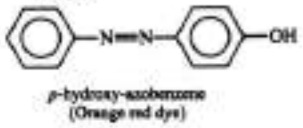
240. (c) The order of reactivity depends upon the stability of the carbocations formed. Maximum is the stability of carbocation, maximum will be the reactivity of its conjugate counter part. Stability of carbocations is in the order.

$$\underset{\text{I(2°, F nearer)}}{FCH_2\overset{+}{C}HCH_3} < \underset{\text{II(2° F away)}}{FCH_2CH_2\overset{+}{C}HCH_3} < \underset{\text{III(2°)}}{CH_3\overset{+}{C}HCH_3} < \underset{\text{IV(Benzyl)}}{Ph\overset{+}{C}H_2}$$

Hence the order of relative reactivity of the alcohols will follow the order : IV > III > II > I.

241. (b) It is a coupling reaction

$$C_6H_5N_2Cl + C_6H_5OH \xrightarrow[\text{Coupling reaction}]{OH^-}$$



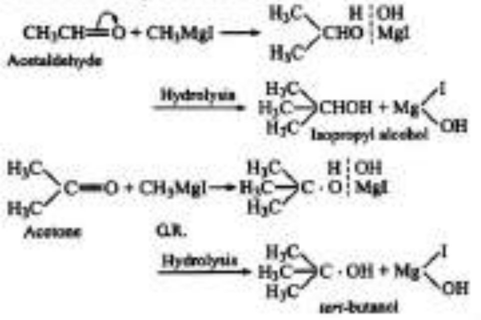
p-hydroxy-azobenzene
(Orange red dye)

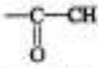
242. (d) Order of acidic strength is :

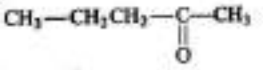
$CH_3OH > HC \equiv CH > C_6H_6 > C_2H_6$

Although all are neutral towards the litmus paper.

243. (b) Fehling solution, Schiff's reagent and Tollen's reagent react only with aldehydes but Grignard reagents react both with aldehydes and ketones.



244. (b) Compounds having,  $-\underset{\underset{O}{\|}}{C}-CH_3$ all sec. alcohol and C_2H_5OH (only in primary alcohol) give positive iodoform test



$$CH_3-CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

(pentanon-2) gives this test.

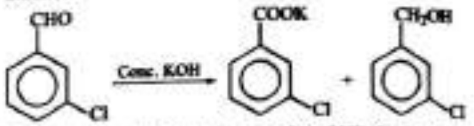
245. (c) The produtt is red ppt of cuprous oxide

$$CH_3CHO + \underset{\text{Fehling solution}}{2Cu^{2+}} + OH^- \longrightarrow CH_3COOH + \underset{\text{red}}{Cu_2O}\downarrow$$

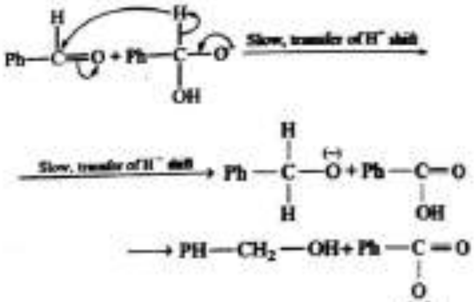
246. (b) Compounds not containing α-H undergo Cannizzaro reaction.

Acetaldehyde does not undergo Cannizzaro reaction since it has α-H atoms while formaldehyde, trimethylacetaldehyde and benzaldehyde undergo Cannizzaro reaction since they do not contain α-hydrogen atoms.

247. (d) *m*-chlorobenzaldehyde does not contains any α-H atom. So it undergo Cannizzaro reaction to form acid salt and alcohol.



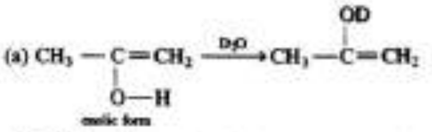
248. (b) In Cannizzaro reaction the transfer of H^- (hydride ion) takes place in slow step



249. (d) Electron withdrawing (nitro group) group facilitates the release of hydride ion.

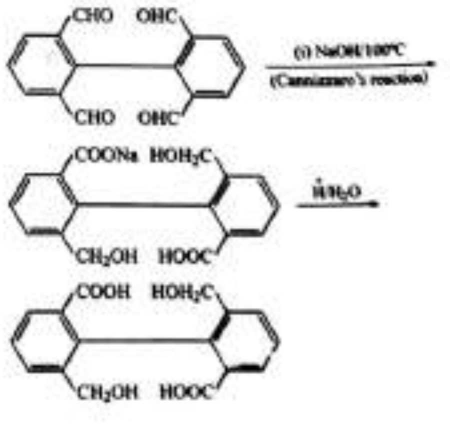
250. (b) CCl_3CHO reacts with water to give a stable chloral monohydrate.

$$\underset{\text{Chloral}}{CCl_3CHO} \xrightarrow{H_2O} \underset{\text{Chloral monohydrate}}{CCl_3CH(OH)_2}$$

251. (a) 

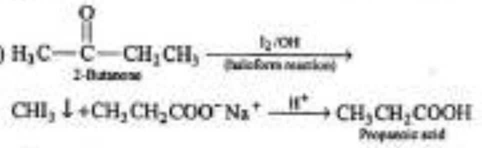
$$CH_3-\underset{\underset{\text{enolic form}}{O-H}}{\underset{|}{C}}=CH_2 \xrightarrow{D_2O} CH_3-\overset{\overset{OD}{|}}{C}=CH_2$$

252. (b) This is an intramolecular Cannizzaro reaction.



253. (c) It is an example of nucleophilic addition on carbonyl group which depends upon positive charge density and steric hindrance around carbonyl group.
Thus CH_3CHO is most reactive and $C_6H_5COC_6H_5$ is least.

254. (c)



$$H_3C-\overset{\overset{O}{\|}}{\underset{\text{2-Butanone}}{C}}-CH_2CH_3 \xrightarrow[\text{(haloform reaction)}]{I_2/OH}$$

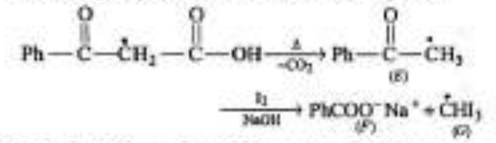
$$CHI_3\downarrow + CH_3CH_2COO^-Na^+ \xrightarrow{H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

255. (c) This reaction is an example of Perkin reaction. This reaction proceeds through the carbanion mechanism. The compound *X* is $(CH_3CO)_2O$

$$C_6H_5CHO + H_3CHCO\cdot O\cdot COCH_3 \xrightarrow{HOH}$$

$$C_6H_5CH{=}\ CHCOOH\cdot COCH_3 + CH_3COOH$$

256. (c) In first step decarboxylation occurs and *E* is formed which is $PhCOCH_3$. The second step is iodoform reaction giving $PhCOO^-Na^+$ (***F***) and CHI_3 (***G***).



257. (b) This is Hofmann bromide reaction. In this reaction primary amine with one carbon less is formed.

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

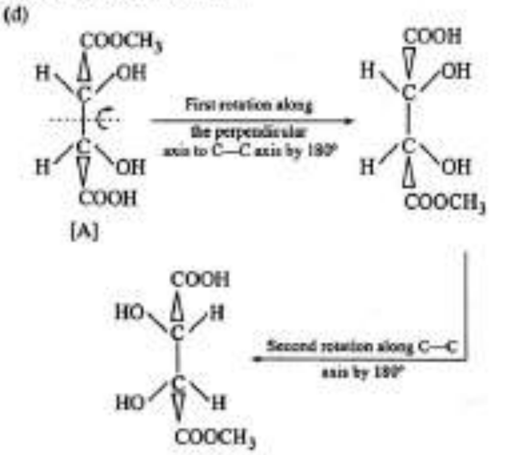
258. (b) In Rosenmund reaction partial hydrogenation occurs

$$\underset{\text{benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow[\text{xylene}]{Pd/BaSO_4} \underset{\text{benzaldehyde}}{C_6H_5CHO} + HCl$$

259. (a) $\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$

260. (d) It is an experimental fact.

261. (d)

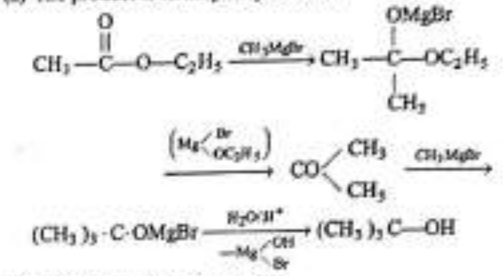


This is perfect mirror image of *B* and thus *A* and *B* are enantiomers.

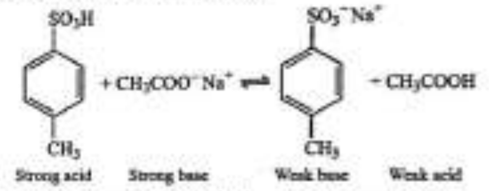
262. (d) The carbon of CO_2 comes from bicarbonate

$$C_2H_5COOH + NaHCO_3 \rightarrow C_2H_5COONa + H_2O + CO_2$$

263. (a) The product is tertiary butyl alcohol



264. (a) This is an acid-base reaction



265. (c) Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form *N*-nitrosoamines.

$$(C_2H_5)_2NH + HONO \longrightarrow \underset{N\text{-nitrosodiethylamine}}{(C_2H_5)_2-N=O} + H_2O$$

266. (b) Carbylamine test is given by only aliphatic and aromatic primary amines. It react, with alkaline $CHCl_3$ to form bad smelling isocyanides.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

267. (d) Propyl chloride reacts with alcoholic KCN to from butane nitrile.

$$CH_3CH_2CH_2Cl + KCN \longrightarrow \underset{\text{Butane nitrile}}{CH_3CH_2CH_2CN} + KCl$$

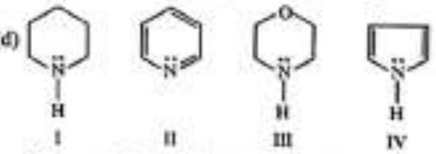
268. (c) Second canonical structure can not be acceptable because N-atom has ten valence electron which is not possible.

269. (a) According to Bronsted Lowry theory, H_2SO_4 is a proton donor species and a stronger acid than HNO_3. Therefore, H_2SO_4 acts as an acid and HNO_3 as base.

$$HNO_3 + H_2SO_4 \longrightarrow H_2^+NO_3 + HSO_4^-$$

$$H_2^+NO_3 \longrightarrow H_2O + NO_2^+$$

270. (d)



In structure I and III the lone pair of N-atom present in sp^3 hybridization structure, I is more basic than III because in structure III the lone pair of electrons shifts towards oxygen atom to a lesser extent. In structure II and IV the N-atom is sp^2 hybridized. In structure IV the lone pair of electrons involves in aromatic sextet but not in structure II.

271. (c) The rate of nitration of benzene C_6H_6 takes place at the same rate because the rate determining step is the formation of carbocation which is same for both the compounds.

272. (a) β-keto carboxylic acid undergoes decarboxylation on heating.

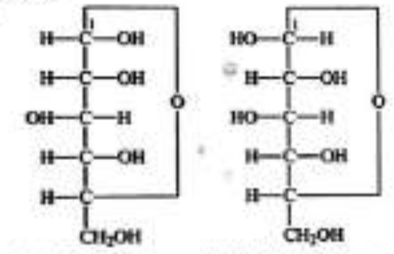
273. (c) 'N' can not accommodate 10 electrons because of non availability of *d*-orbitals.

274. (d) Glucose reduces Tollen's reagent into silver mirror.

$$CH_2OH(CHOH)_4CHO + Ag_2O \rightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + \underset{\text{Silver mirror}}{2Ag}$$

Fructose being a ketohexose reduces Tollen's reagent (ammonical solution of silver nitrate) into silver mirror because the alkaline reagents rearrange fructose to give D-glucose and D-mannose which are strong reducing agents.

275. (b)



α-D(+)-Glucopyranose β-D(+)-Glucopyranose

Two forms of D-glucopyranose are α-D(+)-Glucopyranose and β-D(+)-Glucopyranose. These are anomers (a pair of stereoisomers which differ in configuration only around C_1 are called anomers).

276. (b) Due to H-bonding, stronger in carboxylic acid.

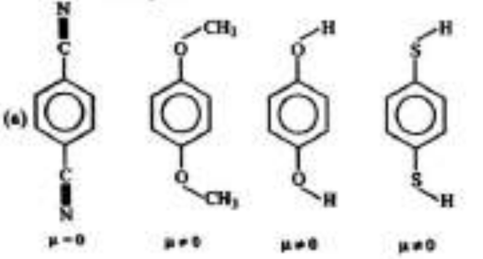
277. (c) Addition of water acc. to Markownikoff rule.

278. (b) Conc. H_3PO_4 acts as dehydrating agent.

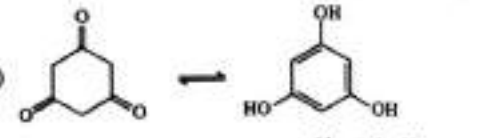
279. (a) $C_6H_5COOH + NaH\overset{14}{C}O_3 \rightarrow C_6H_5COONa + \overset{14}{C}O_2 + H_2O$

280. (b) I represents conjugated diene *i.e.*, most stable ; IV is an isolated diene; III is cumulated diene where II is antiaromatic system.

281. (a)

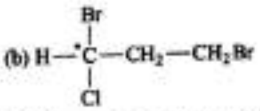


282. (c)



(due to 3α-H-atoms)

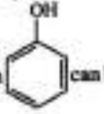
283. (b)



$$H-\overset{\overset{\large Br}{|}}{\underset{\underset{\large Cl}{|}}{\overset{*}{C}}}-CH_2-CH_2Br$$

284. (d) Compounds containing polyvalent functional gps shows only metamerism. Never report chain or position isomerism if functional gp is polyvalent.

285. (d) follow concept.

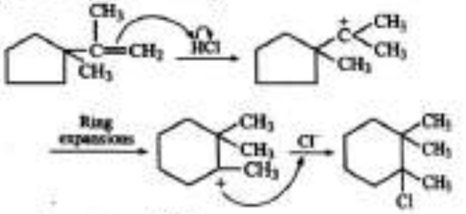
286. (d) Enolic form  can be confirmed by $FeCl_3$ solution.

287. (b) $CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$

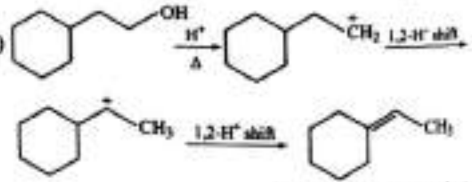
288. (d) It is wurtz reaction.

289. (d) Rest all will give phenol after elimination of HBr.

290. (c) Due to expansion of ring

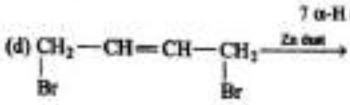


291. (b)



7 α-H atom, major product

292. (d)



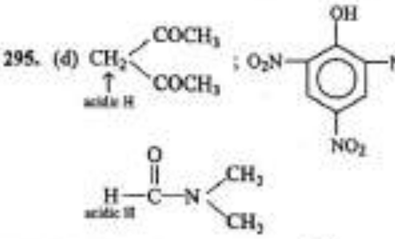
$$\underset{\underset{\large Br}{|}}{CH_2}-CH=CH-\underset{\underset{\large Br}{|}}{CH_2}\xrightarrow{\text{Zn dust}}$$

$$\underset{\text{Conjugated diene}}{CH_2=CH-CH=CH_2} + ZnBr_2$$

293. (a) Clemensen reduction converts $>CO$ gp to $>CH_2$. Here 1,2-methyl shift also occurs during the course of reaction.

294. (c) $CO + NaOH(s) \xrightarrow{\Delta} HCOONa \xrightarrow{HOH} HCOOH$ (reducing agent)

295. (d)



296. (a) $CH_3—CH=CH—Cl \xrightarrow{-HCl} CH_2=C=CH_2$

297. (a) Pyruvic acid is $CH_3 \cdot CO \cdot COOH$ *i.e.*, CH_3CO is attached to C.

298. (c) Br attached on nucleus is weaker leaving gp due to partial bond character.

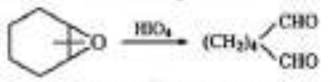
299. (d) $RS^- > CN^- > I^- > RO^- > OH^- > Br^- > C_6H_5O^- > Cl^- > Me_3N$ (Nucleophilicity order)

300. (d) $LiAlH_4$ in ether does not reduces $>C=C<$ to $>CH—C<$

301. (b) Oxidation of unsymmetrical ketone gives two acids. According to Popff's rule the carbonyl gp goes with smaller alkyl gp.

302. (b) *t*-alkyl halides undergoes elimination reaction with sodium alkoxide to give alkene.

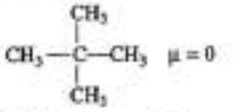
303. (a)



304. (d) All aldehydes restores pink colour to Schiff's reagent readily. Acetone restores colour but slowly. *o*-hydroxy benzaldehyde does not restore pink colour due to intramolecular H-bonding.

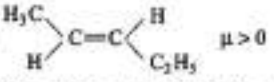
305. (b) The symmetrical molecule has lesser or zero dipole moment.

(a)

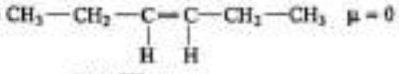


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH_3 \quad \mu = 0$$

(b)

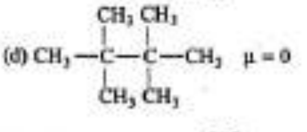


(c)



$$CH_3—CH_2—\underset{H}{C}=\underset{H}{C}—CH_2—CH_3 \quad \mu = 0$$

(d)



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\underset{CH_3}{\overset{CH_3}{C}}—CH_3 \quad \mu = 0$$

306. (b) $ClCH_2=CHCl_2 \xrightarrow[-HCl]{OH^-} CH_2=CCl_2$

307. (a) Due to –ve IE effect of F atom.

308. (d) Rest all shows hydroxylation of ethylene.

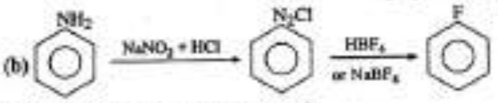
309. (a) The order of ease of abstraction of H-atom is :
Allylic > 3° > 2° > 1° > CH_4 > vinyle

310. (b) N is sp^2 and sp^3 hybridised.

311. (d) A modified or extended Friedel-Craft's reaction

$$C_6H_6 + CH_2Cl_2 \xrightarrow{AlCl_3} C_6H_5CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5$$

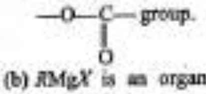
312. (b)



313. (b) Product will be spiro compound.

314. (b) 1,2-bromocyclopentane on heating with I^- in presence of acetone gives cyclopentene.

315. (c) $—NO_2$ group attacks on benzene ring attached to

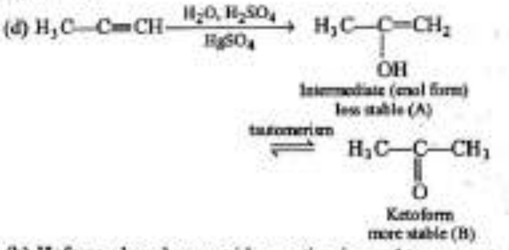


$—O—\underset{\underset{O}{\|}}{C}—$ group.

316. (b) *RMgX* is an organometallic compound having only sigma bonds.

317. (b) It is fact.

318. (d)



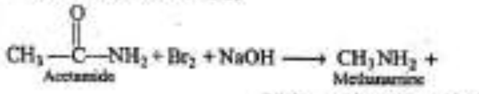
$$H_3C—C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} H_3C—\underset{OH}{C}=CH_2$$

Intermediate (enol form) less stable (A)

$$\underset{tautomerism}{\rightleftharpoons} H_3C—\underset{\underset{O}{\|}}{C}—CH_3$$

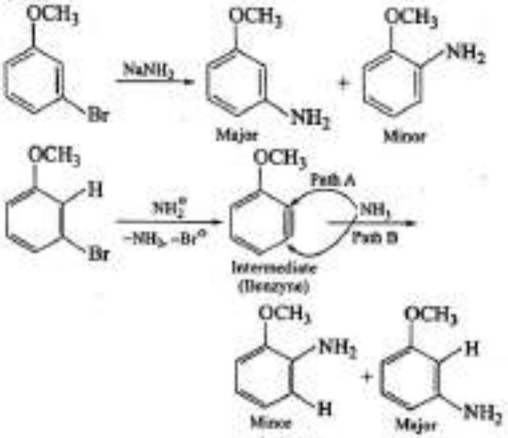
Ketoform more stable (B)

319. (b) Hofmann hypobromamide reaction is used to convert $—CONH_2$ gp to $—NH_2$ gp



$$\underset{Acetamide}{CH_3—\overset{\overset{O}{\|}}{C}—NH_2} + Br_2 + NaOH \longrightarrow \underset{Methanamine}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$

320. (a,b)



Product A is the major product of the reaction formed via path A. This is cine substitution following mechanism of elimination addition reaction.

321. (d) Electron withdrawing groups (–*I* and –*M* effect) decreases basic strength of aniline while electron donating groups (+*I* and +*M* effect) increases basic strength of aniline at para positions.

(I)

(II)

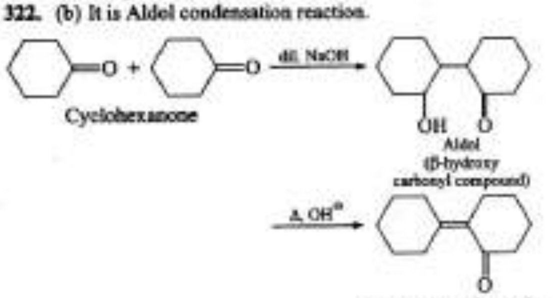
(–*M* effect of —NO_2 group)

(III)

(Hyper conjugation effect of —CH_3 group)

So, the correct order of basic strength of following compounds is : II < I < III.

322. (b) It is Aldol condensation reaction.

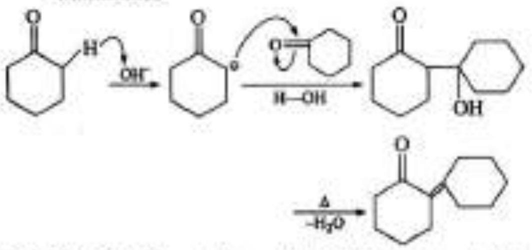


Cyclohexanone

Aldol (β-hydroxy carbonyl compound)

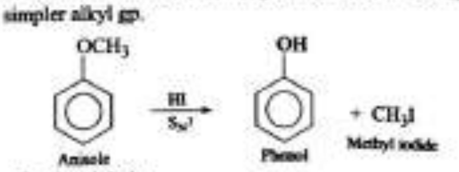
Aldol condensation product (α-β unsaturated)

Mechanism



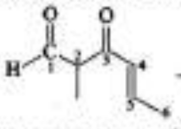
323. (d) It is definition of electrophile. NO_2^+ (nitronium ion) is positively charged electrophile, SO_3 is neutral electrophile.

324. (c) In case of mixed ether, halogen atom is attached to simpler alkyl gp.



325. (d) Denaturation of protein makes the protein inactive as all the properties of protein are lost.

326. (a)

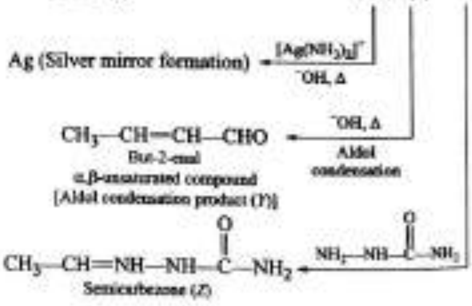


⟶ 3-keto-2-methylhex-4-enal

327. (b) Alkynes are more acidic than alkenes which are further more acidic than alkanes due to the different electronegativity of sp, sp^2 and sp^3 hybridised carbon (order of electro- negativity = $sp > sp^2 > sp^3$) + *I* effect decreases the acidic strength of alkynes so the overall order of acidic strength will be :

$$CH\equiv CH > CH_3—C\equiv CH > CH_2=CH_2 > CH_3—CH_3$$

328. (c)



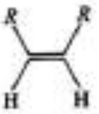
329. (d) Ortho nitrophenol show intramolecular H-bond while paranitrophenol show intermolecular H-bond. Thus b.pt. of *p*-nitrophenol > b.pt. of *o*-nitrophenol. So the mixture of both can be separated by steam distillation which is the technique to separate the components of a mixture on the basis of boiling point.

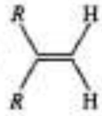
330. (d) Among the three conformers of ethane (Eclipsed, staggered, gauche) bond angle and bond length remains the same while their energy, stability and dihedral angle are different.

331. (d) Presence of three strong electron withdrawing NO_2 groups (–*M* effect) at ortho and para positions enables picric acid (2,4,6-trinitro phenol) to show more acidic nature.

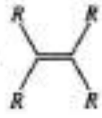
PREVIOUS YEAR OBJECTIVE PROBLEMS (One Answer Correct)

1. Which one of the following alkenes will react fastest with H_2 under catalytic condition ? **(IIT 2000)**

(a)


(b)


(c)


(d)


2. Which of the following compounds will exhibit geometrical isomerism? **(IIT 2000)**

(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene (d) 1,1-diphenyl-1-propene

3. Which of the following has the highest nucleophilicity? **(IIT 2000)**

(a) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

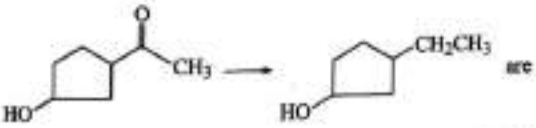
4. Propyne and propene can be distinguished by : **(IIT 2000)**

(a) conc. H_2SO_4 (b) Br_2 in CCl_4
(c) dil. $KMnO_4$ (d) Amm. $AgNO_3$

5. The order of reactivities of the following alkyl halides for a S_N2 reaction is : **(IIT 2000)**

(a) $RF > RCl > RBr > RI$ (b) $RF > RBr > RCl > RI$
(c) $RCl > RBr > RF > RI$ (d) $RI > RBr > RCl > RF$

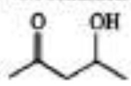
6. The appropriate reagents for the following transformation.

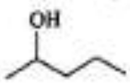


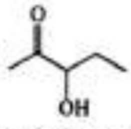
are : **(IIT 2000)**

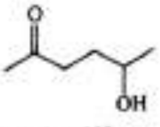
(a) Zn(Hg), HCl (b) $NH_2.NH_2.OH^-$
(c) H_2/Ni (d) $NaBH_4$

7. Which one of the following will most readily be dehydrated in acidic condition : **(IIT 2000)**

(a)


(b)


(c)


(d)


8. Benzoyl chloride is prepared from benzoic acid by : **(IIT 2000)**

(a) Cl_2, $h\nu$ (b) SO_2Cl_2
(c) $SOCl_2$ (d) Cl_2, H_2O

9. Which of the following has the most acidic hydrogen? **(IIT 2000)**

(a) 3-hexanone (b) 2,4-hexanedione
(c) 2,5-hexanedione (d) 2,3-hexanedione

10. Among the following, the strongest base is : **(IIT 2000)**

(a) $C_6H_5NH_2$ (b) p-NO_2—$C_6H_4NH_2$
(c) m-NO_2—$C_6H_4NH_2$ (d) $C_6H_5CH_2NH_2$

11. A S_N2 reaction at an asymmetric carbon of a compound always gives : **(IIT 2001)**

(a) an enantiomer of the substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereoisomer
(d) a single stereoisomer

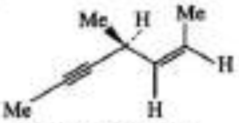
12. The number of isomers for the compound with molecular formula $C_2BrClFI$ is : **(IIT 2001)**

(a) 3 (b) 4
(c) 5 (d) 6

13. In the presence of a peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff addition to alkenes because : **(IIT 2001)**

(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

14. Hydrogenation of the given compound in the presence of poisoned palladium catalyst gives : **(IIT 2001)**



(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture

15. The reaction of propene with HOCl proceeds *via* the addition of : **(IIT 2001)**

(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step

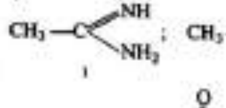
16. 1-propanol and 2-propanol can be best distinguished by : **(IIT 2001)**

(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

17. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives : (IIT 2001)
    (a) Benzyl alcohol and sodium formate
    (b) Sodium benzoate and methyl alcohol
    (c) Sodium benzoate and sodium formate
    (d) Benzyl alcohol and methyl alcohol

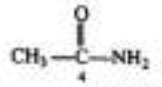
18. The compound that will react most readily with NaOH to form methanol is : (IIT 2001)
    (a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
    (c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$

19. The correct order of basic nature of the following compounds is : (IIT 2001)



; $\underset{2}{CH_3-CH_2-NH_2}$

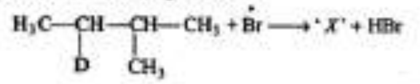
$\underset{3}{(CH_3)_2NH}$;



$\underset{4}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2}$

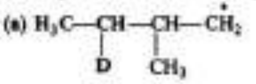
(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4
(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

20. Consider the following reaction :

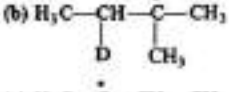


$$H_3C-\underset{D}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CH_3+\dot{B}r\longrightarrow `X' + HBr$$

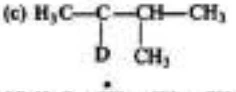
Identify the structure of the major product 'X' : (IIT 2002)

(a)


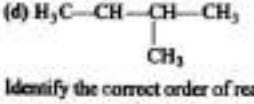
$H_3C-\underset{D}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-\dot{C}H_2$

(b)


$H_3C-\underset{D}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$

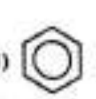
(c)


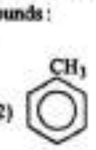
$H_3C-\underset{D}{\underset{|}{\dot{C}}}-\underset{CH_3}{\underset{|}{C}H}-CH_3$

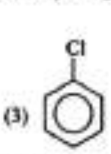
(d)


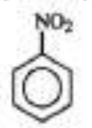
$H_3C-\dot{C}H-\underset{CH_3}{\underset{|}{C}H}-CH_3$

21. Identify the correct order of reactivity in S_E reactions of the following compounds : (IIT 2002)

(1)


(2)


(3)


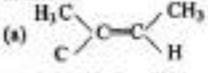
(4)


(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
(c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4

22. Which of the following compounds exhibits stereoisomerism ? (IIT 2002)
    (a) 2-methylbutene-1 (b) 3-methylbutene-1
    (c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

23. The nodel plane in the π-bond of ethene is located in : (IIT 2002)
    (a) the molecular plane
    (b) a plane parallel to the molecular plane
    (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ-bond at right angle
    (d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ-bond

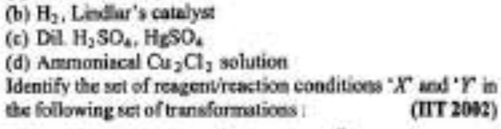
24. Which of the following hydrocarbons has the lowest dipole moment? (IIT 2002)

(a)


(b) $CH_3C\equiv CCH_3$
(c) $CH_3CH_2C\equiv CH$ (d) $CH_2=CH-C\equiv CH$

25. Identify the reagents from the following list which can easily distinguish between 1-butyne and 2-butyne: (IIT 2002)
    (a) Bromine, CCl_4
    (b) H_2, Lindlar's catalyst
    (c) Dil. H_2SO_4, $HgSO_4$
    (d) Ammoniacal Cu_2Cl_2 solution

26. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations : (IIT 2002)



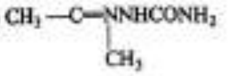
$$CH_3-CH_2-CH_2Br\xrightarrow{X}\text{Product}\xrightarrow{Y}CH_3-\underset{Br}{\underset{|}{C}H}-CH_3$$

(a) X = dilute aqueous NaOH, 20°C ; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

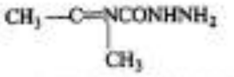
27. Identify the correct order of boiling points of the following compounds : (IIT 2002)
    1. $CH_3CH_2CH_2CH_2OH$ 2. $CH_3CH_2CH_2CHO$
    3. $CH_3CH_2CH_2COOH$
    (a) 1 > 2 > 3 (b) 3 > 1 > 2
    (c) 1 > 3 > 2 (d) 3 > 2 > 1

28. Which of the following acids has the smallest dissociation constant? (IIT 2002)
    (a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
    (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

29. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2\cdot HCl$ and sodium acetate gives a product 'C'. Identify the structure of 'C' : (IIT 2002)
    (a) $CH_3CH_2CH=NNCONH_2$

(b) 

$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=NNHCONH_2$

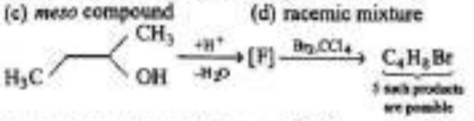
(c) 

$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=NCONHNH_2$

(d) $CH_3CH_2CH=NCONHNH_2$

30. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one Chiral carbon. The ester formed will be : **(IIT 2003)**

(a) optically active mixture (b) pure enantiomer
(c) *meso* compound (d) racemic mixture

31. 

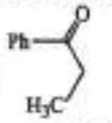
How many structures of F are possible ? **(IIT 2003)**

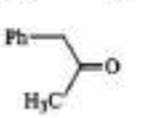
(a) 2 (b) 5
(c) 6 (d) 3

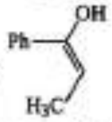
32. Which of the following represents the given mode of hybridization $sp^2-sp^2-sp-sp$ from left to right ? **(IIT 2003)**

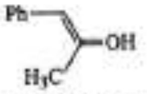
(a) $H_2C=CH—C\equiv CH$ (b) $HC\equiv C—C\equiv CH$
(c) $H_2C=C=C=\dot{C}H_2$ (d) 

33. $Ph—C\equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$, A is : **(IIT 2003)**

(a) 

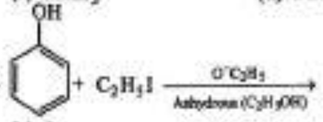
(b) 

(c) 

(d) 

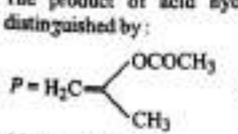
34. Among the following, the molecule with the highest dipole moment is : **(IIT 2003)**

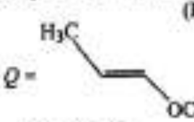
(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

35.  **(IIT 2003)**

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

36. The product of acid hydrolysis of P and Q can be distinguished by : **(IIT 2003)**

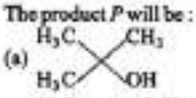


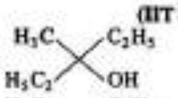


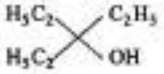
(a) Lucas reagent (b) 2,4-DNP
(c) Fehling's solution (d) NaHSO₃

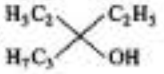
37. Ethyl ester $\xrightarrow[\text{Excess}]{CH_3MgBr} P$

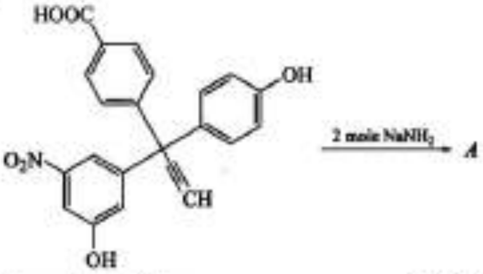
The product P will be : **(IIT 2003)**

(a) 

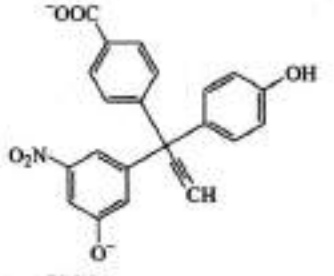
(b) 

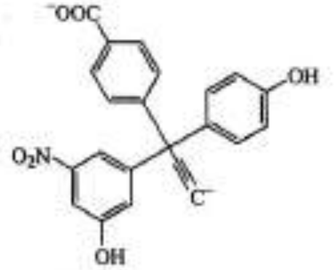
(c) 

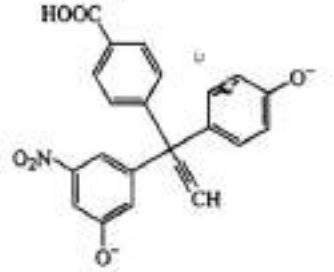
(d) 

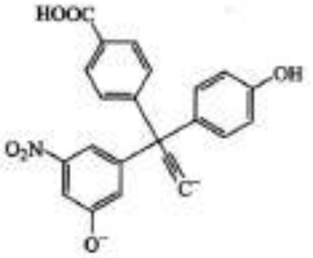
38. 

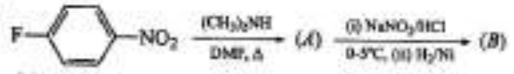
The product A will be : **(IIT 2003)**

(a) 

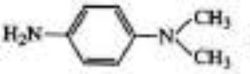
(b) 

(c) 

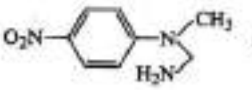
(d)


39.


B is : **(IIT 2003)**

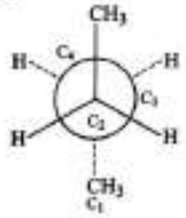
(a)


(b)


(c)


(d)


40. In the given conformation C_2 is rotated about $C_2—C_3$ bond and clockwise by an angle of 120°. Then the formation obtained is : **(IIT 2004)**



(a) Fully eclipsed conformation
(b) Partially eclipsed conformation
(c) Gauche conformation
(d) Staggered conformation

41. On monochlorination of 2-methyl butane, the total number of chiral compound is : **(IIT 2004)**

(a) 2 (b) 4
(c) 6 (d) 8

42. The product of acid catalysed hydration of 2-phenyl propene is : **(IIT 2004)**

(a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol

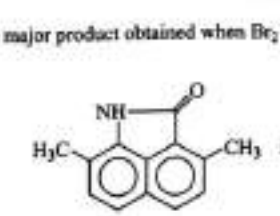
43. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene ? **(IIT 2004)**

(a) H_2 / Pd / $BaSO_4$ (b) H_2 / PtO_2
(c) $NaBH_4$ (d) Li—NH_3 / C_2H_5OH

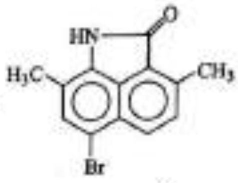
44. Benzamide on reaction with $POCl_3$ gives : **(IIT 2004)**

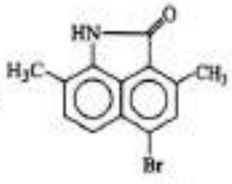
(a) Aniline (b) Chlorobenzene
(c) Benzylamine (d) Benzonitrile

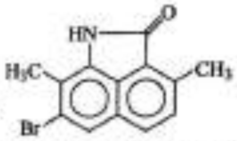
45. The major product obtained when Br_2 / Fe is treated with : **(IIT 2004)**

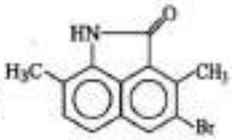


is :

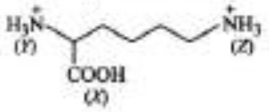
(a)


(b)


(c)


(d)


46. In the compound given below :



The correct order of acidic nature is : **(IIT 2004)**

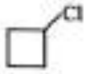
(a) $Z > X > Y$ (b) $X > Y > Z$
(c) $X > Z > Y$ (d) $Y > X > Z$

47. Which of the following resonating structures of 1-methoxy-1, 3-butadiene is least stable : **(IIT 2005)**

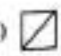
(a) $\overset{-}{C}H_2—CH=CH—CH=\overset{+}{O}—CH_3$
(b) $CH_2=CH—\overset{-}{C}H—CH=\overset{+}{O}—CH_3$
(c) $\overset{-}{C}H_2—\overset{+}{C}H—CH=CH—O—CH_3$
(d) $CH_2=CH—\overset{-}{C}H—\overset{+}{C}H—O—CH_3$

48. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether ? **(IIT 2005)**

(a)


(b)


(c)


(d)


49. When phenyl magnesium bromide reacts with *t*-butanol, the product would be : **(IIT 2005)**

(a) C_6H_6 (b) C_6H_5OH
(c) *t*-butyl benzene (d) *t*-butyl phenyl ether

50. When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$ the gases released respectively are : **(IIT 2006)**

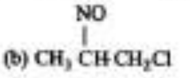
(a) SO_2, NO_2 (b) SO_2, NO
(c) SO_2, CO_2 (d) CO_2, CO_2

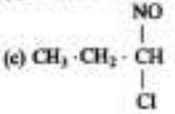
51. The correct increasing order of b.pt. of the following is : (IIT 2006)

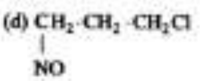
(I) 1, 2-dihydroxy benzene (II) 1,3-dihydroxy benzene
(III) 1,4-dihydroxy benzene (IV) Hydroxy benzene
(a) I < II < III < IV (b) I < II < IV < III
(c) IV < I < II < III (d) IV < II < I < III

52. The product formed in the reaction,
$CH_3-CH=CH_2+NOCl \longrightarrow$ is : (IIT 2006)

(a) $CH_3CHCl\cdot CH_2NO$

(b)

$CH_3\,\underset{}{\overset{NO}{CH}}\,CH_2Cl$

(c)

$CH_3\cdot CH_2\cdot \overset{NO}{\underset{Cl}{CH}}$

(d)

$\underset{NO}{CH_2}\cdot CH_2\cdot CH_2Cl$

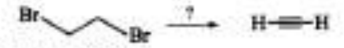
53. In $CH_3NH_2+CHCl_3+KOH \longrightarrow A+KCl+H_2O$, A is : (IIT 2006)

(a) CH_3CN (b) CH_3NHCH_3
(c) $CH_3\,\overset{-}{N}\overset{+}{C}$ (d) $CH_3\,\overset{+}{N}\equiv\overset{-}{C}$

54. The IUPAC name of C_6H_5COCl is : (IIT 2006)

(a) Benzoyl chloride
(b) Benzene chloroketone
(c) Benzene carbonyl chloride
(d) Chlorophenyl ketone

55. The reagent (s) used for the following conversion are : (IIT 2007)



(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) Zn/CH_3OH
(d) aqueous KOH followed by $NaNH_2$

56. The number of structural isomers for C_6H_{14} is : (IIT 2007)

(a) 3 (b) 4
(c) 5 (d) 6

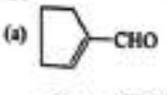
57. The number of stereoisomers obtained by bromination of *trans*-2-butene is : (IIT 2007)

(a) 1 (b) 2
(c) 3 (d) 4

58. Sodium extract of aniline on treatment with $FeSO_4$ and H_2SO_4 in presence of air gives a prussian blue precipitate. The blue colour is due to : (IIT 2007)

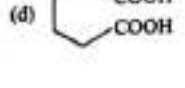
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_3[Fe(CN)_6]_3$

59. Cyclohexane on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with KOH(*aq.*) yields compound F. Compound F is : (IIT 2007)

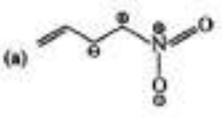
(a)


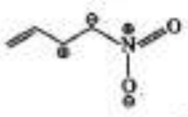
(b)

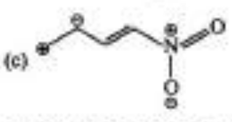

(c)

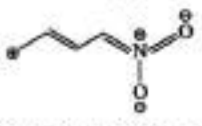

(d)


60. Among the following, the least stable resonance structure is: (IIT 2007)

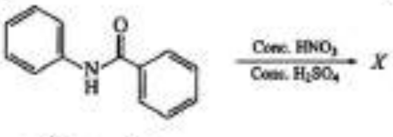
(a)


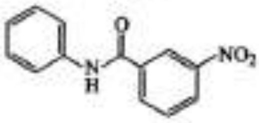
(b)


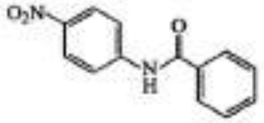
(c)


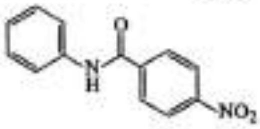
(d)


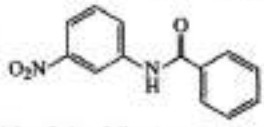
61. In the following reactions, the structure of major product X is : (IIT 2007)

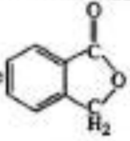


(a)


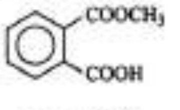
(b)


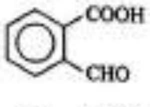
(c)


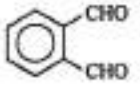
(d)


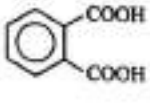
62. Which of the following on reaction with conc. NaOH followed by acidification gives the lactone


as the only product : (IIT 2006)

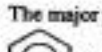
(a)


(b)


(c)


(d)


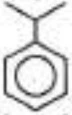
63. The major product *P* and *Q* in the reaction

 + $ClCH_2CH_2 \cdot CH_3 \xrightarrow{AlCl_3} P \xrightarrow{H_2O} Q$ + phenol are :

(IIT 2006)

(a)  + CH_3CH_2CHO

(b)  + CH_3CHO

(c)  + CH_3COCH_3

(d)  + CH_3CH_2CHO

64. The smallest ketone and its next homologous are reacted with $NH_2OH$to form oximes as : **(IIT 2006)**

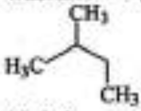
(a) two different oximes

(b) three different oximes

(c) two oximes are optically active

(d) three oximes are optically active

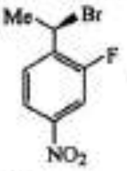
65. What are *P* and *Q* in the reaction : **(IIT 2006)**

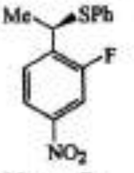
 $\xrightarrow[h\nu]{Cl_2} P, \underset{\text{Isomers}}{(C_5H_{11}Cl)} \xrightarrow[\text{distillation}]{\text{Fractional}} Q$ is:

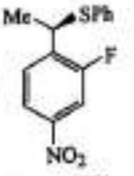
(a) 6, 6 (b) 6, 4

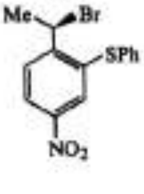
(c) 4, 4 (d) 3, 3

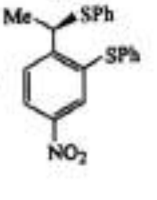
66. The major product of the following reaction is : **(IIT 2008)**

 $\xrightarrow[\text{dimethyl formamide}]{\ominus\oplus \atop \text{PhSNa}}$

(a) 

(b) 

(c) 

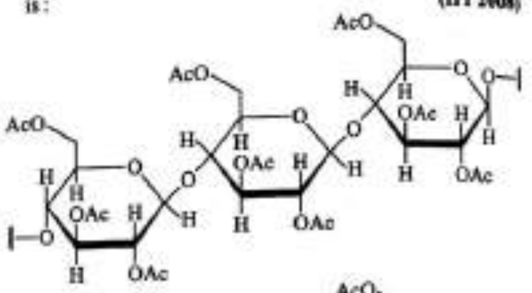
(d) 

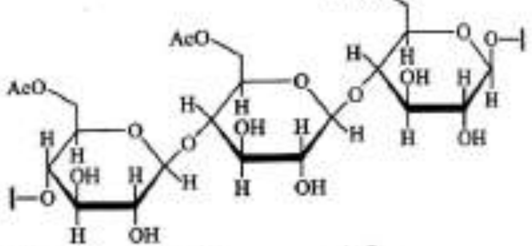
67. Hyperconjugation involves overlap of the following orbitals: **(IIT 2008)**

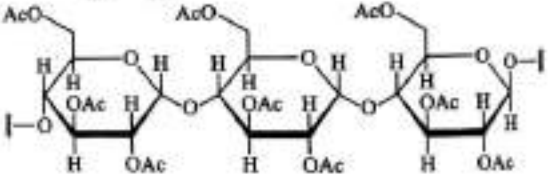
(a) $\sigma - \sigma$ (b) $\sigma - p$

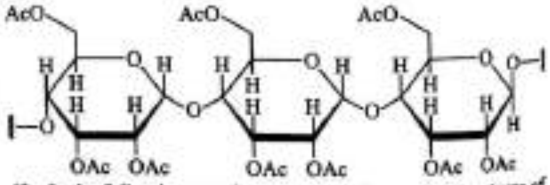
(c) $p - p$ (d) $\pi - \pi$

68. Cellulose upon acetylation with excess acetic anhydride/ H_2SO_4(catalytic) gives cellulose triacetate whose structure is : **(IIT 2008)**

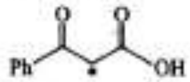
(a) 

(b) 

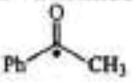
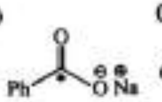
(c) 

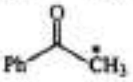
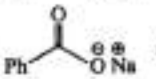
(d) 

69. In the following reaction sequence, the correct structures of *E*, *F* and *G* are :

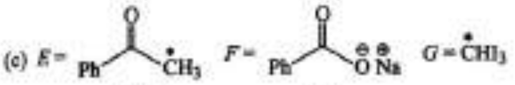
 $\xrightarrow{\text{Heat}} [E] \xrightarrow[NaOH]{I_2} [F] + [G]$

(*implies ^{13}C labelled carbon) **(IIT 2008)**

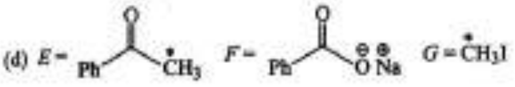
(a) *E* =  *F* =  $G = CHI_3$

(b) *E* =  *F* =  $G = CHI_3$

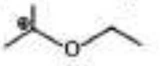
(c)



(d)

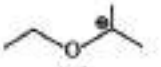


70. The correct stability order for the following species is :

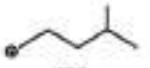


(I)

(II)



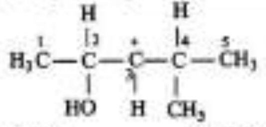
(III)



(IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

71. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is : **(IIT 2009)**



$$H_3\overset{1}{C}-\underset{HO}{\overset{H}{\overset{|2}{C}}}-\underset{H}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{\overset{|4}{C}}}-\overset{5}{C}H_3$$

(a) CH_3 at C-4 (b) H at C-4
(c) CH_3 at C-2 (d) H at C-2

72. The correct stability order of the following resonance structures is : **(IIT 2009)**

$H_2C=\overset{+}{N}=\overset{-}{N}$ (I)

$H_2\overset{+}{C}-N=\overset{-}{N}$ (II)

$H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (III)

$H_2\overset{-}{C}-N=\overset{+}{N}$ (IV)

(a) (I) > (II) > (IV) > (III) (b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV) (d) (III) > (I) > (IV) > (II)

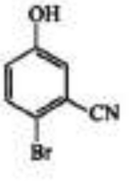
73. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is : **(IIT 2009)**

(a) 2 (b) 4
(c) 7 (d) 6

74. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is : **(IIT 2009)**

(a) Nylon (b) Poly (vinyl chloride)
(c) Cellulose (d) Natural Rubber

75. The IUPAC name of the following compound is : **(IIT 2009)**



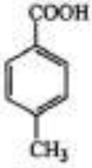
(a) 4-Bromo-3-cyanophenol
(b) 2-Bromo-5-hydroxybenzonitrile
(c) 2-Cyano-4-hydroxybromobenzene
(d) 6-Bromo-3-hydroxybenzonitrile

76. The correct acidity order of the following is : **(IIT 2009)**

(I)

(II)

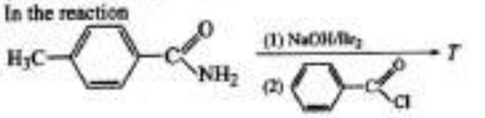
(III)



(IV)

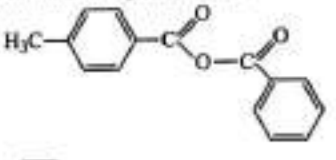
(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

77. In the reaction

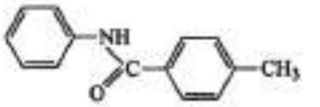


the structure of the product *T* is : **(IIT 2010)**

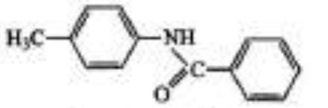
(a)



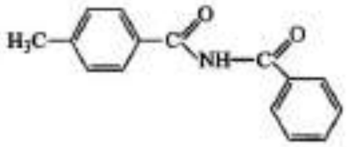
(b)



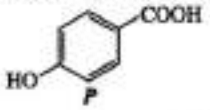
(c)



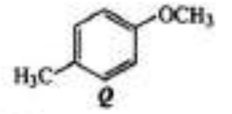
(d)



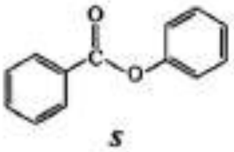
78. The compounds *P*, *Q* and *S*



P

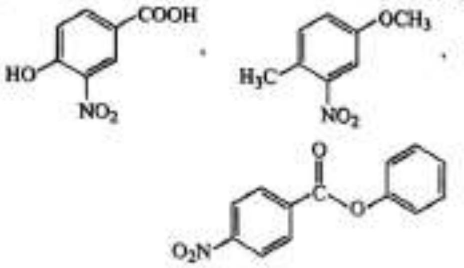


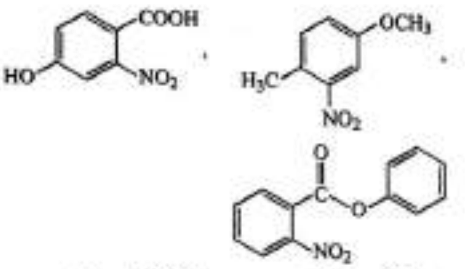
Q

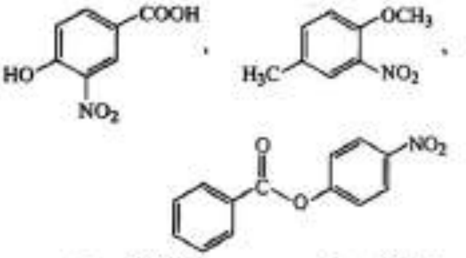


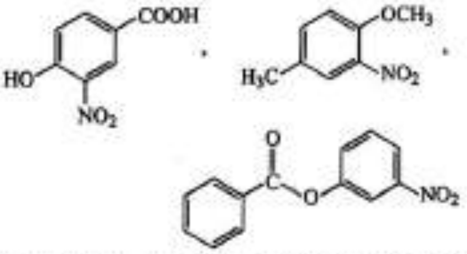
S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is: **(IIT 2010)**

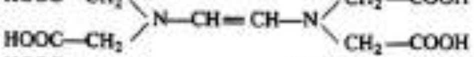
(a)


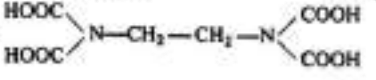
(b)


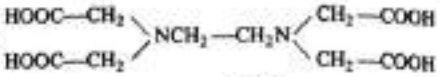
(c)


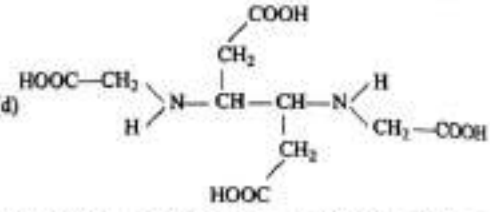
(d)


79. Correct structure of ethylenediaminatetraacetic acid (EDTA) is: **(IIT 2010)**

(a)


(b)


(c)


(d)


80. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and alkyne. The bromoalkane and alkyne respectively are: **(IIT 2010)**

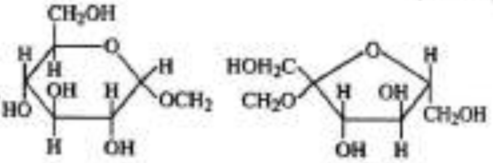
(a) $BrCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$ and $CH_3CH_2C \equiv CH$

(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C \equiv CH$

(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C \equiv CH$

(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C \equiv CH$

81. The correct statement about the following disaccharide is: **(IIT 2010)**



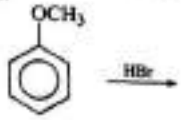
(a) Ring (a) is pyranose with α-glucosidic link

(b) Ring (a) is furanose with α-glucosidic link

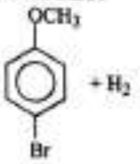
(c) Ring (b) is furanose with α-glucosidic link

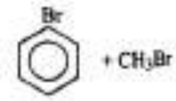
(d) Ring (b) is pyranose with β-glucosidic link

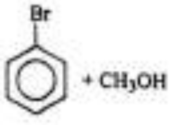
82. In the reaction:

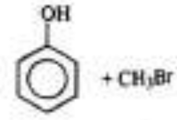


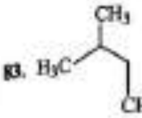
The products are: **(IIT 2010)**

(a)


(b)


(c)


(d)


83. 

$\xrightarrow{Cl_2, h\nu}$ *N* (isomeric products) $C_5H_{11}Cl$

$\xrightarrow{\text{Fractional distillation}}$ *M* (isomeric products)

What are *N* and *M* ?

(a) 6, 6 (b) 6, 4

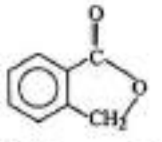
(c) 4, 4 (d) 3, 3 **(IIT 2006)**

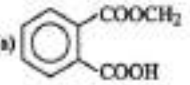
84. Which of the following compounds form two isomeric oximes on reacting with NH_2OH ?

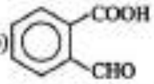
(a) *R*—CHO (b) *R*—CO*R*

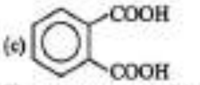
(c) *R*—CO*R*' (d) HCHO **(IIT 2006)**

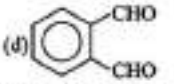
85. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product ? **(IIT 2006)**



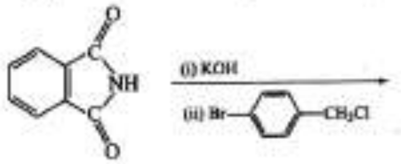
(a) 

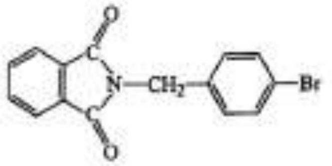
(b) 

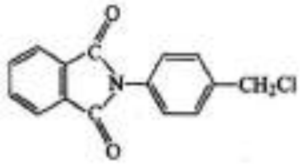
(c) 

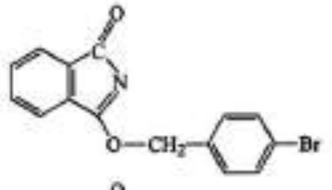
(d) 

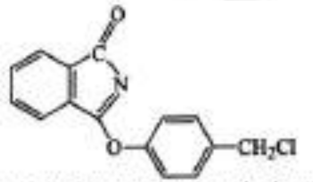
86. The major product of the following reaction is : **(IIT 2011)**



(a) 

(b) 

(c) 

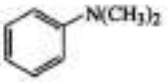
(d) 

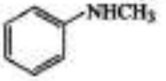
87. Among the following compounds, the most acidic is : **(IIT 2011)**

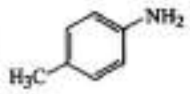
(a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid

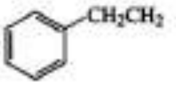
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid

88. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is : **(IIT 2011)**

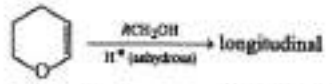
(a) 

(b) 

(c) 

(d) 

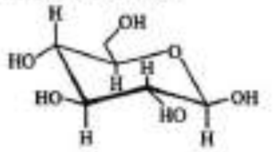
89. The major product of the following reaction is : **(IIT 2011)**



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

90. The following carbohydrate is : **(IIT 2011)**



(a) a ketohexose (b) an aldohexose

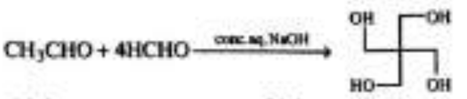
(c) an α-furanose (d) an α-pyranose

91. The carboxyl functional group (— COOH) is present in: **(IIT 2012)**

(a) picric acid (b) barbituric acid

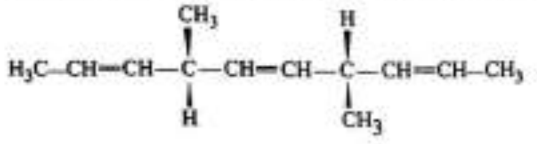
(c) ascorbic acid (d) aspirin

92. The number of aldol reaction(s) that occurs in the given transformation is : **(IIT 2012)**



(a) 1 (b) 2
(c) 3 (d) 4

93. The number of optically active products obtained from the complete ozonolysis of the given compound is: **(IIT 2012)**



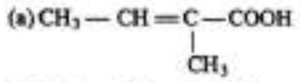
$$H_3C{-}CH{=}CH{-}\underset{H}{\overset{CH_3}{C}}{-}CH{=}CH{-}\underset{CH_3}{\overset{H}{C}}{-}CH{=}CH{-}CH_3$$

(a) 0 (b) 1
(c) 2 (d) 4

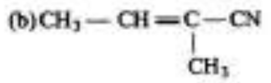
94. The major product H of the given reaction sequence is:

$$CH_3-CH_2-CO-CH_3 \xrightarrow{^{\ominus}CN} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

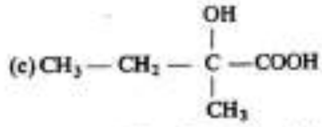
(IIT 2012)

(a)


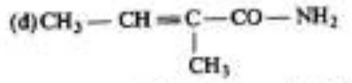
$$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-COOH$$

(b)


$$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CN$$

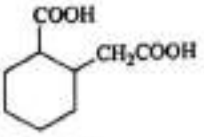
(c)


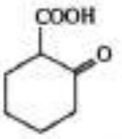
$$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-COOH$$

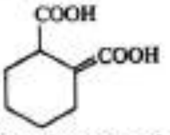
(d)


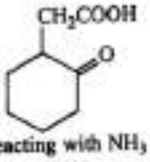
$$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CO-NH_2$$

95. The compound that undergoes decarboxylation most readily under mild condition is: **(IIT 2012)**

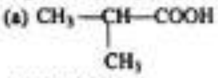
(a)


(b)


(c)


(d)


96. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is: **[JEE (Main) 2013]**

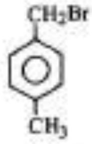
(a)


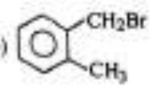
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH$$

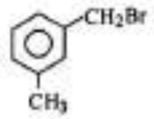
(b) CH_3CH_2COOH

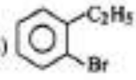
(c) CH_3COOH (d) $CH_3CH_2CH_2COOH$

97. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[JEE (Main) 2013]**

(a)


(b)


(c)


(d)


98. A compound with molar mass 180 is acylated with CH_3COCl to get a compound with molar mass 390. The number of amino groups present per molecule of the former compound is: **[JEE (Main) 2013]**

(a) 4 (b) 6
(c) 2 (d) 5

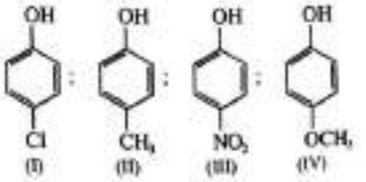
99. A solution of (–) –1 – chloro – 1 – phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of: **[JEE (Main) 2013]**

(a) carbocation (b) free radical
(c) carbanion (d) carbene

100. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts the fastest and by what mechanism? **[JEE (Main) 2013]**

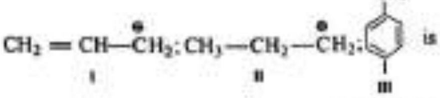
(a) secondary alcohol by S_N2
(b) tertiary alcohol by S_N2
(c) secondary alcohol by S_N1
(d) tertiary alcohol by S_N1

101. Arrange the following compounds in order of decreasing acidity: **[JEE (Main) 2013]**



(a) III > I > II > IV (b) IV > III > I > II
(c) II > IV > I > III (d) I > II > III > IV

102. The order of stability of the following carbocations



is : **[JEE (Main) 2013]**

(a) I > II > III (b) III > I > II
(c) III > II > I (d) II > III > I

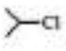
103. Synthesis of each molecule of glucose in photosynthesis involves : **[JEE (Main) 2013]**

(a) 8 molecules of ATP (b) 6 molecules of ATP
(c) 18 molecules of ATP (d) 10 molecules of ATP

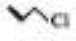
104. KI in acetone, undergoes S_N2 reaction with each of *P*, *Q*, *R* and *S*. The rates of the reaction vary as :

H_3C-Cl

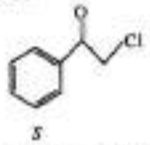
P



Q



R



S

[JEE (Advanced) I 2013]

(a) $P > Q > R > S$ (b) $S > P > R > Q$
(c) $P > R > Q > S$ (d) $R > P > S > Q$

105. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is :

[JEE (Advanced) I 2013]

(a) Benzoic acid (b) Bezenesulphonic acid
(c) Salicylic acid (d) Carbolic acid (Phenol)

106. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to :

[JEE (Advanced) I 2013]

(a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations

(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations

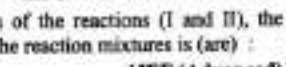
(c) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations

(d) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations

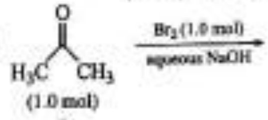
107. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are) :

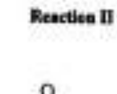
[JEE (Advanced) II 2013]

Reaction I :

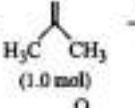


Reaction II :

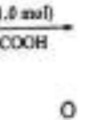




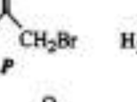
P



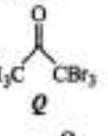
Q



R



S



T

$CHBr_3$

U

(a) Reaction **I** : ***P*** and Reaction **II** : ***P***

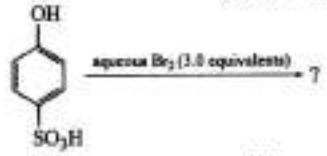
(b) Reaction **I** : ***U***, acetone and Reaction **II** : ***Q***, acetone

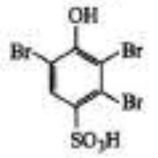
(c) Reaction **I** : ***T***, ***U***, acetone and Reaction **II** : ***P***

(d) Reaction **I** : ***R***, acetone and Reaction **II** : ***S***, acetone

108. The major product(s) of the following reaction is (are) :

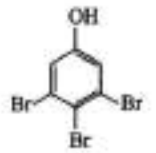
[JEE (Advanced) I 2013]



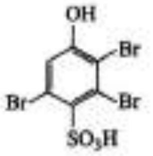


P

Q



R



S

(a) *P* (b) *Q*
(c) *R* (d) *S*

109. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE (Main) 2013]**

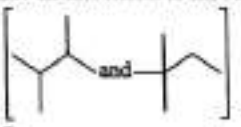
(a) Ammonia (b) Phosgene
(c) Methylisocyanate (d) Methylamine

110. For the identification of β-naphthol using dye test, it is necessary to use : **[JEE (Advanced II) 2014]**

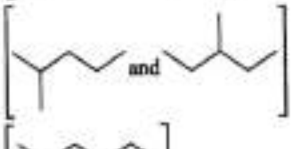
(a) dichloromethane solution of β-naphthol
(b) acidic solution of β-naphthol
(c) neutral solution of β-naphthol
(d) alkaline solution of β-naphthol

111. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

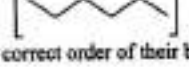
(I)



(II)



(III)



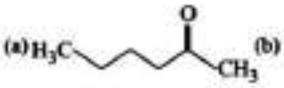
The correct order of their boiling point is :

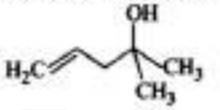
[JEE (Advanced II) 2014]

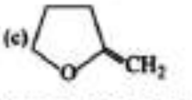
(a) I > II > III (b) III > II > I
(c) II > III > I (d) III > I > II

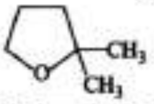
112. The major product in the following reaction is :

[JEE (Advanced II) 2014]

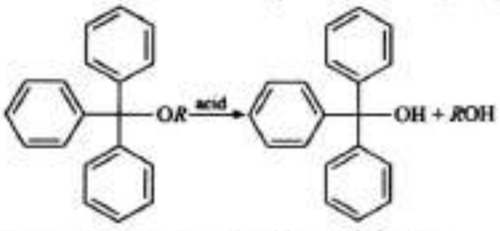
(a)


(b)


(c)


(d)


113. The acidic hydrolysis of ether (X) shown below is fastest when : [JEE (Advanced II) 2014]



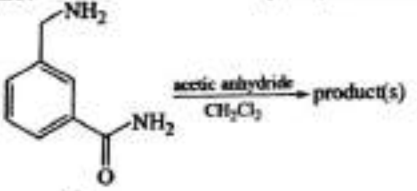
(a) one phenyl group is replaced by a methyl group

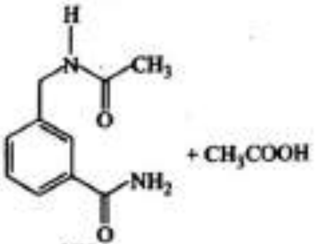
(b) one phenyl group is replaced by a para- methoxyphenyl group

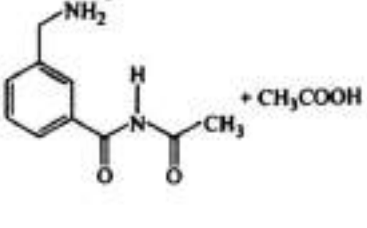
(c) two phenyl groups are replaced by two para-methoxyphenyl groups

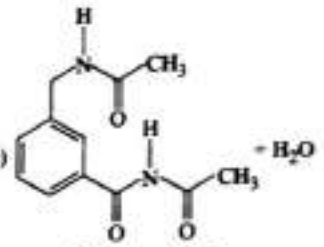
(d) no structural change is made to X

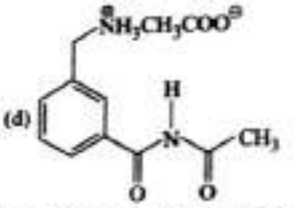
114. In the reaction shown below, the major product(s) formed is/are : [JEE (Advanced I) 2014]



(a)


(b)


(c)


(d)


115. In S_N2 reactions, the correct order of reactivity for the following compounds : CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is : [JEE (Main) 2014]

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

116. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is : [JEE (Main) 2014]

(a) an alkanol (b) an alkanediol

(c) an alkyl cyanide (d) an alkyl isocyanide

117. The most suitable reagent for the conversion of $R—CH_2—OH \longrightarrow R—CHO$ is : [JEE (Main) 2014]

(a) $KMnO_4$

(b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC (Pyridinium Chlorochromate)

118. The major organic compound formed by the reaction of 1, 1, 1- trichloroethane with silver powder is :

[JEE (Main) 2014]

(a) Acetylene (b) Ethene

(c) 2-Butyne (d) 2-Butene

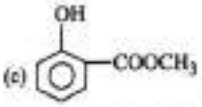
119. Sodium phenoxide when heated with CO_2 under pressure a 125°C yields a product which on acetylation produces C.

The major product C would be : [JEE (Main) 2014]

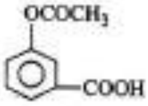
(a)


(b)


(c)



(d)



120. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE (Main) 2014]**

(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

121. For which of the following molecule significant $\mu \neq 0$? **[JEE (Main) 2014]**

(a) Only (i) (b) (i) and (ii)
(c) Only (iii) (d) (iii) and (iv)

122. In the reaction,

$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.\ KOH} C$, the product C is: **[JEE (Main) 2014]**

(a) Acetaldehyde (b) Acetylene
(c) Ethylene (d) Acetyl chloride

123. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The precentage of nitrogen in the compound is: **[JEE (Main) 2014]**

(a) 6% (b) 10%
(c) 3% (d) 5%

124. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is:
(at. mass Ag = 108; Br = 80) **[JEE (Main) 2015]**

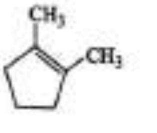
(a) 24 (b) 36
(c) 48 (d) 60

125. Which of the following compounds will exhibit geometrical isomerism? **[JEE (Main) 2015]**

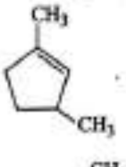
(a) 1-Phenyl-2-butene
(b) 3-Phenyl-1-butene
(c) 2-Phenyl-1-butene
(d) 1, 1-Diphenyl-1-propane

126. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE (Main) 2015]**

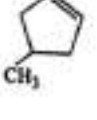
(a)



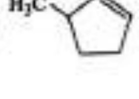
(b)



(c)



(d)



127. The synthesis of alkyl fluorides is best accomplished by: **[JEE (Main) 2015]**

(a) Free radical fluorination
(b) Sandmeyer's reaction
(c) Finkelstein reaction
(d) Swart's reaction

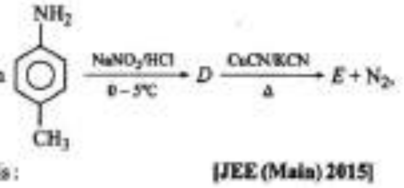
128. In the following sequence of reactions:

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C,$$

the product C is: **[JEE (Main) 2015]**

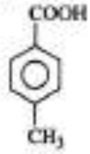
(a) C_6H_5COOH (b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

129. In the reaction

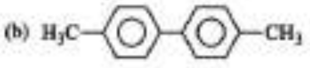


the product E is: **[JEE (Main) 2015]**

(a)

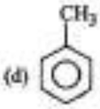


(b)



(c)

(d)



130. Which polymer is used in the manufacture of paints and lacquers? **[JEE (Main) 2015]**

(a) Bakelite (b) Glyptal
(c) Polypropene (d) Poly vinyl chloride

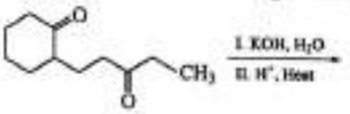
131. Which of the vitamins given below is water soluble? **[JEE (Main) 2015]**

(a) Vitamin C (b) Vitamin D
(c) Vitamin E (d) Vitamin K

132. Which of the following compounds is not an antacid? **[JEE (Main) 2015]**

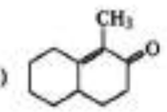
(a) Aluminium hydroxide (b) Cimetidine
(c) Phenelzine (d) Ranitidine

133. The major product of the following reaction is:



[JEE (Advanced I) 2015]

(a)



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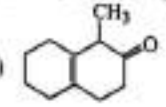
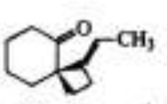
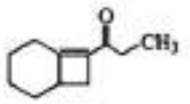
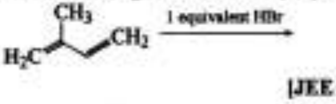


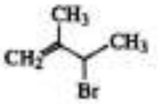
(c) 

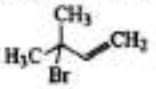
(d) 

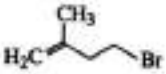
134. In the following reaction, the major product is :

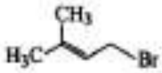


[JEE (Advanced I) 2015]

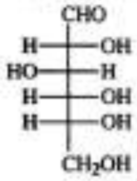
(a) 

(b) 

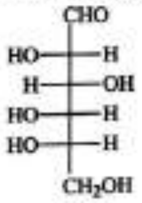
(c) 

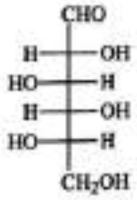
(d) 

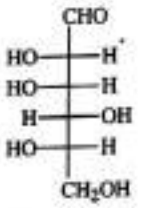
135. The structure of D-(+)-glucose is :

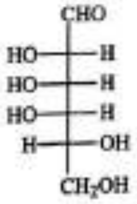


The structure of L(–)-glucose is :

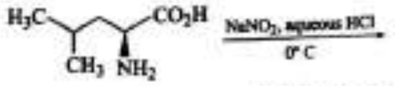
(a) 

(b) 

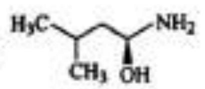
(c) 

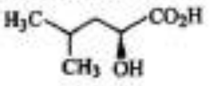
(d) 

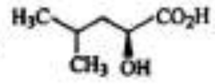
136. The major product of the reaction is :

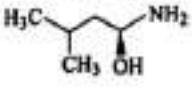


[JEE (Advanced I) 2015]

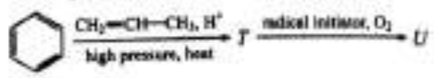
(a) 

(b) 

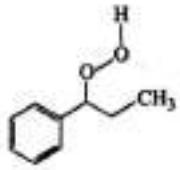
(c) 

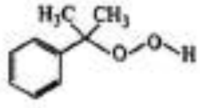
(d) 

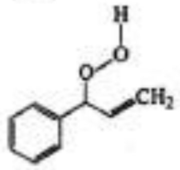
137. The major product U in the following reactions is :

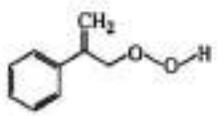


[JEE (Advanced II) 2015]

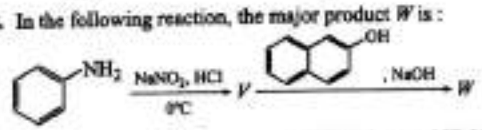
(a) 

(b) 

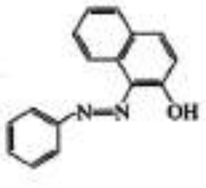
(c) 

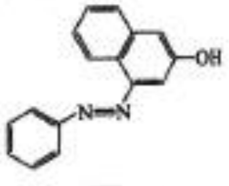
(d) 

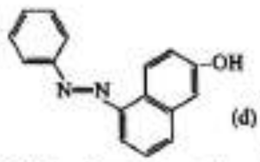
138. In the following reaction, the major product W is :

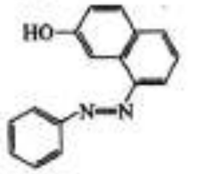


[JEE (Advanced II) 2015]

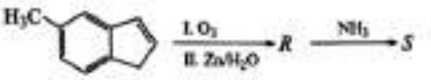
(a) 

(b) 

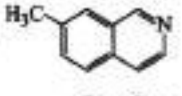
(c) 

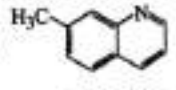
(d) 

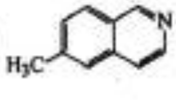
139. In the following reactions, the product S is :

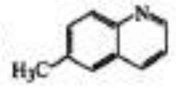


[JEE (Advanced II) 2015]

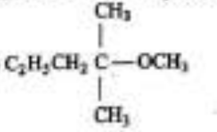
(a) 

(b) 

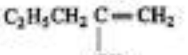
(c) 

(d) 

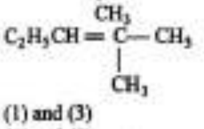
140. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields : **[JEE (Main) 2016]**

(1) 

$C_2H_5CH_2C(CH_3)_2-OCH_3$

(2) 

$C_2H_5CH_2C(CH_3)=CH_2$

(3) 

$C_2H_5CH=C(CH_3)-CH_3$

(a) (1) and (3)　　(b) (3) only

(c) (1) and (2)　　(d) All of these

141. Which of the following statements about low density polythene is **FALSE**? **[JEE (Main) 2016]**

(a) It is a poor conductor of electricity

(b) Its synthesis requires dioxygen or a peroxide initiator as a catalyst

(c) It is used in the manufacture of buckets, dust-bins etc.

(d) Its synthesis requires high pressure

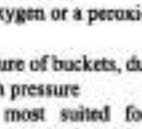
142. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is : **[JEE (Main) 2016]**

(a) fractional distillation

(b) steam distillation

(c) distillation under reduced pressure

(d) simple distillation

143. The absolute configuration of  is: **[JEE (Main) 2016]**

(a) $(2S, 3R)$　　(b) $(2S, 3S)$

(c) $(2R, 3R)$　　(d) $(2R, 3S)$

144. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of : **[JEE (Main) 2016]**

(a) Lead　　(b) Nitrate

(c) Iron　　(d) Fluoride

145. Thiol group is present in : **[JEE (Main) 2016]**

(a) Cystine　　(b) Cysteine

(c) Methionine　　(d) Cytosine

146. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[JEE (Main) 2016]**

(a) four moles of NaOH and two moles of Br_2

(b) two moles of NaOH and two moles of Br_2

(c) four moles of NaOH and one mole of Br_2

(d) one mole of NaOH and one mole of Br_2

147. The reaction of propene with HOCl $(Cl_2 + H_2O)$ proceeds through the intermediate : **[JEE (Main) 2016]**

(a) $CH_3-CH^+-CH_2-Cl$

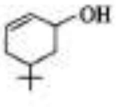
(b) $CH_3-CH(OH)-CH_2^+$

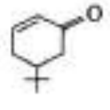
(c) $CH_3-CHCl-CH_2^+$

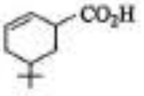
(d) $CH_3-CH^+-CH_2-OH$

148. The product of the reaction given below is :

[JEE (Main) 2016]

(a) 

(b) 

(c) 

(d) 

149. On complete hydrogenation, natural rubber produces: **[JEE (Advanced) I 2016]**

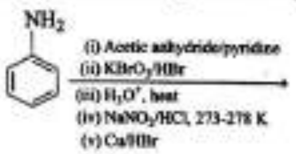
(a) ethylene-propylene copolymer

(b) vulcanised rubber

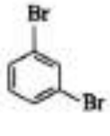
(c) polypropylene

(d) polybutylene

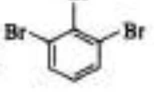
150. The product(s) of the following reaction sequence is(are):



[JEE (Advanced) I 2016]

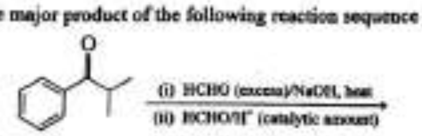
(a) 

(b) 

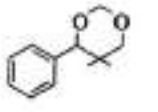
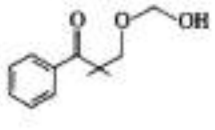
(c) 

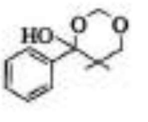
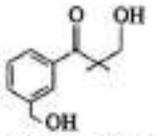
(d) 

151. The major product of the following reaction sequence is :

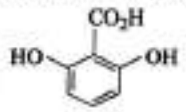
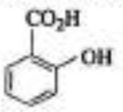


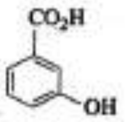
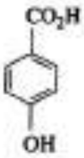
[JEE (Advanced) II 2016]

(a) 
(b) 

(c) 
(d) 

152. The correct order of acidity for the following compounds is :

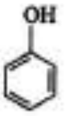
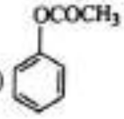
(I) 
(II) 

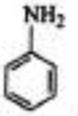
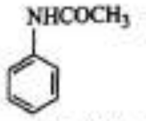
(III) 
(IV) 

[JEE (Advanced) II 2016]

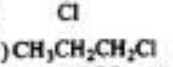
(a) I > II > III > IV
(b) III > I > II > IV
(c) III > IV > II > I
(d) I > III > IV > II

153. Which of the following compounds will form significant amount of *meta* product during mono-nitration reaction? [JEE (Main) 2017]

(a) 
(b) 

(c) 
(d) 

154. The increasing order of the reactivity of the following halides for the S_{N1} reaction is : [JEE (Main) 2017]

(i) 
$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$

(ii) $CH_3CH_2CH_2Cl$

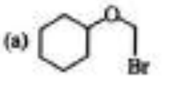
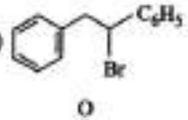
(iii) $p—H_3CO—C_6H_4—CH_2Cl$

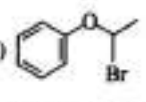
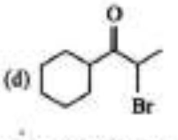
(a) (iii) < (ii) < (i)
(b) (ii) < (i) < (iii)
(c) (i) < (iii) < (ii)
(d) (ii) < (iii) < (i)

155. The formation of which of the following polymers involves hydrolysis reaction? [JEE (Main) 2017]

(a) Nylon 6
(b) Bakelite
(c) Nylon 6, 6
(d) Terylene

156. Which of the following, upon treatment with *tert*.-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine? [JEE (Main) 2017]

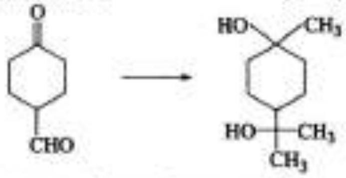
(a) 
(b) 

(c) 
(d) 

157. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : [JEE (Main) 2017]

(a) six
(b) zero
(c) two
(d) four

158. The correct sequence of reagents for the following conversion will be : [JEE (Main) 2017]



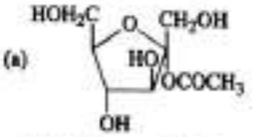
(a) $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH, CH_3MgBr

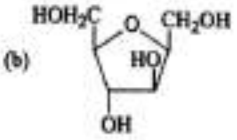
(b) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+OH^-$

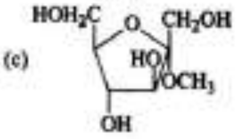
(c) CH_3MgBr, $[Ag(NH_3)_2]^+OH^-$, H^+/CH_3OH

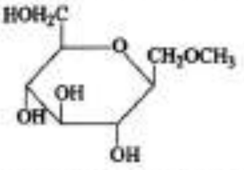
(d) $[Ag(NH_3)_2]^+OH^-$, CH_3MgBr, H^+/CH_3OH

159. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? [JEE (Main) 2017]

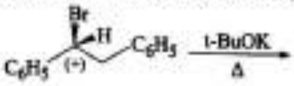
(a) 

(b) 

(c) 

(d) 

160. The major product obtained in the following reaction is :



[JEE (Main) 2017]

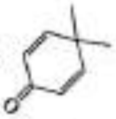
(a) $(\pm)C_6H_5CH(OtBu)CH_2C_6H_5$
(b) $C_6H_5CH{-}CHC_6H_5$
(c) $(+)C_6H_5CH(OtBu)CH_2C_6H_5$
(d) $(-)C_6H_5CH(OtBu)CH_2C_6H_5$

161. Which of the following molecules is least resonance stabilized? **[JEE (Main) 2017]**

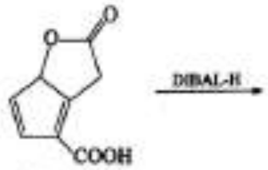
(a) 

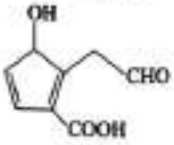
(b) 

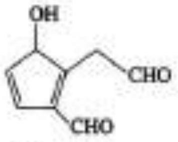
(c) 

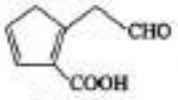
(d) 

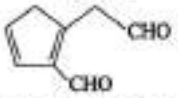
162. The major product obtained in the following reaction is: **[JEE (Main) 2017]**



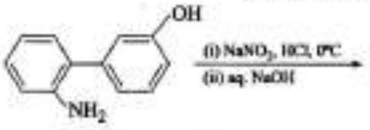
(a) 

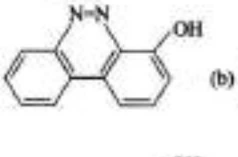
(b) 

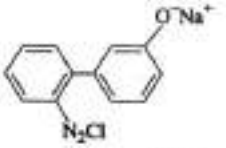
(c) 

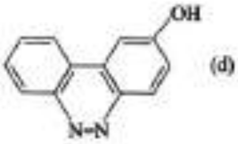
(d) 

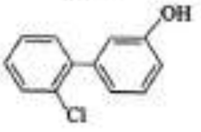
163. The major product of the following reaction is : **[JEE (Advanced-II) 2017]**



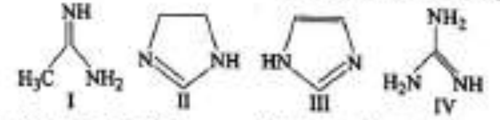
(a) 

(b) 

(c) 

(d) 

164. The order of basicity among the following compounds is: **[JEE (Advanced-II) 2017]**

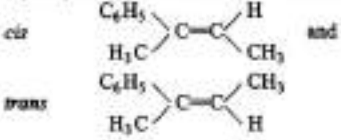


(a) II > I > IV > III
(b) IV > II > III > I
(c) I > IV > III > II
(d) IV > I > II > III

PREVIOUS YEAR OBJECTIVE PROBLEMS SOLUTION

1. (a) More is the heat of hydrogenation of alkene, easier is its hydrogenation or more is its reactivity.

2. (a) 1-phenyl-2-butene has two geometrical isomers as :



3. (c) Stronger is the acid, weaker is its conjugate base or weaker is nucleophile. The order of acidic nature $HF > H_2O > NH_3 > CH_4$.

4. (d) Propyne has one acidic hydrogen and thus, forms propylides with $AgNO_3$ in ammonia.

$$CH_3C{\equiv}CH + Ag_2O \longrightarrow \underset{\text{Silver propylide}}{CH_3C{\equiv}C{\cdot}Ag}$$

5. (d) The rate of reaction follows $RI > RBr > RCl > RF$ whether it obeys S_N1 or S_N2 mechanism.

6. (b) Both Zn-Hg/HCl and $NH_2 \cdot NH_2/OH^-$ reduce $>C{=}O$ gp. to $>CH_2$ but reduction with Zn-Hg/HCl is not useful for acid sensitive substances.

7. (a) It undergoes dehydration easily as the product obtained is conjugated which is more stable.

8. (c) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl + SO_2$

—OH group of —COOH is replaced by PCl_5 or $SOCl_2$.

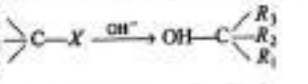
9. (b) Two electron withdrawing groups attached on $H_2C <$ group makes the H-atom of $H_2C <$ (or methylene group) acidic in nature and the compounds are called reactive methylene compounds.

$$H_2C\begin{cases} COCH_3 \\ COCH_2CH_3 \end{cases}$$

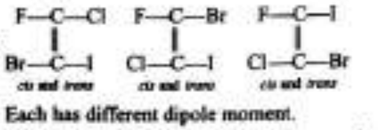
*R*CO is electron withdrawing group.

10. (d) Aliphatic amines are more basic.

11. (d) S_N2 reaction at an asymmetric carbon always leads to 100% inversion in molecule, *i.e.*, a stereoisomer.



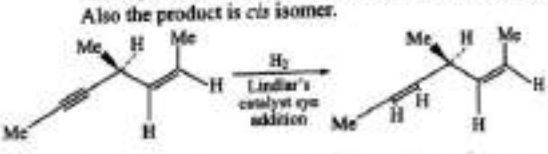
12. (d)



Each has different dipole moment.

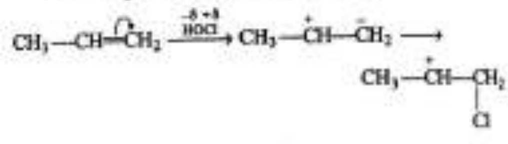
13. (c) In addition of HCl on alkene in presence of peroxide, the second step of chain propagation is endothermic whereas in HI, first step of chain propagation is endothermic.

14. (b) Lindlar's catalyst (Pd on $CaCO_3$ deactivated by lead acetate) is used to convert a triple bond to double bond. Also the product is *cis* isomer.



The product has a plane of symmetry and thus, is optically inactive.

15. (b) Addition is electrophilic in alkene and thus, Cl^+ being an electrophile attacks negative centre.



$$CH_3{-}CH{=}CH_2 \xrightarrow{\overset{-\delta\ +\delta}{HOCl}} CH_3{-}\overset{+}{C}H{-}\overset{-}{C}H_2 \longrightarrow CH_3{-}\overset{+}{C}H{-}\underset{\displaystyle Cl}{\underset{|}{C}H_2}$$

16. (c) $CH_3CH_2CH_2OH \xrightarrow{Cu,\ \Delta} CH_3CH_2CHO \xrightarrow{\text{Fehling sol.}}$

Red ppt.

$$CH_3CHOHCH_3 \xrightarrow{Cu,\ \Delta} CH_3COCH_3$$

17. (a) This is crossed Cannizzaro's reaction :

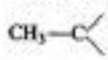
$$HCHO + C_6H_5CHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

18. (a) $(CH_3)_4N^+I^- \xrightarrow[\Delta,\ P]{NaOH} (CH_3)_4N^+OH + NaI$

$$\hookrightarrow (CH_3)_3N + CH_3OH$$

The reaction will be more spontaneous when it has the best leaving group, *i.e.*, I^-. Also methyl group with +ve *N* is more active due to +ve *IE* of CH_3 group.

19. (b) 2° amines are more basic than 1° amines due to +ve *IE* of $—CH_3$ group. In amide the resonance gives rise to less availability to electron pair for coordination and thus, it is less basic. The negative charge developed on N in



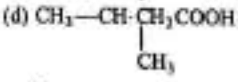
$$CH_3{-}C\begin{cases} NH \\ NH_2 \end{cases}$$

due to resonance makes it more basic.

20. (b) Br is less reactive and more selective and thus, formation of 3° free radical will be the major product.

21. (c) C_6H_6 ring is activated for S_E reaction by the +*I* effect as well as hyperconjugation of CH_3 gp. —Cl deactivates ring as −*I* effect predominates over + *M* effect. $—NO_2$ group deactivates ring by −*I* effect as well as by −*M* effect.

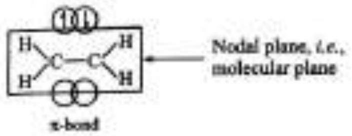
22. (d)



$$CH_3{-}CH{\cdot}\underset{\displaystyle CH_3}{\underset{|}{\overset{*}{C}H_2}}COOH;$$

$\overset{*}{C}$ is asymmetric or Chiral carbon.

23. (a) A π-bond has a nodal plane passing through the two bonded nuclei, *i.e.*, molecular plane.



24. (b) $CH_3C\equiv CCH_3$ is linear at $C\equiv C$ and symmetrical and thus, dipole moment is zero.

25. (d) Ammoniacal Cu_2Cl_2 gives red precipitate with terminal alkynes (1-butyne) only.

26. (b) $CH_3CH_2CH_2Br \xrightarrow[\text{Dehydrobromination } (-HBr)]{\text{NaOH (alc.)}} CH_3CH{=}CH_2$

$$\xrightarrow[\text{20°C Acc. to Markownikoff's rule}]{\text{HBr/acetic acid}} CH_3CHBr\cdot CH_3$$

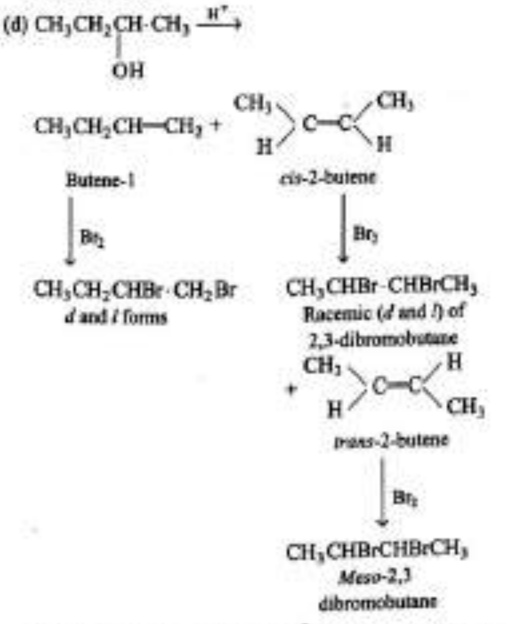
27. (b) More is the tendency for hydrogen bonding, higher will be the boiling point. In carboxylic acids H-bonding is more than alcohols.

28. (c) $BrCH_2CH_2COOH$ is the weakest acid and has lowest dissociation constant. $-I$ effect of Br is lesser than F and is far away from —COOH group.

29. (a) $CH_3CH_2\cdot CH_2OH \xrightarrow{[O]} CH_3CH_2CHO \xrightarrow{H_2NCONHNH_2}$
$CH_3CH_2CH{=}N\cdot NHCONH_2$

30. (a) The product will be optically active because the chiral carbon atoms of both the acid and alcohol retain their configuration.

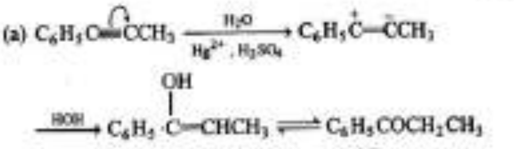
31. (d)



F has only three structures. $F \xrightarrow{Br_2}$ in all 5 compounds.

32. (a) $\underset{sp^2}{CH_2}{=}\underset{sp^2}{CH}{-}\underset{sp}{C}{\equiv}\underset{sp}{CH}$

33. (a)

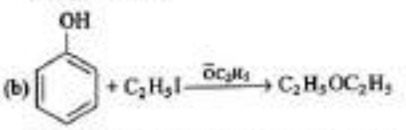


$$C_6H_5C\equiv CCH_3 \xrightarrow[Hg^{2+},\,H_2SO_4]{H_2O} C_6H_5\overset{+}{C}{-}\overset{-}{C}CH_3$$

$$\xrightarrow{HOH} C_6H_5\cdot\overset{OH}{\overset{|}{C}}{=}CHCH_3 \rightleftharpoons C_6H_5COCH_2CH_3$$

34. (a) $\mu_{CCl_4} = 0, \mu_{CHCl_3} = 1.0\text{ D}, \mu_{CH_2Cl_2} = 1.6\text{ D},$
$\mu_{CH_3Cl} = 1.86\text{ D}$

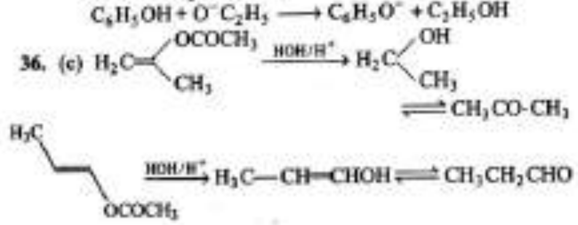
35. (b)



$C_2H_5O^-$ will abstract proton from phenol producing phenoxide ion. Now $C_6H_5O^-$ and $C_2H_5O^-$ (in excess) will try to attack methylene carbon of ethyl iodide. Since, $C_2H_5O^-$ is a better nucleophile and thus, it will succeed to give ether.

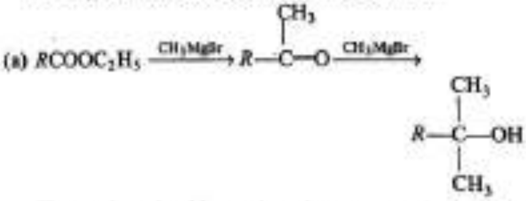
$C_6H_5OH + O^-C_2H_5 \longrightarrow C_6H_5O^- + C_2H_5OH$

36. (c)



Aldehyde formed will reduce Fehling solution.

37. (a)

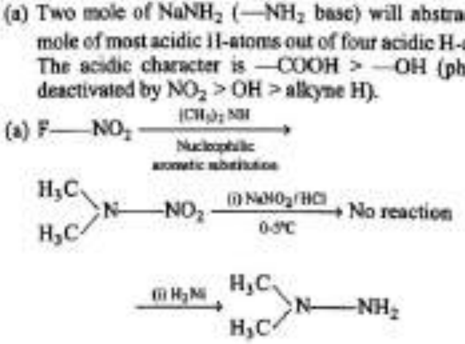


$$RCOOC_2H_5 \xrightarrow{CH_3MgBr} R{-}\overset{CH_3}{\overset{|}{C}}{=}O \xrightarrow{CH_3MgBr} R{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}OH$$

The product should contain at least two methyl groups and one OH group.

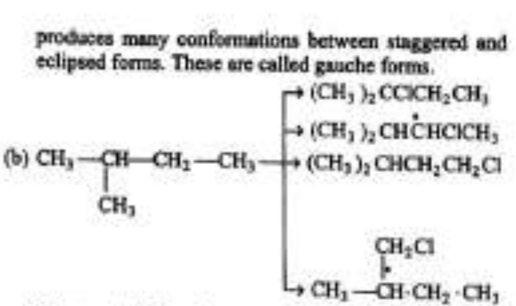
38. (a) Two mole of $NaNH_2$ ($-NH_2$ base) will abstract two mole of most acidic H-atoms out of four acidic H-atoms. The acidic character is —COOH > —OH (phenolic deactivated by NO_2 > OH > alkyne H).

39. (a)



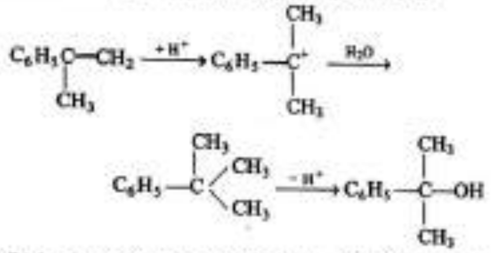
40. (d) The given molecule is the staggered form of compound. A rotation of 60° converts staggered conformation into an eclipsed conformation and *vice-versa*. Rotation between 0° to 60° and more than 60° but less than 120°

produces many conformations between staggered and eclipsed forms. These are called gauche forms.

41. (b) 

Thus, out of four isomers only two have chiral carbon atoms. Each has two isomer.

42. (c) The reaction proceeds *via* carbocation formation.



43. (d) Reduction of alkyne to alkene by Li—NH_3/C_2H_5OH is known as Birch reaction. The product formed is *trans*-hex-2-ene.

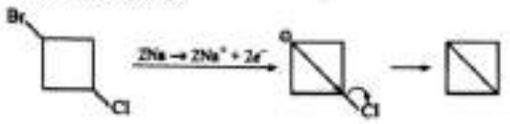
44. (d) $C_6H_5CONH_2 \xrightarrow[-H_2O]{POCl_3} C_6H_5CN$

45. (a) Electrophilic substitution involves the attack of electrophile on *o*- and *p*-position. The ring attached with NH has rich electron density. As ortho position is occupied, *p*-position is attached by Br^+.

46. (b) The ease with which any compound or group can lose H^+ is called acidic nature. Position of *X* is most acidic due to resonance stabilization of —COOH. (*Y*) is more acidic than (*Z*) due to $-I$ effect of —COOH group.

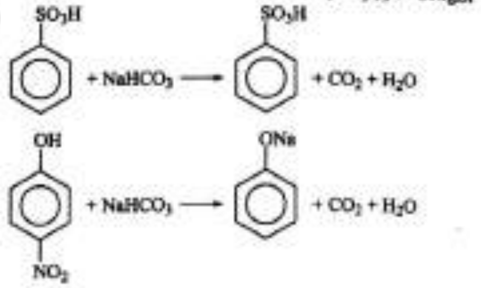
47. (c) The octet of all atoms are complete in structure of options (a) and (b). In structure of option (d) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure of option (c).

48. (d) This is a internal Wurtz's type reaction and the only obvious choice is :



49. (a) $(CH_3)_3C{\cdot}OH + C_6H_5MgBr \longrightarrow C_6H_6 + (CH_3)_3C{\cdot}OMgBr$

50. (d)



51. (c) Due to chelation in I and dipole moment.

52. (a) Follow Markownikoff addition (NO^+Cl^-).

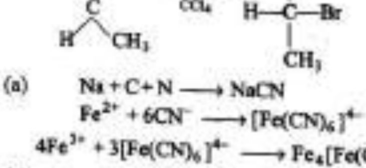
53. (d) Isocyanide test of carbylamine reaction.

54. (c) Follow IUPAC rule.

55. (b) Elimination of HBr by KOH gives less reactive vinyl bromide. To eliminate HBr from vinyl bromide strong base $NaNH_2$ is used.

56. (c) *n*-hexane, 2-methyl pentane, 3-methyl pentane, 2,3-dimethyl butane, 2,2-dimethyl butane.

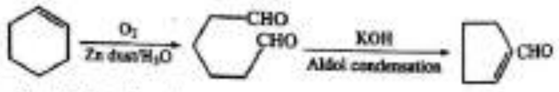
57. (a) Anti addition of Br_2 on *trans* alkene products *meso* compound.



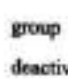
58. (a)

$$Na + C + N \longrightarrow NaCN$$
$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$
$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$$

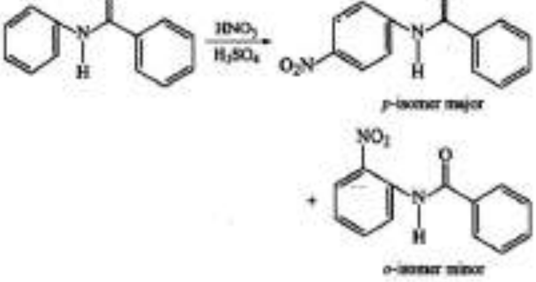
59. (a)



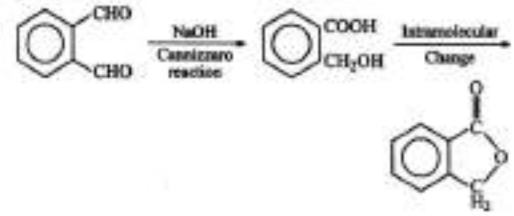
60. (a) Similar charge on nearest atoms give rise to lesser stability.

61. (b) —$\ddot{N}H$ group is *o*-, *p*- directing as well as an activating group whereas  $>C{=}O$ group is *m*-directing and deactivating. When two different nature groups are

present in benzene ring, the *o*-, *p*-directing group predominates.

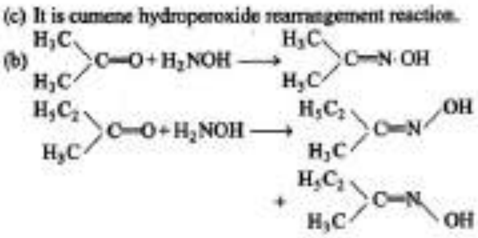


62. (c)



63. (c) It is cumene hydroperoxide rearrangement reaction.

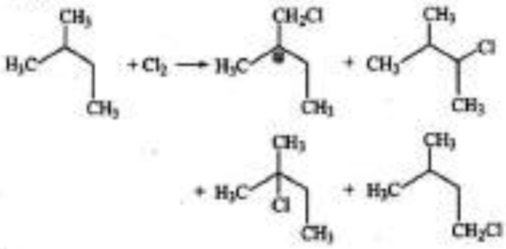
64. (b)



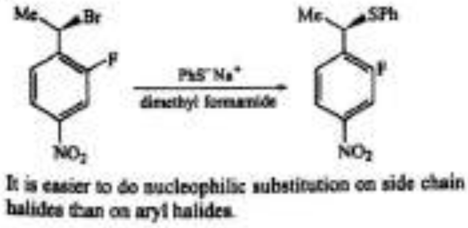
$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C{=}O + H_2NOH \longrightarrow \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C{=}N\cdot OH$$

$$\begin{matrix}H_5C_2\\H_3C\end{matrix}\!\!>\!C{=}O + H_2NOH \longrightarrow \begin{matrix}H_5C_2\\H_3C\end{matrix}\!\!>\!C{=}N\diagup OH + \begin{matrix}H_5C_2\\H_3C\end{matrix}\!\!>\!C{=}N\diagdown OH$$

65. (b)



66. (a)

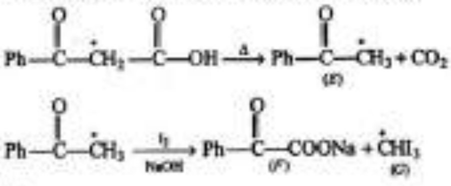


It is easier to do nucleophilic substitution on side chain halides than on aryl halides.

67. (b) Hyperconjugation involves $\sigma - p$ orbitals.

68. (a) Like cellulose which has β 1-4 glycosidic linkage.

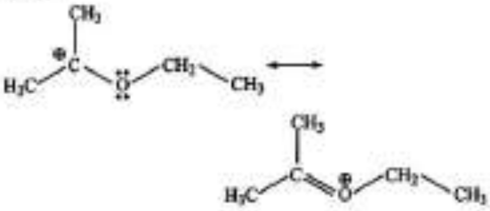
69. (c)



$$Ph{-}\overset{O}{\overset{\|}{C}}{-}\dot{C}H_2{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow{\Delta} Ph{-}\underset{(E)}{\overset{O}{\overset{\|}{C}}}{-}\dot{C}H_3 + CO_2$$

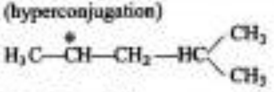
$$Ph{-}\overset{O}{\overset{\|}{C}}{-}\dot{C}H_3 \xrightarrow[NaOH]{I_2} Ph{-}\underset{(F)}{\overset{O}{\overset{\|}{C}}}{-}COONa + \underset{(G)}{\dot{C}HI_3}$$

70. (d) (i)



Stabilizes by resonance and have six α-hydrogen atoms (hyperconjugation)

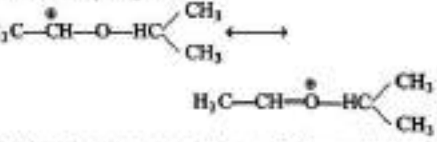
(ii)



$$H_3C{-}\overset{\oplus}{C}H{-}CH_2{-}HC\begin{matrix}CH_3\\CH_3\end{matrix}$$

Have five α-hydrogen atoms.

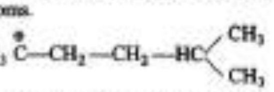
(iii)



$$H_3C{-}\overset{\oplus}{C}H{-}O{-}HC\begin{matrix}CH_3\\CH_3\end{matrix} \longleftrightarrow H_3C{-}CH{=}\overset{\oplus}{O}{-}HC\begin{matrix}CH_3\\CH_3\end{matrix}$$

Stabilizes by resonance and have only three α-hydrogen atoms.

(iv)



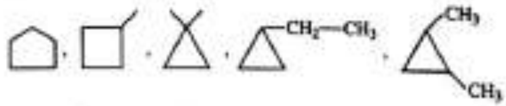
$$H_3\overset{\oplus}{C}{-}CH_2{-}CH_2{-}HC\begin{matrix}CH_3\\CH_3\end{matrix}$$

Have only two α-hydrogen atoms.

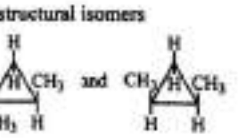
71. (d) Due to H^- shift from C_2 to C_3. Driving force is conjugation from oxygen. Also bulky gp. hinders in hydride shift.

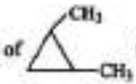
72. (b) Stability of cononical form ∝ negative formal charge on more electronegative atom ∝ minimum distance between unlike charges.

73. (d)



are five structural isomers



are geometrical isomers of  thus, is all six.

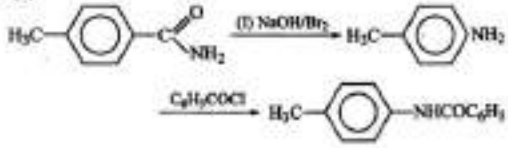
74. (d) Natural rubber involves weak van der Waals' forces.

75. (b) Priority order is CN > ON > Br.

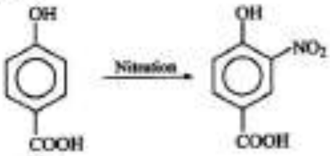
76. (a) Electron repelling gp. decreases the strength of aromatic carboxylic acid and phenol.

Benzoic acid	*p*-methyl benzoic acid
C_6H_5COOH	1.26×10^{-5}
$K_a: 6.76 \times 10^{-5}$	
Phenol	*p*-chlorophenol
1.05×10^{-10}	4.16×10^{-10}

77. (c)

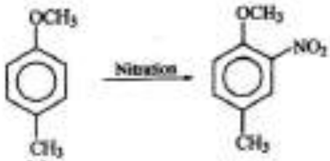


78. (c)



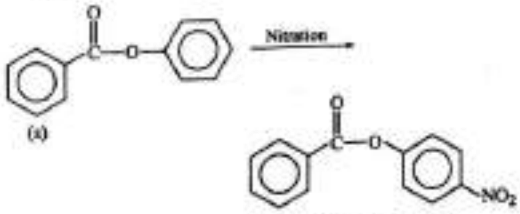
[NO_2 attacks at *o*-, *p*- with respect to OH]

(p)



[NO_2 attacks at *o*-, *p*- with respect to CH_3 and OCH_3 both]

(q)



[NO_2^+ attacks at *o*-, *p*- with respect to $—OCOC_6H_5$]

79. (c) It is the formula of EDTA.

80. (d) $CH_3 \cdot CH_2 \cdot C{\equiv}CH + NaNH_2 \rightarrow CH_3CH_2 \cdot C{\equiv}C^-Na^+$

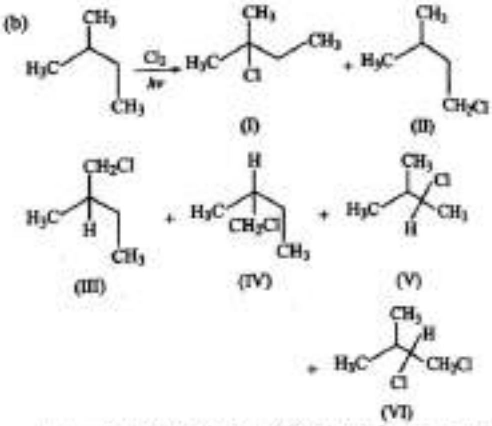
$CH_3CH_2CH_2CH_2Br$

$\underset{\text{Octyne-3}}{CH_3CH_2 \cdot C{\equiv}C—CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3} \leftarrow$

81. (a) These are facts.

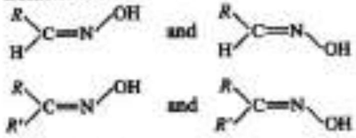
82. (d) 

83. (b)

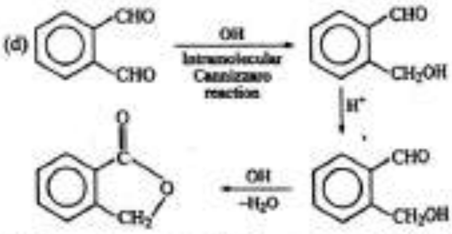


In these (iii) + (iv) and (v) + (vi) are enantiomers to each other. Thus total six isomers will be possible for *N*. In these only four isomers will be obtained on fractional distillation without resolution because enantiomers cannot be separated by fractional distillation, Hence $N = 6, M = 4$

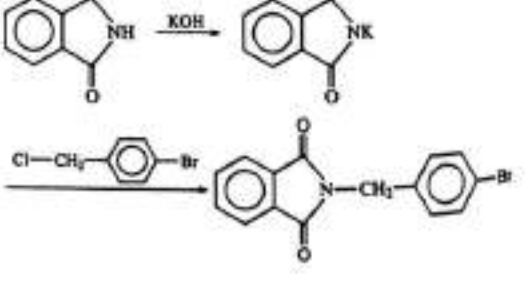
84. (c) An aldehyde and a unsymmetrical ketone form two isomeric oxime



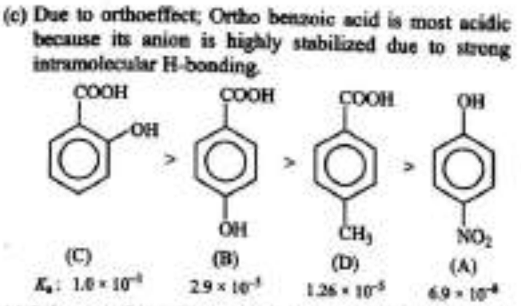
85. (d)



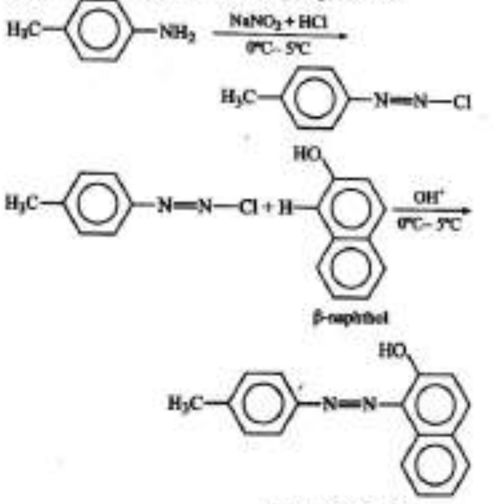
86. (a) The replacement of Cl is due to the formation of stable benzyl carbocation. Alternatively Cl is present in side chain and thus replaced whereas Br is attached in benzene nucleus.



87. (c) Due to orthoeffect; Ortho benzoic acid is most acidic because its anion is highly stabilized due to strong intramolecular H-bonding.

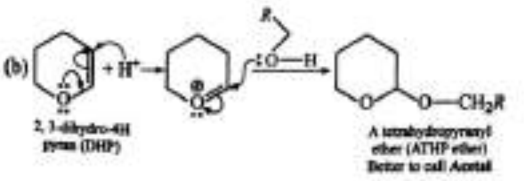


88. (c) It is a test for $-NH_2$ gp. attached on benzene nucleus following diazotisation and coupling reaction.



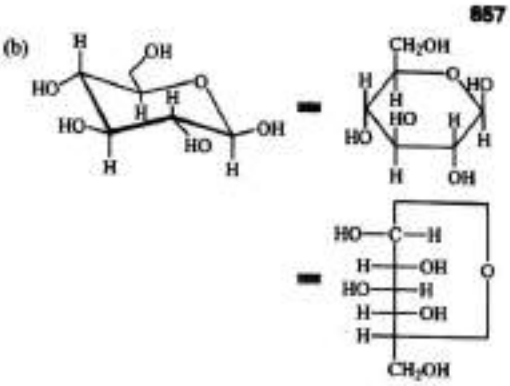
Brilliant Colour Dye

89. (b)



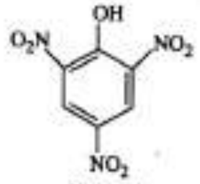
Note : Because of its special structure, there are two ether oxygen attached to same carbon, making it acetal.

90. (b)

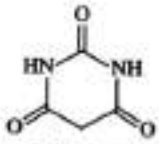


In β-D glucopyranose all the OH groups and CH_2OH group occupy equatorial position in the most stable conformer.

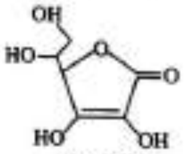
91. (d) Aspirin is acetyl salicylic acid.



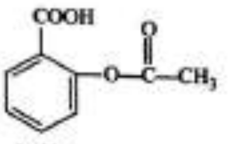
Picric acid



Barbituric acid



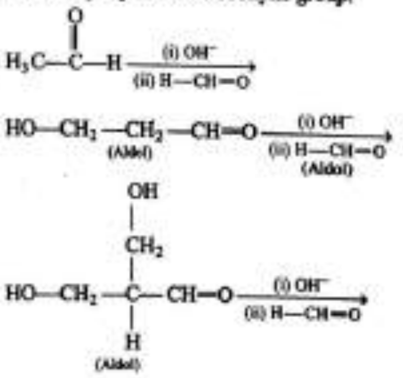
Ascorbic acid



Aspirin

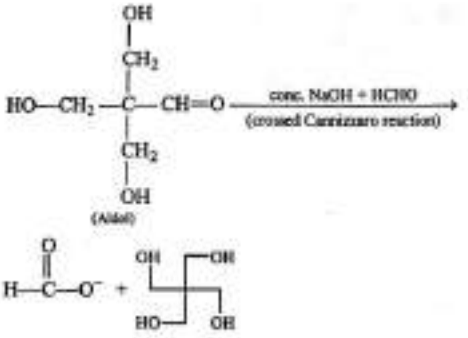
Thus, only aspirin has carboxylic group.

92. (c)

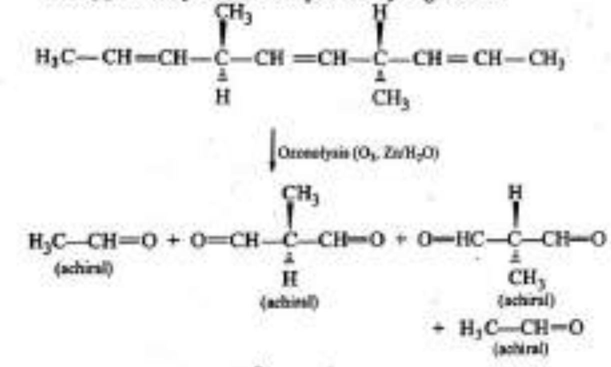


$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{(ii) } H-CH=O]{\text{(i) } OH^-} \underset{\text{(Aldol)}}{HO-CH_2-CH_2-CH=O} \xrightarrow[\substack{\text{(ii) } H-CH=O \\ \text{(Aldol)}}]{\text{(i) } OH^-}$$

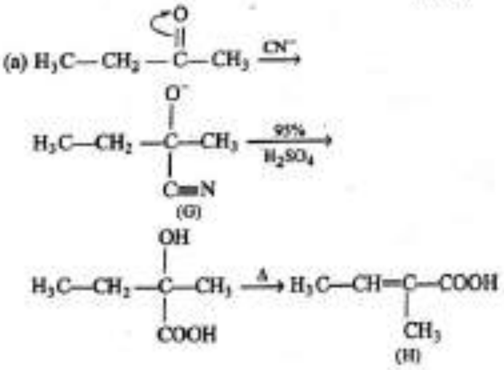
$$\underset{\text{(Aldol)}}{HO-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{\overset{\displaystyle CH_2}{|}}}{C}-CH=O} \xrightarrow[\text{(ii) } H-CH=O]{\text{(i) } OH^-}$$



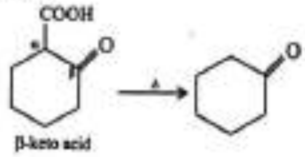
93. (a) Ozonolysis of the compound may be given as:



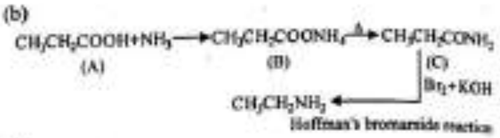
94. (a)



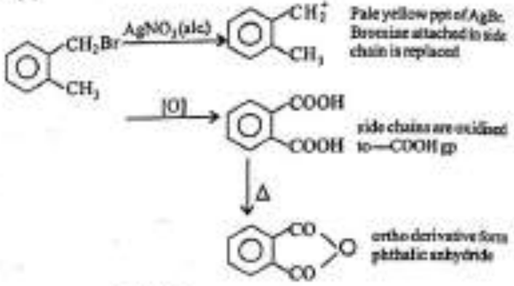
95. (b) β-keto acids undergo decarboxylation most easily on heating.



96. (b)



97. (b)



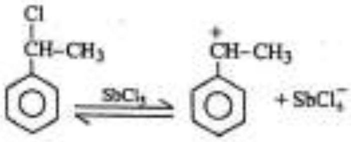
98. (d) $-NH_2 \xrightarrow[-HCl]{CH_3COCl} -NHCOCH_3$

Presence of one $-NH_2$ shows an increase of molar mass by 42 units (one $CH_3CO - 1H$)

Total increase 210 unit

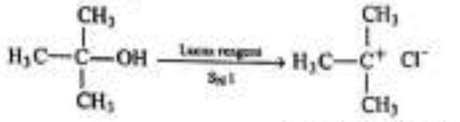
$\therefore$ No. of $-NH_2$ gps in molecules $= \frac{210}{42} = 5$

99. (a)



(The attack on this carbocation takes place from either side and thus recemisation occures)

100. (d)



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH \xrightarrow[S_N1]{\text{Lucas reagent}} H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}}\ Cl^-$$

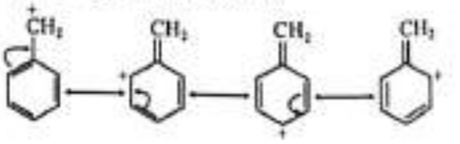
(most stable 3° carbocation)

101. (a) p-nitrophenol is strongest acid among all

102. (b) More is the no. of canonical forms, more is stability

$CH_2=CH-CH_2^+ \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$

$CH_3\cdot CH_2\cdot CH_2^+$ has no resonance



103. (c)

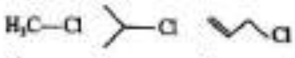
$$12NADP + 18ADP + 12H_2O \xrightarrow{h\nu} 18ATP + 12NADPH + 6O_2$$

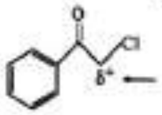
$$6CO_2 + 12NADPH + 18ATP \xrightarrow{dark} C_6H_{12}O_6 + 12NADP + 18ADP + 6H_2O$$

Net reaction $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$

One carbon atom of glucose requires 3ATP for its synthesis in photosynthesis.

104. (b)



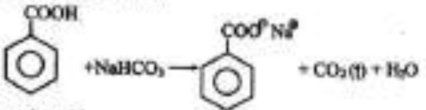


more charge as a result of – I.E. of Cl due to electron withdrawing nature of Cl as well as $>C=O$ group stabilises its transition state.

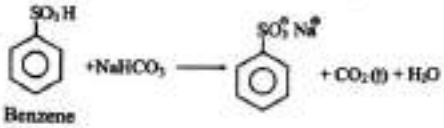
$$\text{Rate of } S_N2 \propto \frac{1}{\text{steric hendrance}}$$
$$\propto \delta^+ \text{ charge on carbon}$$
$$\propto \text{Stability of transition state}$$

So, $S > P > R > Q$

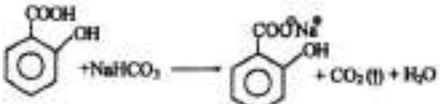
105. (d) Organic molecules having —COOH group liberate CO_2 with $NaHCO_3$ solution



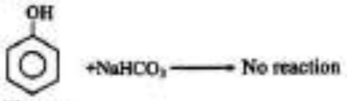
Benzoic acid



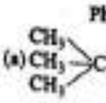
Benzene Sulphonic acid



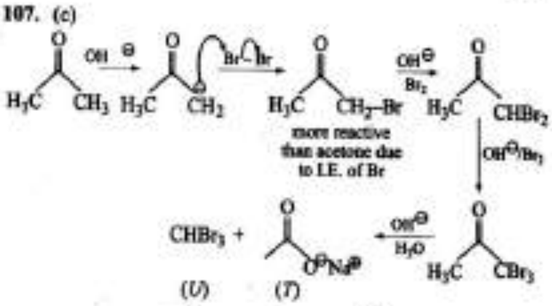
Salicylic acid

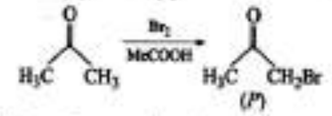


Phenol

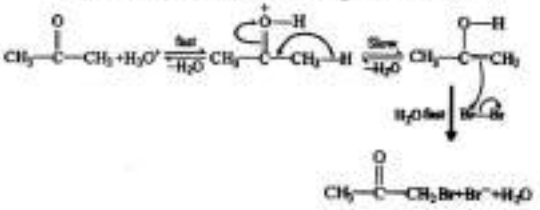
106. (a)  $(CH_3)_3C^+$; Carbon showing sp^2 hybridisation has one p orbital vacant. Thus $\sigma - p$ empty orbital hyperconjugation. $CH_3—CH=CH—CH_3$; The hyperconjugation involves σ of CH_3 gp and π bond of its nearest C *i.e.* $\sigma - \pi^*$ electron delocalization.

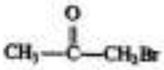
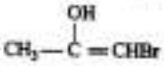
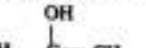
107. (c)



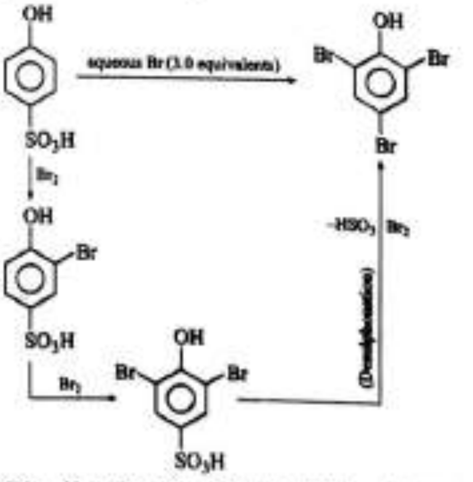


In acidic medium reaction takes place via enol form



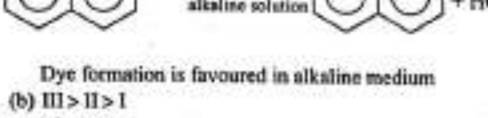
The enol form of  $CH_3—\overset{\overset{O}{\|}}{C}—CH_2Br$ *i.e.*,  $CH_3—\overset{\overset{OH}{|}}{C}=CHBr$ is less reactive than enol form of CH_3COCH_3 *i.e.*,  $CH_3—\overset{\overset{OH}{|}}{C}=CH_2$ and thus only monosubstitution takes place at α – C.

108. (b)



109. (c) $CH_3—N=C=O$ (methyl isocyanate) was leaked.

110. (d)

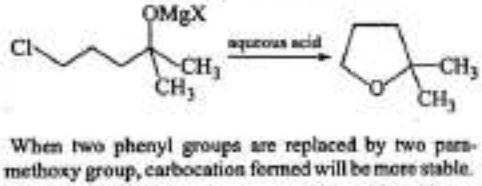


Dye formation is favoured in alkaline medium

111. (b) III > II > I

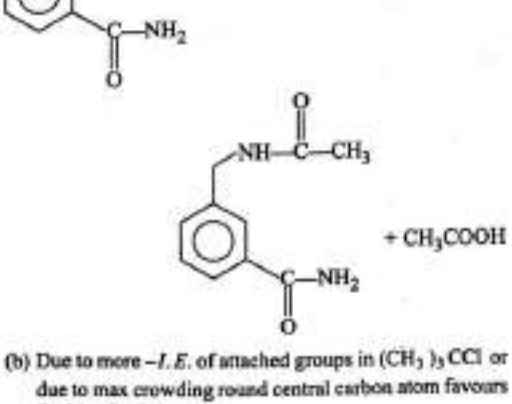
More the branching in an alkane, lesser will be the surface area, as the shape approaches to spherical, leading to decrease in van der Waals' forces. Therefore lesser will be the boiling point.

112. (d)



113. (c) When two phenyl groups are replaced by two para-methoxy group, carbocation formed will be more stable.

114. (a) Amino gp. $(-NH_2)$ undergo acetylation and amide gp. $(-CONH_2)$ does not undergo acylation therefore acetic anhydride shows acetylation with amino gp.



115. (b) Due to more $-I.E.$ of attached groups in $(CH_3)_3CCl$ or due to max crowding round central carbon atom favours S_N1 mechanism.

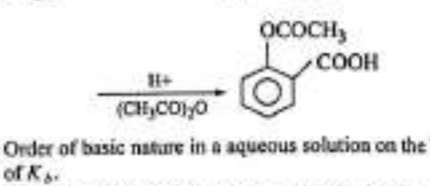
116. (d) This is carbylamine reaction

$$RNH_2 + CHCl_3 + 3KOH(alc.) \longrightarrow \underset{\text{unpleasant smell}}{RNC} + 3KCl + 2H_2O$$

117. (d) PCC is milder oxidant and oxidises alcohol to aldehyde only.

118. (c) $CH_3{\cdot}CCl_3 + Cl_3C{\cdot}CH_3 \xrightarrow{\text{Ag powder}} CH_3C \equiv CCH_3$

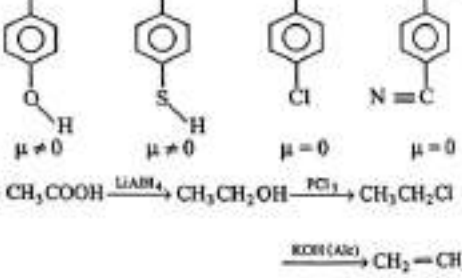
119. (a)



120. (a) Order of basic nature in a aqueous solution on the basis of K_b.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$

121. (d)



122. (c) $CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl$

$$\xrightarrow{KOH(Alc)} CH_2 = CH_2$$

123. (b) Meq. of acid (H_2SO_4) taken $= \frac{1}{10} \times 2 \times 60 = 12$

Meq. of acid used by NaOH = Meq. of NaOH $= \frac{1}{10} \times 20 = 2$

$\therefore$ Meq. of acid used by $NH_3 = 12 - 2 = 10 =$ Meq. of NH_3

$$\% \text{ of N} = \frac{\text{Meq. of } NH_3 \times 1.4}{\text{Mass. of organic compound}} = \frac{10 \times 1.4}{1.4} = 10$$

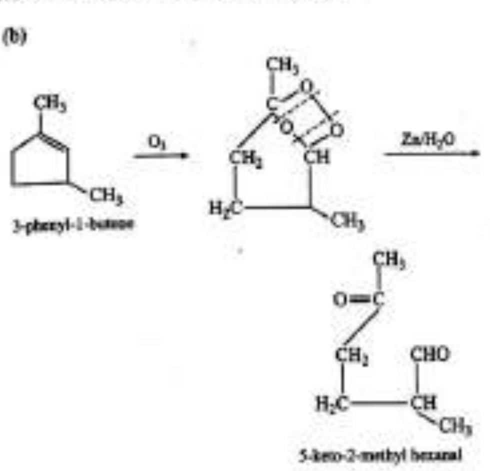
124. (a)
$$\%Br = \frac{\text{At. mass of Br}}{\text{Molar mass of AgBr}} \times \frac{\text{mass of AgBr}}{\text{mass of organic compound}} \times 100$$

$$= \frac{80}{188} \times \frac{141}{250} \times 100 = 24\%$$

125. (a) $\begin{matrix} C_{ab} \\ \| \\ C_{ab} \end{matrix}$ type molecules show geometrical isomerism.

Cis   Trans

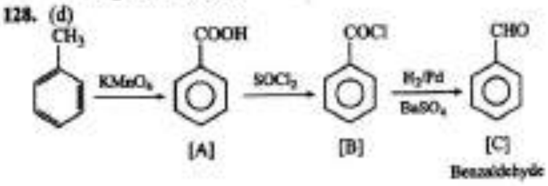
126. (b)



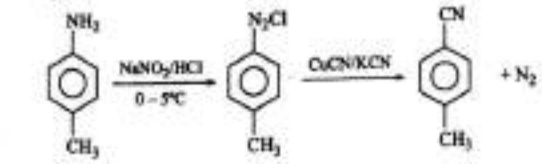
127. (d) $R-I + AgF \longrightarrow R-F + AgI$

This is Swart's reaction to prepare alkyl fluorides more conveniently by heating chloro or bromo alkane with inorganic fluorides.

128. (d)



129. (c)

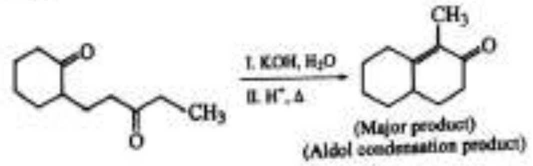


130. (b) Glyptal is used in the manufacture of paints and lacquers.

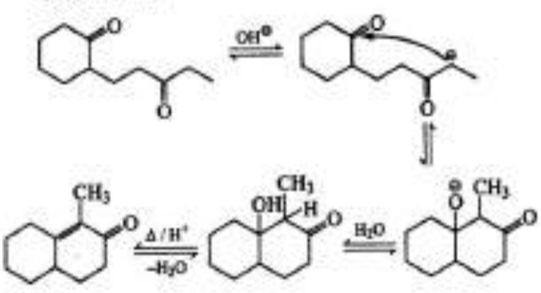
131. (a) Vitamins 'B' and 'C' are water soluble. Vitamins A, D, E, K are water insoluble.

132. (c) Phenelzine is antidepressent (a tranquilizer) and not antacid. Rest all are antacids.

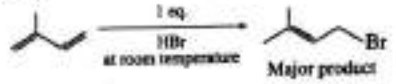
133. (a)



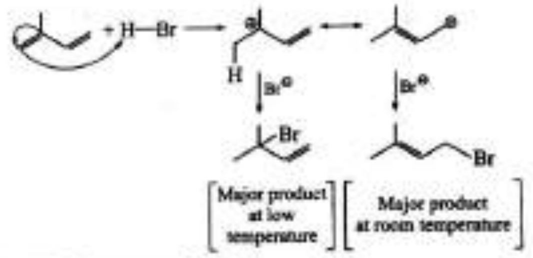
Mechanism :



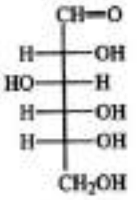
134. (d)



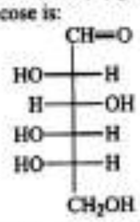
Mechanism :



135. (a) The structure of $D(+)$-glucose is:



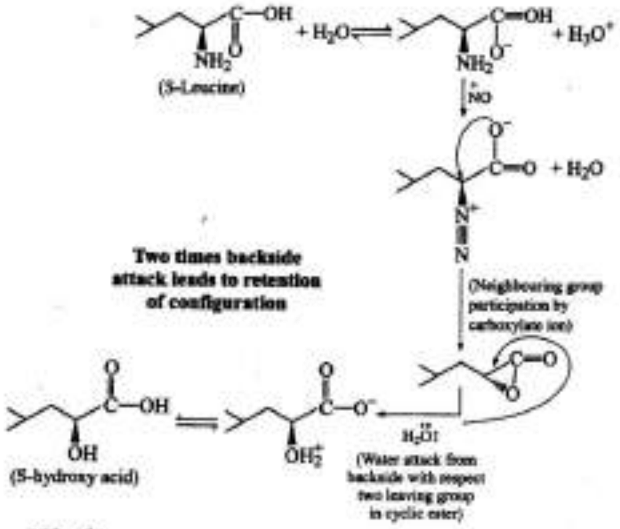
The structure of $L(-)$ glucose which is enantiomer of $D(+)$-glucose is:



136. (c) $NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

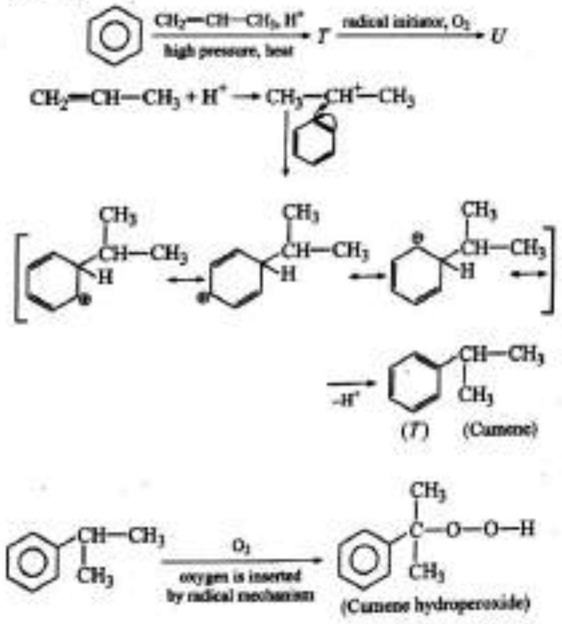
$HNO_2 + HCl \rightleftharpoons H_2\overset{\oplus}{O}NO + Cl^-$

$H_2\overset{\oplus}{O}NO \longrightarrow H_2O + NO^+$



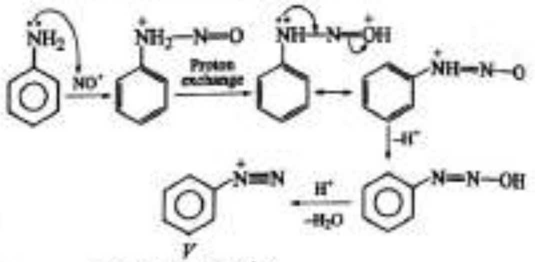
Two times backside attack leads to retention of configuration

137. (b)



138. (a) $NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

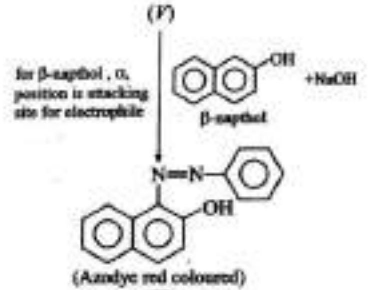
$HNO_2 + HCl \rightleftharpoons H_2NO_2^+ + Cl^-$



Benzenediazonium ion

$H_2NO_2^+ \longrightarrow H_2O + NO^+$

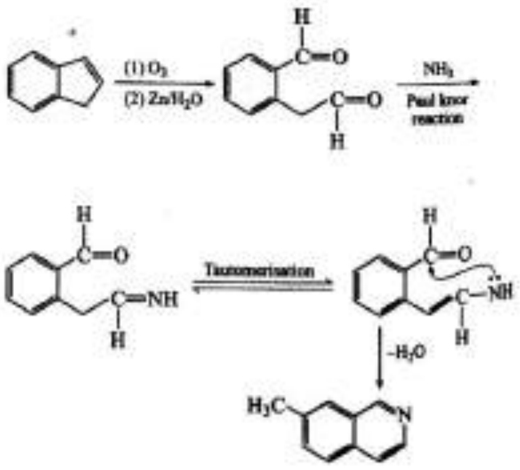
(V)



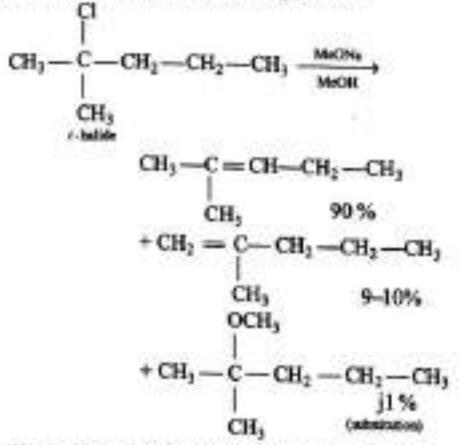
(Azodye red coloured)
(W)

The formation of V is example of diazotisation reaction. The formation of W from V is example of diazocoupling reaction.

139. (a)



140. (d) *t*-halides predominantly show E_2 reactions



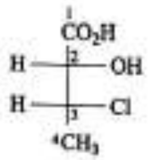
Elimination reactions predominate over substitution and thus all the products are possible.

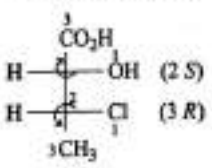
141. (c) Buckets, dustbins are manufactured by high density polythene.

142. (c) Glycerol being high boiling point liquid (290°C) is made to boil at lower temperature by lowering pressure on its surface, *i.e.*, at reduced pressure. Glycerol is therefore separated from spent-lye by distillation under reduced pressure without decomposition. Note that glycerol decomposes at its boiling point.

143. (a) Carbon number 2 and 3 are chiral. On 2nd carbon two vertical positions are attached with carbon ($CHClCH_3$ and COOH) and horizontal position with OH and H. O has high priority than H.

On 3rd carbon two vertical position are attached with carbon [CHOH(COOH) and CH_3] and horizontal positions with H and Cl. Cl has high priority than H.





(2nd carbon seems to be *R* but H on horizontal position and thus *S*)

(3rd carbon seems to be *S* but H on horizontal position and thus *R*)

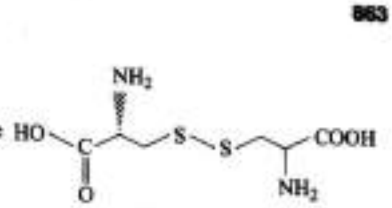
144. (b) Highest concentration of nitrate (100 ppm) is reported.

	International standard Beuro	NCERT
Lead	15 ppb	50 ppb
Nitrate	50 ppm	50 ppm

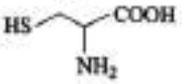
Note : Again there may be two answers according to ISB of environmental pollution.

145. (b)

Cystine

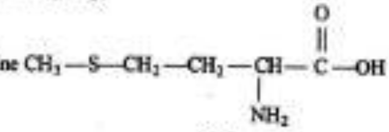


Cysteine



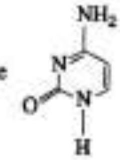
(— SH is thiol group)

Methionine

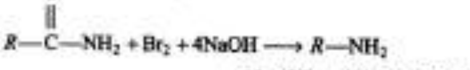


$$CH_3-S-CH_2-CH_2-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$$

Cytosine

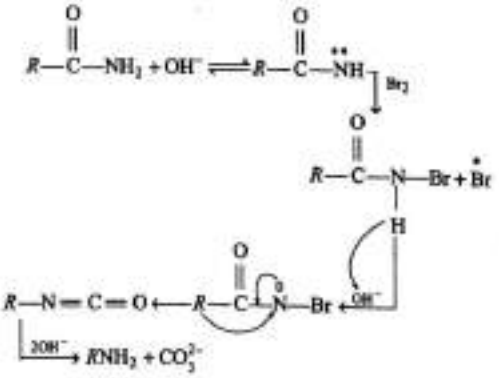


146. (c) Hofmann bromamide degradation reaction.



$$R-\overset{\overset{O}{\|}}{C}-NH_2+Br_2+4NaOH\longrightarrow R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

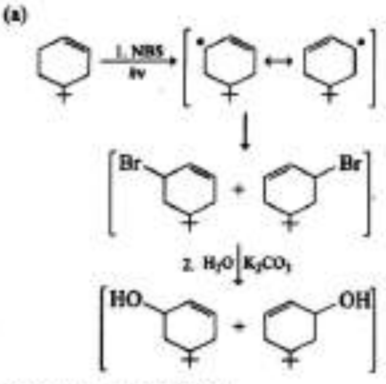
1 mole bromine and 4 moles of NaOH are used for one mole of amine produced.



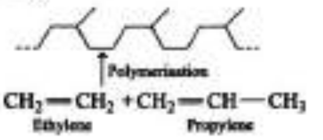
147. (a) The reaction proceeds through formation of carbonium ion

$$CH_3-CH^+-CH_2-Cl$$

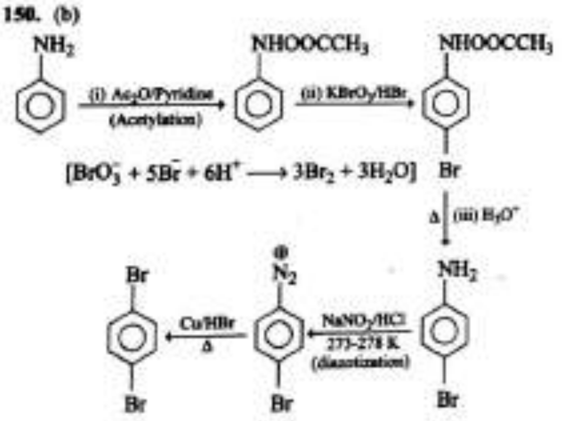
148. (a)



149. (a) Natural rubber $\xrightarrow{H_2/Ni}$

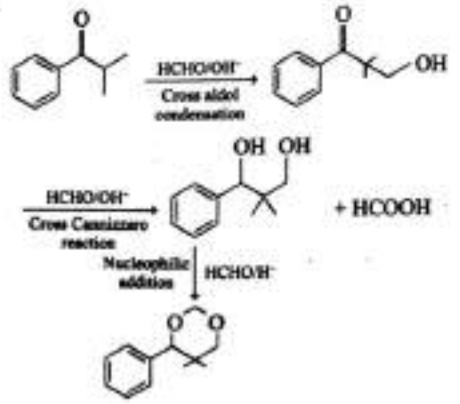


150. (b)

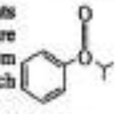


$[BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O]$

151. (a)



or choices (b) and (c) represents hemiacetals (O—C—OH) and are unstable. Choice (d) can be formed from only when it undergoes Gatterman-Koch reaction if aromatic ring is electron rich.

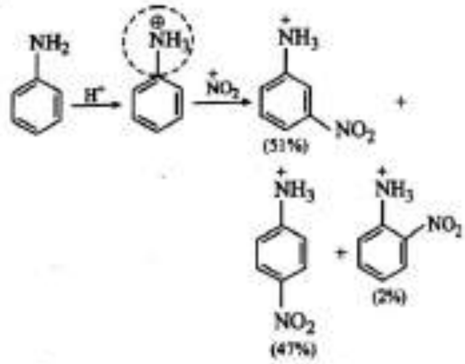


152. (a) *Ortho* substituted benzoic acid is more acidic than *meta* and *para* isomers due to *ortho* effect.

or

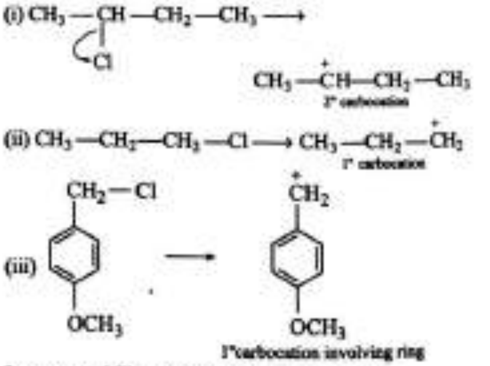
Conjugate base of *ortho* hydroxybenzoic acid is more acidic than its *meta* and *para* isomers due to strong H-bonding.

153. (c)



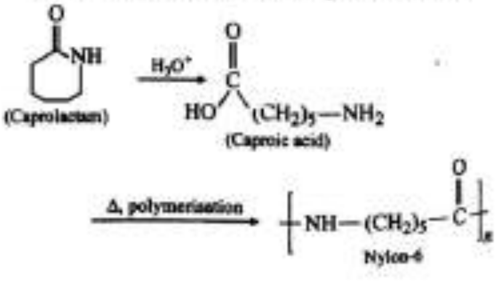
NH_3^+ is *meta* directing gp. and deactivating gp.

154. (b) Rate of S_{N^1} reaction = stability of carbocation



Increase stability of carbocation is II < I< III.

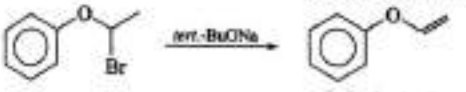
155. (a) Caprolactam is hydrolysed to produce caproic acid which undergoes condensation to produce Nylon-6.



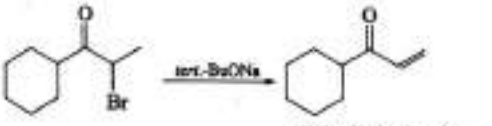
156. (a)

(fails to decolourise the colour of bromine)

(it decolourises bromine solution due to unsaturation)

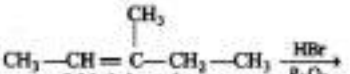


(it decolourises bromine solution due to unsaturation)

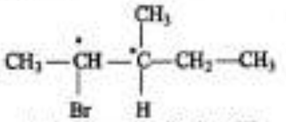


(it decolourises bromine solution due to unsaturation)

157. (d)



$$\underset{\text{3-Methylpent-2-ene}}{CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3}\xrightarrow[R_2O_2]{HBr}$$

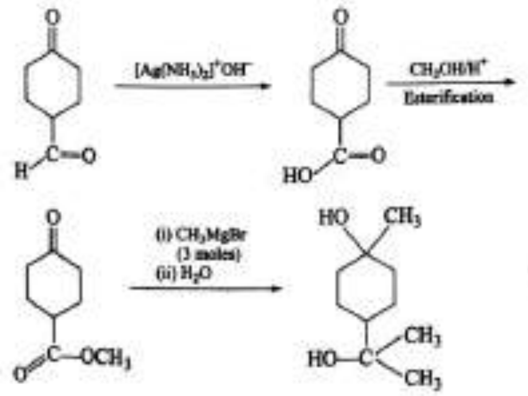


$$CH_3-\underset{\underset{Br}{|}}{\overset{\bullet}{C}H}-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{\overset{*}{C}}}-CH_2-CH_3$$

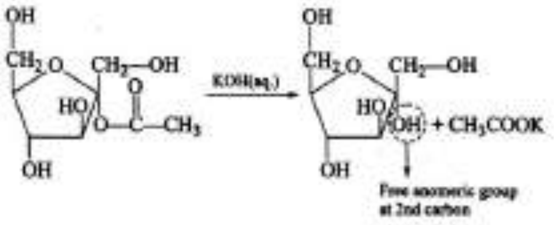
Antimarkownikov Product (X)

Product (X) contains two chiral centres* and unsymmetrical. Thus, total stereoisomers = $2^2 = 4$.

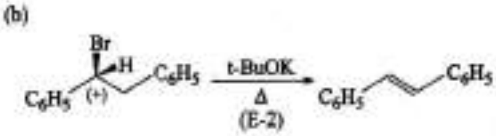
158. (a)



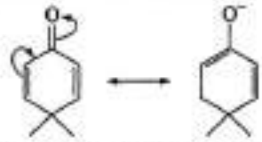
159. (a) Sugars having free anomeric — OH group are reducing sugars.



160. (b)

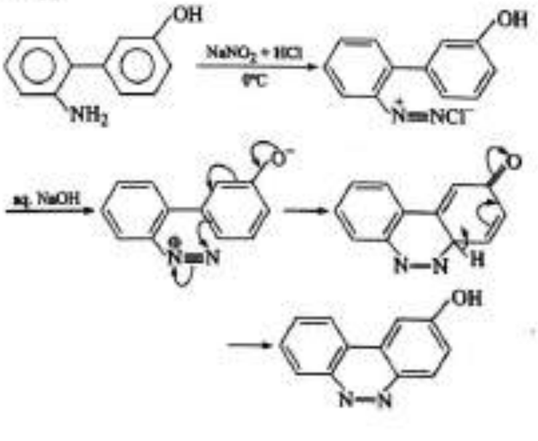


161. (d) All are stabilized by resonance. First three being aromatic are more stabilized. The fourth one being non-aromatic is least stabilized.

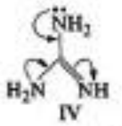


162. (b) DIBAL—H is a reducing agent and reduces cyanide, esters, amides, lactones, esters and carboxylic acids into corresponding aldehydes.

163. (c)

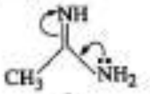


164. (d)



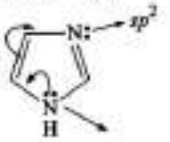
IV

Resonance with two $-\ddot{N}H_2$ groups increases electron density on '*N*' of $=NH$



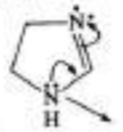
I

Lesser increase of electron density on $=NH$ due to only one resonance with one $-NH_2$



III

The lone pair of electron of NH is used in aromatic sextet and thus least basic.



II

The lone pair of electron of NH is not involve in aromaticity. So more available also, 'N' is bonded to sp^3 C on one side.

$\therefore$ IV > I > II > III

OBJECTIVE PROBLEMS (More Than One Answer Correct)

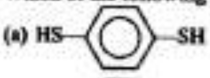
1. Select the correct statements :
   (a) A compound having enantiomers must be chiral
   (b) A compound having enantiomers must have chiral centres
   (c) Mirror image molecules are always enantiomers
   (d) 2,3-pentadiene has two enantiomers

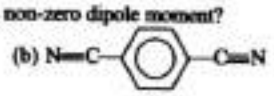
2. Select the correct statements :
   (a) All asymmetric carbons are stereocentres
   (b) A compound with open chain structure is chiral if it has no plane of symmetry
   (c) A molecule containing chiral centres must be chiral
   (d) Prefix D-refers for dextrotatory nature of compound

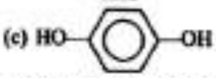
3. In *sp*-hybridization of carbon, if $2s$ and $2p_x$ undergo hybridization, then the two *sp*-orbitals :
   (a) are perpendicular to p_y (b) are perpendicular to p_z
   (c) are perpendicular to p_x (d) are at 120° to p_y and p_z

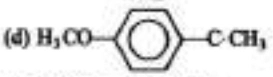
4. Select the electrophiles :
   (a) $\ddot{N}F_3$ (b) PCl_3 (c) CCl_4 (d) $\ddot{C}Cl_2$

5. Which of the following has non-zero dipole moment?

(a)


(b)


(c)


(d)


6. Which of the following represents the correct order ?
   (a) Stability : $\overset{+}{C}H_3 > CH_3-\overset{+}{C}H_2 < CH_3-\overset{+}{C}H-CH_3$ $< (CH_3)_3\overset{+}{C}$
   (b) Stability : $\overset{\bullet}{C}H_3 < CH_3-\overset{\bullet}{C}H_2 < CH_3-\overset{\bullet}{C}H-CH_3$ $< (CH_3)_3\overset{\bullet}{C}$
   (c) Hyperconjugation : $CH_3- < CH_3-CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
   (d) Basic nature : $\bar{C}H_3 > N\bar{H}_2 > \bar{O}H > \bar{F}$

7. Which of the following represents the correct order ?
   (a) $+I$ effect : $CH_3- < CH_3-CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
   (b) $-I$ effect : $NO_2 > SO_3H > F > NH_2$
   (c) Stability : Allyl carbocation > vinyl carbocation
   (d) Stability : $CH\equiv\bar{C} < CH_3-C\equiv\bar{C} < CH_2=\bar{C}H$ $< CH_3-\bar{C}H_2$

8. Which are not the correct orders for C—Cl bond length in?
   I. CH_3-CH_2-Cl II. $CH_2=CH-Cl$
   III. C_6H_5-Cl
   (a) I > III > II (b) I > II > III
   (c) III > I > II (d) III > II > I

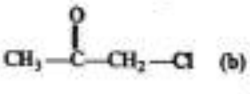
9. Which of the following are correctly shown for conjugated compounds :
   (a) Stability of conjugated compounds ∝ No. of resonating structures
   (b) Bond energy of conjugated compounds ∝ No. of resonating structures
   (c) Bond length of a functional group $\propto \frac{1}{\text{Bond strength}}$
   (d) Reactivity of a functional group due to breaking of bond $\propto \frac{1}{\text{No. of resonating structures}}$

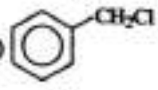
10. Which of the following are correct for N-compounds?
    (a) Basic nature ∝ stability of cation
    (b) Stability of cation ∝ degree of solvation
    (c) Basic nature ∝ degree of solvation
    (d) Basic nature $\propto \frac{1}{\text{electronegativity of N}}$

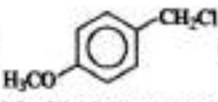
11. Select the correct statements :
    (a) Carbocations are electrophiles
    (b) Carbocation is diamagnetic in nature
    (c) Triphenyl methyl carbocation in propeller in shape
    (d) Carbocation are trigonal planar

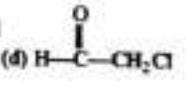
12. Which hybridizations are present in pyrolle :
    (a) sp (b) sp^2
    (c) sp^3 (d) sp^3d

13. Which of the following will not show S_N1 reactions ?

(a)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-Cl$

(b)


(c)


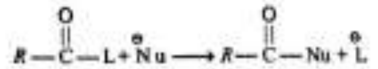
(d)

$H-\overset{O}{\overset{\|}{C}}-CH_2Cl$

14. Which of the following will give S_N reactions ?
    (a) $R-NH_2$ (b) $R-OH$
    (c) $R-N_3$ (d) $R-Br$

15. Which of the following on subjecting for S_N2 reaction will show Walden inversion ?
    (a) CH_3CHDBr (b) CH_3CH_2Br
    (c) $C_6H_5CH_2Br$ (d) $C_2H_5-CHDBr$

16. Which of the following reactions do not represent trans-esterification?
    (a) $C_6H_5COOC_2H_5 + NaOH \longrightarrow C_6H_5COONa + C_2H_5OH$
    (b) $C_6H_5COOC_2H_5 + H_2O \longrightarrow C_6H_5COOH + C_2H_5OH$
    (c) $C_6H_5COOC_2H_5 + CH_3OH \longrightarrow C_6H_5COOCH_3 + C_2H_5OH$
    (d) $C_6H_5COCl + CH_3OH \longrightarrow C_6H_5COOCH_3$

17. Which statements are correct for the given reaction, if it takes place?



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-L+\overset{\ominus}{N}u \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Nu+\overset{\ominus}{L}$$

(a) Basic nature of $\overset{\ominus}{Nu}$ should be greater than $\overset{\ominus}{L}$

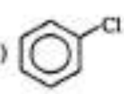
(b) Basic nature of $\overset{\ominus}{L}$ should be greater than $\overset{\ominus}{Nu}$

(c) Acyl carbon is nucleophile

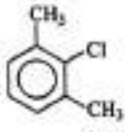
(d) Acyl carbon is electrophile

18. Which of the following will not give reaction according to benzyne mechanism on treating with KNH_2/NH_3?

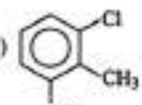
(a)



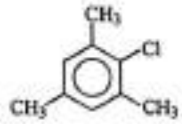
(b)



(c)

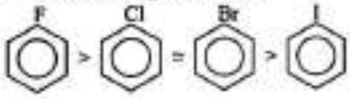


(d)



19. The correct orders of reactivity are represented in :

(a) Halobenzenes S_N reactions :



(b) Activating nature of groups in benzene :
$-NH_2 > -OH > -CH_3 > -Cl$

(c) Reactivity following S_N2 :
$R-I > R-Br > R-Cl > R-F$

(d) Reactivity following S_N1:
$RI > RBr > RCl > RF$

20. Which of the following will give alkene ?

(a) $CH_3-CHBr-CHBr\cdot CH_3 \xrightarrow{NaI/Acetone}$

(b) $CH_3\cdot CHBr\cdot CHBr\cdot CH_3 \xrightarrow{Zn/CH_3COOH}$

(c) $CH_3\cdot CHBr-CH_2\cdot CH_3 \xrightarrow{NaI/Acetone}$

(d) $CH_3CHBr\cdot CH_2CH_3 \xrightarrow{KOH\ alc.}$

21. Select the correct statements :

(a) According to Markownikoff's rule—"Richer becomes richer".

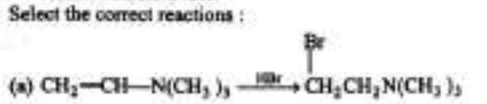
(b) Markownikoff's rule can be used for addition of unsymmetrical alkenes.

(c) Markownikoff's rule can be used if substituents present on doubly bonded carbons have +*I* groups.

(d) Addition of HCl on $C_6H_5-CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ follows Markownikoff's rule.

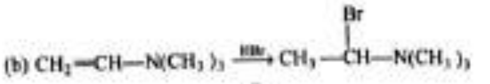
22. Select the correct reactions :

(a)



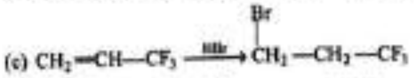
$$CH_2=CH-N(CH_3)_3 \xrightarrow{HBr} \overset{\overset{\displaystyle Br}{|}}{C}H_2CH_2N(CH_3)_3$$

(b)



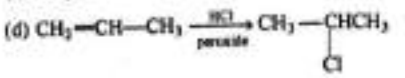
$$CH_2=CH-N(CH_3)_3 \xrightarrow{HBr} CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-N(CH_3)_3$$

(c)



$$CH_2=CH-CF_3 \xrightarrow{HBr} \overset{\overset{\displaystyle Br}{|}}{C}H_2-CH_2-CF_3$$

(d)



$$CH_2=CH-CH_3 \xrightarrow[peroxide]{HCl} CH_3-\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3$$

23. Select the correct statements about : $CH_3CH=CH_2 \xrightarrow[NaCl]{Br_2}$

(a) $CH_3\cdot CHCl\cdot CH_2Br$ is major product and $CH_3CHBr\cdot CH_2Br$ is minor product

(b) $CH_3\cdot CHCl\cdot CH_2Br$ is minor product and $CH_3CHBr\cdot CH_2Br$ is major product

(c) Formation of cyclobromium cation takes place as an intermediate

(d) Formation of cyclochloronium cation takes place as an intermediate

24. Which statements are correct for the following reaction ?

$$CH_3-CH=CH_2+HBr \xrightarrow{dibenzoyl\ peroxide} CH_3CH_2\cdot CH_2Br$$

(a) Initiation step involves formation of $C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}-\dot{O}$, $\dot{H}$ and $\dot{Br}$ radicals

(b) In propagation step $\dot{Br}$ attacks first to react with π system of alkene

(c) In propagation step $\dot{H}$ attacks first to react with π system of alkene

(d) Initiation step starts with formation of $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\dot{O}$

25. About a reaction producing more than one product, through common intermediate, the :

(a) product formed most rapidly is called kinetic product

(b) product formed most stable is called thermodynamic product

(c) process giving kinetic product in excess is called kinetically controlled process

(d) process giving thermodynamic product in excess is called thermodynamically controlled process

26. Which of the following are nucleophilic additions ?

(a) $CH\equiv CH+HCN \longrightarrow$

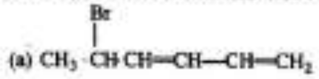
(b) $CH\equiv CH+HCl \longrightarrow$

(c) $CH\equiv CH+ROH \xrightarrow{KOH}$

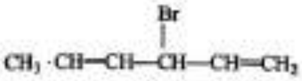
(d) $CH\equiv CH+\ddot{C}H_2 \longrightarrow$

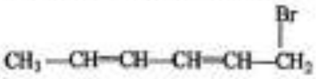
27. Hexa-1,3,5-triene on reaction with 1 equivalent of HBr gives:

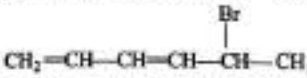
(a)



$$CH_3\cdot\overset{\overset{\displaystyle Br}{|}}{C}H\,CH=CH-CH=CH_2$$

(b) 
$CH_3\cdot CH{=}CH{-}\overset{\overset{\displaystyle Br}{|}}{CH}{-}CH{=}CH_2$

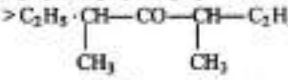
(c) 
$CH_3{-}CH{=}CH{-}CH{=}CH{-}\overset{\overset{\displaystyle Br}{|}}{CH_2}$

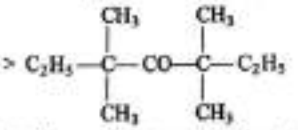
(d) 
$CH_2{=}CH{-}CH{=}CH{-}\overset{\overset{\displaystyle Br}{|}}{CH}{-}CH_3$

28. Select the correct statements about addition of Br_2 on *cis*-but-2-ene:
    (a) It is stereospecific reaction
    (b) Stereochemistry of product depends upon stereochemistry of substrate
    (c) Br_2 always shows antiaddition
    (d) Cis-2-butene with Br_2 gives enantiomers of 2,3-dibromobutane

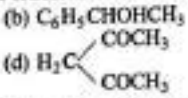
29. Which of the following will produce geometrical isomers on treating with NH_2OH :
    (a) CH_3COCH_3
    (b) HCHO
    (c) $CH_3CO\cdot CH_2CH_3$
    (d) CH_3CHO

30. Select of correct reactivity orders for nucleophilic addition of carbonyl compounds :
    (a) cyclopropanone > cyclobutanone > cyclopentanone > cyclohexanone
    (b) $FCH_2{-}CHO > CH_3CHO > C_6H_5CHO > CH_3COCH_3$
    (c) $ClCH_2CHO > HCHO > CH_3COCH_2Cl > CH_3COCH_3$
    (d) $C_2H_5COC_2H_5 > C_2H_5{-}CO\cdot CH_2\cdot CH(CH_3)_2$


$>C_2H_5\cdot\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CO{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}C_2H_5$


$>C_2H_5{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CO{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}C_2H_5$

31. Select the correct statements about reactions of carbonyl compounds with alcohols :
    (a) These reactions are addition reactions and reversible in nature
    (b) Aldehydes form hemi-acetal and acetal in acid medium
    (c) Ketone forms hemi-ketal and ketal in basic medium
    (d) Hemi-acetal and hemi-ketal are formed when pH > 7 whereas acetal and ketals when pH < 7

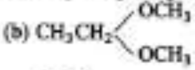
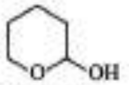
32. Which of the following gives iodoform test with NaOI?
    (a) $\Delta{-}COCH_3$
    (b) $C_6H_5CHOHCH_3$
    (c) $CH_2BrCOCH_3$
    (d) 
    $H_2C\!\begin{smallmatrix}COCH_3\\COCH_3\end{smallmatrix}$

33. Which of the following will decarboxylate on heating?
    (a) CH_3COCH_2COOH
    (b) $HOOC\cdot CH_2CH_2COOH$
    (c) $CH_3CO\cdot CH_2\cdot COCH_3$
    (d) $CH_3\cdot CH_2COCH_2COOH$

34. Which are correct about the reaction :

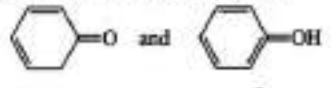
$$CH_3CHO + CH_3\cdot CH_2CHO \xrightarrow[10^\circ C]{OH^-} :$$

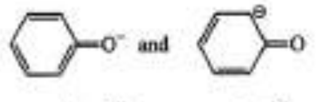
    (a) The reaction is crossed aldol addition
    (b) The reaction is mixed aldol addition
    (c) The reaction gives four aldols
    (d) The products formed can be separated easily

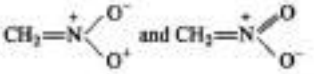
35. Which of the following compounds will give positive Tollens reagent test?
    (a) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(OH)OCH_3$
    (b) 
    $CH_3CH_2\!\begin{smallmatrix}OCH_3\\OCH_3\end{smallmatrix}$
    (c) 

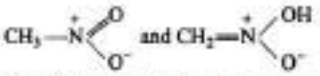
    (d) CH_3CHO

36. Which of the following are tautomers?

(a) 

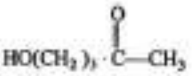
(b) 

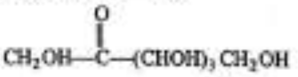
(c) 
$CH_2{=}\overset{+}{N}\!\begin{smallmatrix}O^-\\O^+\end{smallmatrix}$ and $CH_2{=}\overset{+}{N}\!\begin{smallmatrix}{=}O\\O^-\end{smallmatrix}$

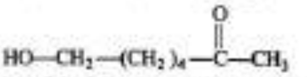
(d) 
$CH_3{-}\overset{+}{N}\!\begin{smallmatrix}{=}O\\O^-\end{smallmatrix}$ and $CH_2{=}\overset{+}{N}\!\begin{smallmatrix}OH\\O^-\end{smallmatrix}$

37. Which of the following form stable hemi-ketal?

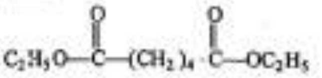
(a) 
$C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5$

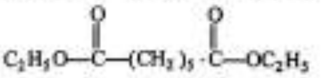
(b) 
$HO(CH_2)_3\cdot\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$

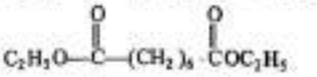
(c) 
$CH_2OH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CHOH)_3CH_2OH$

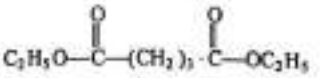
(d) 
$HO{-}CH_2{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$

38. Which of the following will show Dieckmann condensation reactions?

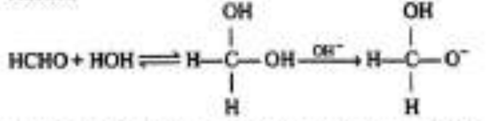
(a) 
$C_2H_5O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4\cdot\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5$

(b) 
$C_2H_5O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_5\cdot\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5$

(c) 
$C_2H_5O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_6\cdot\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5$

(d) 
$C_2H_5O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_3\cdot\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5$

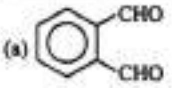
39. When an aldehyde is treated with formaldehyde in presence of an aqueous base, the formaldehyde is always oxidised and the other aldehyde is reduced. The reasons for this are :
   (a) Formaldehyde is a better reductant than the other aldehyde
   (b) In an aqueous basic solution it exists as a conjugate base of its hydrate which is one of the intermediates of the reaction

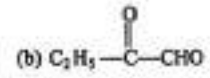


$$HCHO + HOH \rightleftharpoons H-\underset{H}{\overset{OH}{C}}-OH \xrightarrow{OH^-} H-\underset{H}{\overset{OH}{C}}-O^-$$

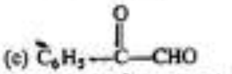
   (c) It has two α-H-atoms on carbonyl group whereas other aldehydes have only one α-H-atom
   (d) The reaction is called crossed Cannizzaro reaction

40. Which of the following will show intramolecular Cannizzaro reaction ?

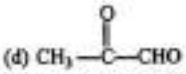
(a) 

(b) 

$C_2H_5-\overset{\overset{O}{\|}}{C}-CHO$

(c) 

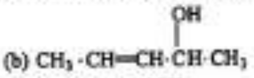
$C_6H_5-\overset{\overset{O}{\|}}{C}-CHO$

(d) 

$CH_3-\overset{\overset{O}{\|}}{C}-CHO$

41. Which of the following alcohols are not oxidised by MnO_2?

(a) $C_6H_5CH_2OH$

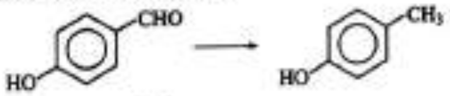
(b) 

$CH_3\cdot CH=CH\cdot\overset{OH}{CH}\cdot CH_3$

(c) $C_6H_5CH_2CH_2OH$

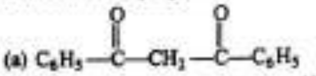
(d) $CH_3CH=CHOH$

42. The reductants used for are :



   (a) Zn-Hg/conc. HCl
   (b) NH_2NH_2/alc. KOH
   (c) $HS-(CH_2)_3-SH/H^+$, Ni/H_2
   (d) red P + HI

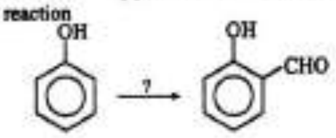
43. Which of the following will yield a hydrocarbon when treated with CH_3MgBr?

(a) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-C_6H_5$

(b) $CH\equiv CH$ (c) $R-OH$ (d) H_2SO_4

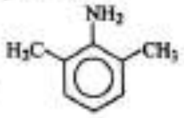
44. The reaction



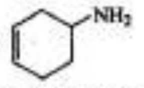
can be made by :
   (a) $CHCl_3$/alc. KOH followed by hydrolysis
   (b) HCN/HCl/anhy. $AlCl_3$
   (c) $(CH_2)_6N_4$/OH followed by hydrolysis
   (d) CrO_3

45. Which of the following gives carbylamine test?

(a) 

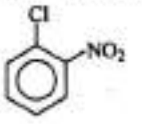
(b) 

(c) $CH_2=CH-CH_2NH_2$

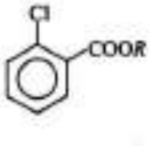
(d) 

46. Which of the following will give Ullmann reaction :

(a) 

(b) 

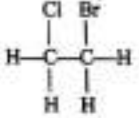
(c) 

(d) 

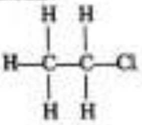
47. Nitration of salicylic acid gives :
   (a) 3-nitro phenol
   (b) Picric acid
   (c) 2,4,6-tri nitro phenol
   (d) 2,4,6-tri nitro benzoic acid

48. Which of the following will give white ppt. with $AgNO_3$ in presence of HNO_3?
   (a) $C_6H_5NH_3^+Cl^-$
   (b) C_6H_5Cl
   (c) 2,4,6-tri nitro chloro benzene
   (d) CH_3SH

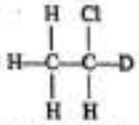
49. Which have asymmetric carbon atoms?

(a) 

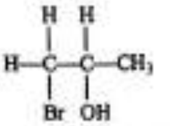
$H-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Br}{C}}-H$

(b) 

$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl$

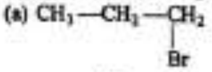
(c) 

$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-D$

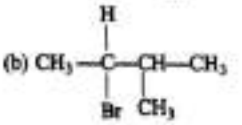
(d) 

$H-\underset{Br}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$

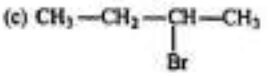
50. Which of the following have asymmetric carbon atoms?

(a) 

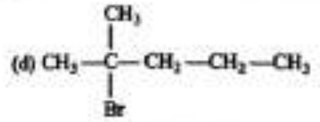
$CH_3-CH_2-\underset{Br}{CH_2}$

(b) 

$CH_3-\underset{Br}{\overset{H}{C}}-\underset{CH_3}{CH}-CH_3$

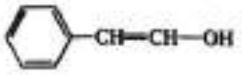
(c) 

$CH_3-CH_2-\underset{Br}{CH}-CH_3$

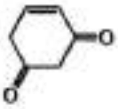
(d) 

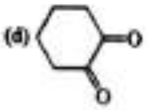
$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_2-CH_3$

51. Tautomerism is exhibited by :

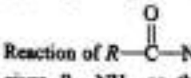
(a) 

(b) 

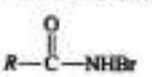
(c) 

(d) 

52. Which of the following compounds will show geometrical isomerism ?
    (a) 2-butene (b) Propene
    (c) 1-phenyl propene (d) 2-methyl-2-butene
53. Which of the following will give yellow precipitate with I_2/NaOH?
    (a) $ICH_2COCH_2CH_3$ (b) $CH_3COOCOCH_3$
    (c) CH_3CONH_2 (d) $CH_3CH(OH)CH_2CH_3$



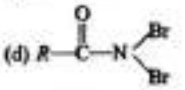
54. Reaction of $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediate involved in this reaction are :

(a) 

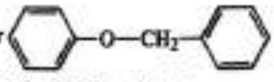
$R-\overset{O}{\overset{\|}{C}}-NHBr$

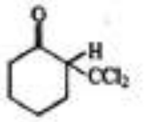
(b) $R-NHBr$

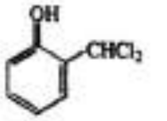
(c) $R-N=C=O$

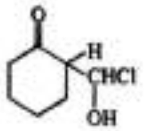
(d) 

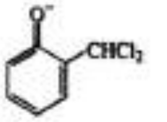
$R-\overset{O}{\overset{\|}{C}}-N\langle{}^{Br}_{Br}$

55. The ether  when treated with HI produces :
    (a) $C_6H_5CH_2I$ (b) $C_6H_5CH_2OH$
    (c) C_6H_5I (d) C_6H_5OH
56. Which of the following will undergo aldol condensation?
    (a) Acetaldehyde (b) Propanaldehyde
    (c) Benzaldehyde (d) Trideutero acetaldehyde
57. Which will react with acetone to give a product containing $\rangle C{=}N$, linkage?
    (a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
    (c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$
58. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates :

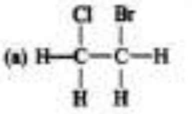
(a) 

(b) 

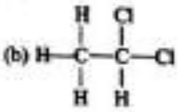
(c) 

(d) 

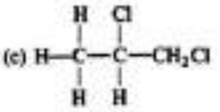
59. A new carbon-carbon bond formation is possible in :
    (a) Cannizzaro reaction (b) Friedel-Crafts alkylation
    (c) Clemmensen reduction (d) Reimer-Tiemann reaction
60. *p*-chloroaniline and anilinium hydrochloride can be distinguished by :
    (a) Sandmeyer reaction (b) $NaHCO_3$
    (c) $AgNO_3$ (d) Carbylamine test
61. Toluene when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the CH_3 group :
    (a) is para directing
    (b) is meta directing
    (c) activates the ring by hyperconjunction
    (d) deactivates ring
62. Resonance structure of a molecule should have :
    (a) identical arrangement of atoms
    (b) nearly the same energy content
    (c) the same number of paired electrons
    (d) identical bonding
63. Phenol is less acidic than :
    (a) acetic acid (b) *p*-methoxyphenol
    (c) *p*-nitrophenol (d) ethanol
64. Dipole moment is shown by :
    (a) 1, 4-dichlorobenzene
    (b) *cis*-1, 2-dichloroethane
    (c) *trans*-1, 2-dichloroethene
    (d) *trans*-1, 2-dichloro-2-pentene
65. Only two isomeric monochloro derivatives are possible for :
    (a) *n*-butane (b) 2, 4-dimethylpentane
    (c) benzene (d) 2-methylpropane
66. Which of the following have asymmetric carbon atom ?

(a) 

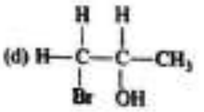
$H-\overset{Cl}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H$

(b) 

$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-Cl$

(c) 

$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-CH_2Cl$

(d) 

$H-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{OH}{C}}-CH_3$

67. The compound in which C uses its sp^3-hybrid orbitals for bond formation is :
(a) HCOOH (b) $(H_2N)_2CO$
(c) $(CH_3)_3COH$ (d) CH_3CHO

68. Among the following compounds, which will react with acetone to give a product containing $>C{=}N{-}$ bond ?
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$

69. An aromatic molecule will :
(a) have $4n\pi$ electrons
(b) have $(4n+2)\pi$ electrons
(c) be planar
(d) be cyclic

70. Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to :
(a) the formation of less stable carbonium ion
(b) resonance stabilization
(c) longer carbon halogen bond
(d) sp^2-hybridized carbon attached to the halogen

71. The compound used as refrigerant are :
(a) NH_3 (b) CCl_4
(c) CF_4 (d) CF_2Cl_2

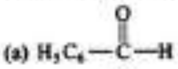
72. Which of the following compounds will give a yellow precipitate with iodine and alkali ?
(a) 2-Hydroxypropane (b) acetophenone
(c) methyl acetate (d) acetamide

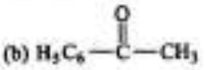
73. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$ the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are ?
(a) The electron density on *meta* carbon is more than that on *ortho* and *para* positions
(b) The intermediate carbonium ion formed after initial attach of Br^+ at the *meta* position is least destablished
(c) Loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position
(d) Easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* position

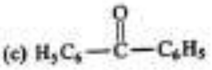
74. Base catalysed aldol condensation occurs with :
(a) Propionaldehyde
(b) Benzaldehyde
(c) 2-methylpropionaldehyde
(d) 2, 2-dimethylpropionaldehyde

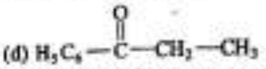
75. Which of the following compounds will react with ethanolic KCN ?
(a) ethyl chloride (b) acetyl chloride
(c) chlorobenzene (d) benzaldehyde

76. Keto-enol tautomerism is observed in :

(a) 
$H_5C_6{-}\overset{O}{\overset{\|}{C}}{-}H$

(b) 
$H_5C_6{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

(c) 
$H_5C_6{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5$

(d) 
$H_5C_6{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_3$

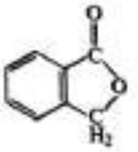
77. Which of the following are example of aldol condensation ?
(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3COH(CH_3)CH_2COCH_3$
(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

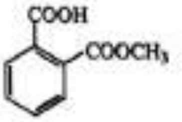
78. The smallest ketone and its next homologue are reacted with NH_2OH to from oxime : (IIT 2006)
(a) Two different oximes are formed
(b) Three different oximes are formed
(c) Two oximes formed are optically active
(d) All oximes formed are optically active

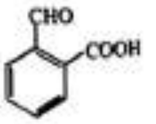
79. The product of reaction of alcoholic silver nitrite with ethyl bromide are :
(a) ethane (b) ethene
(c) nitroethane (d) ethyl nitrite

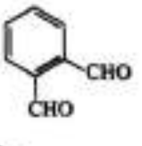
80. A positive carbylamine test is given by :
(a) *N*, *N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine

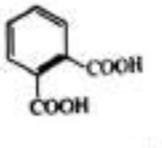
81. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following : (IIT 2006)

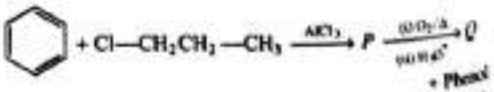


(a) 

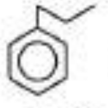
(b) 

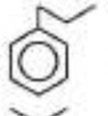
(c) 

(d) 

82. 

The major products *P* and *Q* are : (IIT 2006)

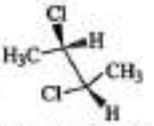
(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

83. The correct statement(s) about the compound given below is (are) : **(IIT 2008)**



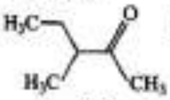
(a) The compound is optically active

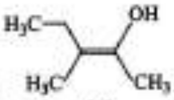
(b) The compound possesses centre of symmetry

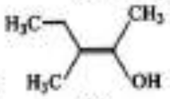
(c) The compound possesses plane of symmetry

(d) The compound possesses axis of symmetry

84. The correct statement(s) concerning the structures *E*, *F* and *G* is (are) : **(IIT 2008)**


(*E*)


(*F*)


(*G*)

(a) *E*, *F* and *G* are resonance structures

(b) *E*, *F* and *E*, *G* are tautomers

(c) *F* and *G* are geometrical isomers

(d) *F* and *G* are diastereomers

85. The correct statement(s) about the compound

$H_3C(HO)HC—CH=CH—CH(OH)CH_3$ (*X*) is(are) :

(IIT 2009)

(a) The total number of stereoisomers possible for *X* is 6

(b) The total number of diastereomers possible for *X* is 3

(c) If the stereochemistry about the double bond in *X* is *trans*, the number of enantiomers possible for *X* is 4

(d) If the stereochemistry about the double bond in *X* is *cis*, the number of enantiomers possible for *X* is 2

86. In the reaction

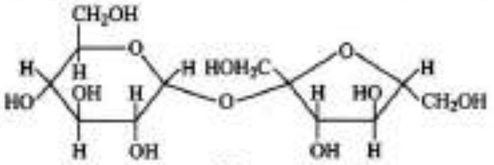
$$2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$$

the amine(s) *X* is(are) : **(IIT 2009)**

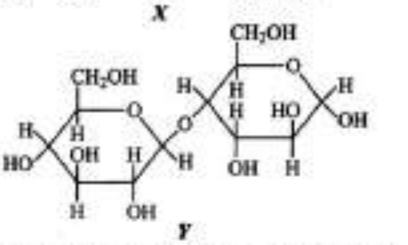
(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

87. The correct statement(s) about the following sugars *X* and *Y* is(are) : **(IIT 2009)**



X



Y

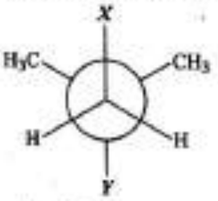
(a) *X* is a reducing sugar and *Y* is a non-reducing sugar

(b) *X* is a non-reducing sugar and *Y* is a reducing sugar

(c) The glucosidic linkages in *X* and *Y* are α and β, respectively

(d) The glucosidic linkages in *X* and *Y* are β and α, respectively

88. In the Newmann projection for 2,2-dimethylbutane.



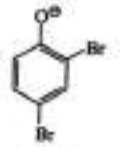
X and *Y* can respectively be : **(IIT 2010)**

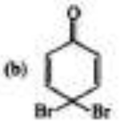
(a) H and H (b) H and C_2H_5

(c) C_2H_5 and H (d) CH_3 and CH_3

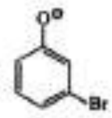
89. In the reaction

the intermediate(s) is(are) : **(IIT 2010)**

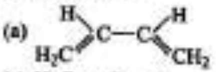
(a) 

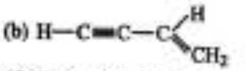
(b) 

(c) 

(d) 

90. Amongst the give options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) : **(IIT 2011)**

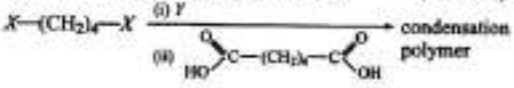
(a) 

(b) 

(c) $H_2C{=}C{=}O$

(d) $H_2C{=}C{=}CH_2$

91. The correct functional group X and the reagent/reaction condition Y in the following scheme are : **(IIT 2011)**



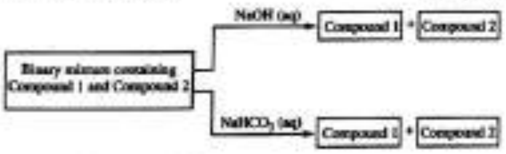
(a) $X = COOCH_3$, $Y = H_2$ / Ni / heat

(b) $X = CONH_2$, $Y = H_2$ / Ni / heat

(c) $X = CONH_2$, $Y = Br_2$ / NaOH

(d) $X = CN$, $Y = H_2$ / Ni / heat

92. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. **(IIT 2012)**



(a) C_6H_5OH and C_6H_5COOH

(b) C_6H_5COOH and $C_6H_5CH_2OH$

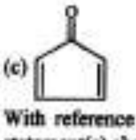
(c) $C_6H_5CH_2OH$ and C_6H_5OH

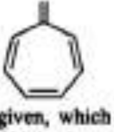
(d) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

93. Which of the following molecules, in pure form, is(are) **unstable** at room temperature? **(IIT 2012)**

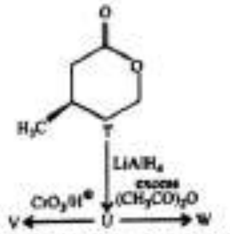
(a) 

(b) 

(c) 

(d) 

94. With reference to the scheme given, which of the given statement(s) about T, U, V and W is(are) correct? **(IIT 2012)**



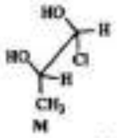
(a) **T** is soluble in hot aqueous NaOH.

(b) **U** is optically active.

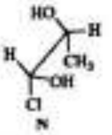
(c) Molecular formula of **W** is $C_{10}H_{18}O_4$.

(d) **V** gives effervescence on treatment with aqueous $NaHCO_3$.

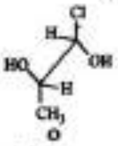
95. Which of the given statement(s) about **N, O, P** and **Q** with respect to **M** is (are) correct? **(IIT 2012)**



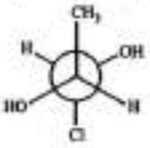
M



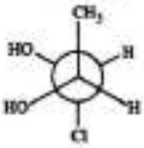
N



O



P



Q

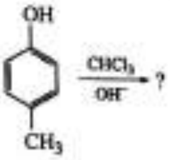
(a) M and N are non-mirror image stereoisomers.

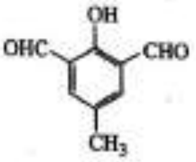
(b) M and O are identical.

(c) M and P are enantiomers.

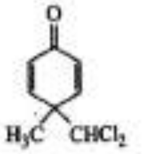
(d) M and Q are identical.

96. In the following reaction, the product(s) formed is (are) : **[JEE (Advanced) II 2013]**

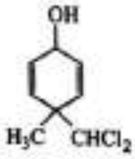




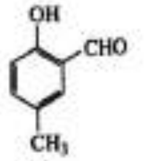
P



Q



R

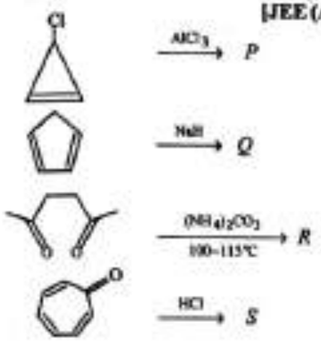


S

(a) P (Major)　　(b) Q (Minor)
(c) R (Minor)　　(d) S (Major)

97. Among P, Q, R and S, the aromatic compound(s) is/are :

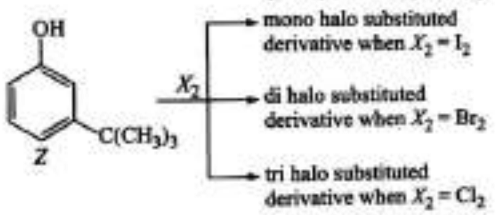
[JEE (Advanced) I 2013]



(a) P　　(b) Q
(c) R　　(d) S

98. The reactivity of compound Z with different halogens under appropriate conditions is given below :

[JEE (Advanced) I 2014]



The observed pattern of electrophilic substitution can be explained by

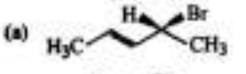
(a) the steric effect of the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group

99. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are :

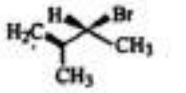
[JEE (Advanced) I 2014]

(a) *tert*-butanol and 2-methylpropan-2-ol
(b) *tert*-butanol and 1,1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol
(d) isobutyl alcohol and 2-methylpropan-1-ol

100. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) :

(a)


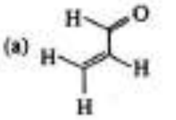
(b)

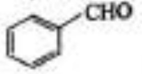

(c)


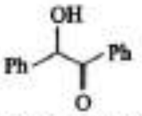
(d)

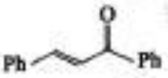

101. Positive Tollens' test is observed for:

[JEE (Advanced) I 2016]

(a)


(b)


(c)


(d)


102. The correct statement(s) about the following reaction sequence is(are):

$$\text{Cumene }(C_9H_{12}) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2} P \xrightarrow{CHCl_3/NaOH} Q\text{ (major)} + R\text{ (minor)}$$

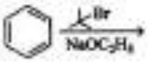
$$Q \xrightarrow[PhCH_2Br]{NaOH} S$$

[JEE (Advanced) I 2016]

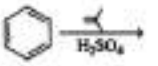
(a) R is steam volatile
(b) Q gives dark violet coloration with 1% aqueous $FeCl_3$ solution
(c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
(d) S gives dark violet coloration with 1% aqueous $FeCl_3$ solution

103. Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) :

[JEE (Advanced) II 2016]

(a)


(b)


(c)


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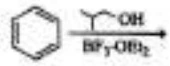
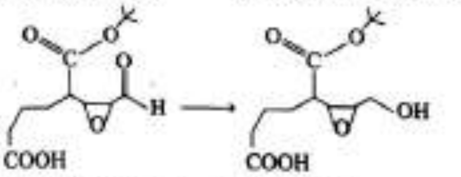


104. Reagent(s) which can be used to bring about the following transformation is(are) :　　**[JEE (Advanced) II 2016]**



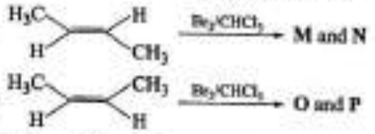
(a) $LiAlH_4$ in $(C_2H_5)_2O$　　(b) BH_3 in THF
(c) $NaBH_4$ in C_2H_5OH　　(d) Raney Ni/H_2 in THF

105. The IUPAC name(s) of the following compound is (are):

[JEE (Advanced) I 2017]

(a) 4-methylchlorobenzene
(b) 4-chlorotoluene
(c) 1-chloro-4-methylbenzene
(d) 1-methyl-4-chlorobenzene

106. The correct statement(s) for the following addition reactions is (are) : **[JEE (Advanced) I 2017]**



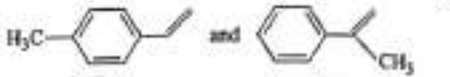
(a) (M and O) and (N and P) are two pairs of diastereomers
(b) Bromination proceeds through *trans*-addition in both the reactions
(c) O and P are identical molecules
(d) (M and O) and (N and P) are two pairs of enantiomers

107. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction. **[JEE (Advanced) II 2017]**

(i) $P \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2} Q\ (C_8H_8O)$

(ii) $R \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2} S\ (C_8H_8O)$

The option(s) with suitable combination of P and R, respectively, is (are) :

(a)


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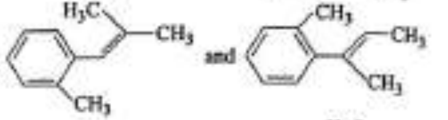

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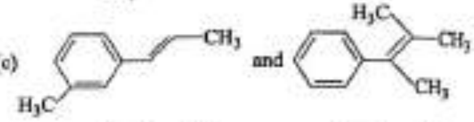

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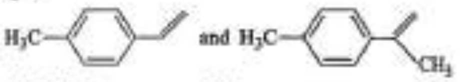
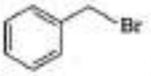
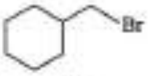


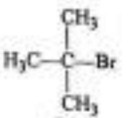
108. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is (are):



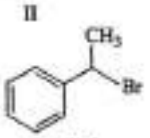
I



II



III



IV

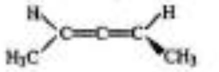
[JEE (Advanced) II 2017]

(a) I and II follow S_N2 mechanism
(b) the order of reactivity for I, III and IV is : IV > I > III
(c) I and III follow S_N1 mechanism
(d) compound IV undergoes inversion of configuration

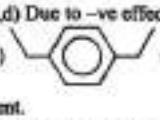
SOLUTIONS (More Than One Answer Correct)

1. (a,c,d) 2,3-pentadiene has two stereo centres C^1 and C^3, but no chiral centres

and



2. (a,b,c) Prefix D-refers for configuration of the compound.
3. (a,b) p_x, p_y and p_z are at 90° and *sp*-orbitals are linear.
4. (a,b,c,d) Due to –ve effect of halogen atoms.
5. (a,c,d)



structure has non-zero dipole moment.

6. (a,b,c) Increase in electronegativity (along the period) gives rise to increase in basic nature

$$\bar{C}H_3 < \bar{N}H_2 < \bar{O}H < \bar{F}$$

7. (a,b,c) More is the *s* character on adjacent carbon to $\bar{C}$, more is stability

$$\underset{sp}{CH}\equiv\bar{C} > CH_3-C\equiv\bar{C} > CH_2=\bar{C}H > CH_3-\bar{C}H_2$$

8. (a,c,d) CH_3-CH_2-Cl No resonance

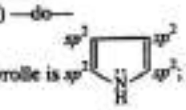
$CH_2=CH-Cl$ 2 resonating structures

C_6H_5-Cl 4 resonating structures

Bond length of functional group

$$= \frac{1}{\text{No. of resonating structures}}$$

9. (a,b,c,d) These are facts.
10. (a,b,c,d) —do—
11. (a,b,c,d) —do—
12. (b,c) Pyrolle is

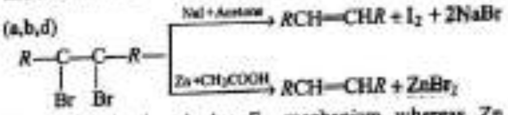


; N has sp^3-hybridisation

13. (a,d)

S_N1 reactions are favoured if unsaturation is at β-carbon
S_N2 reactions are favoured if unsaturation is at α-carbon and substrate containing carbonyl group at β-carbon does not give S_N1 reaction.

14. (b,c,d) $R-NH_2$ does not give S_N reactions as $-NH_2$ is poor leaving group.
15. (a,d) Only optically active compounds show Walden inversion.
16. (a,b,d) *Trans* esterification is the reaction of ester with alcohol.
17. (a,d) If $\overset{\ominus}{L}$ is the best leaving group, a nucleophile (*i.e.*, less basic nature) then only the reaction is possible.
18. (b,d) Aryl halides having no H-atom at ortho position do not show benzyne mechanism.
19. (a,b,c,d) All the facts are based on electronic displacement and mechanism.
20. (a,b,d)

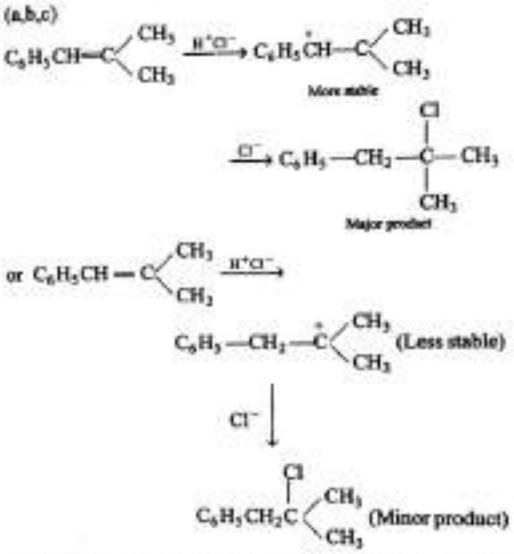


$$R-\underset{Br}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}-R \begin{cases} \xrightarrow{\text{NaI + Acetone}} RCH=CHR + I_2 + 2NaBr \\ \xrightarrow{\text{Zn + CH}_3\text{COOH}} RCH=CHR + \underline{ZnBr_2} \end{cases}$$

The debromination is by E_2 mechanism whereas Zn behaves as a nucleophile.

$$RCHBr\cdot CH_2\cdot CH_3 \xrightarrow{\text{KOH alc.}} RCH=CH\cdot CH_3 + HBr$$

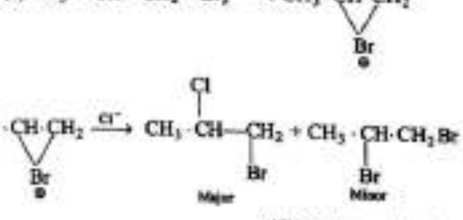
21. (a,b,c)



$$C_6H_5CH=C\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{H^+Cl^-} C_6H_5\overset{+}{C}H-C\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{Cl^-} C_6H_5-CH_2-\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3$$

$$\text{or } C_6H_5CH=C\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{H^+Cl^-} C_6H_5-CH_2-\overset{+}{C}\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{Cl^-} C_6H_5CH_2\overset{Cl}{\overset{|}{C}}\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

22. (a,c) Anti Markownikoff addition is observed when one doubly bonded carbon is attached with powerful electron withdrawing group. Kharash effect is not observed in HCl.
23. (a,c)

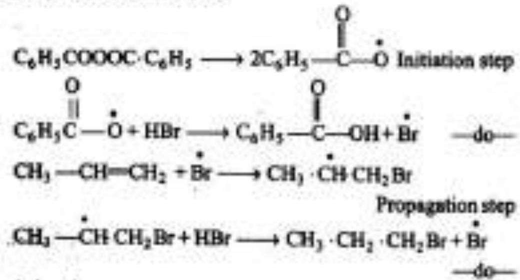


$$CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3\cdot CH\cdot CH_2 \ (\overset{\oplus}{Br} \text{ bridged})$$

$$CH_3\cdot CH\cdot CH_2 \xrightarrow{Cl^-} CH_3\cdot\overset{Cl}{\overset{|}{C}H}-\underset{Br}{\underset{|}{C}H_2} + CH_3\cdot\underset{Br}{\underset{|}{C}H}\cdot CH_2Br$$

(Cl⁻ is more reactive than Br⁻)

24. (b,d) The mechanism is :



$$C_6H_5COOOC \cdot C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \text{ Initiation step}$$

$$C_6H_5\overset{O}{\overset{\|}{C}}-\dot{O}+HBr \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OH+\dot{B}r \quad \text{—do—}$$

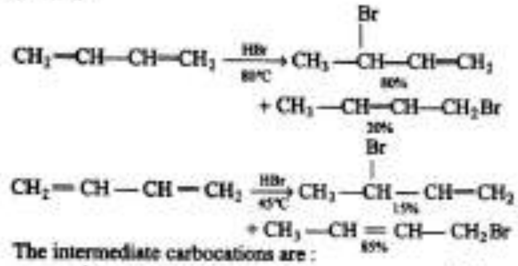
$$CH_3-CH=CH_2+\dot{B}r \longrightarrow CH_3 \cdot \dot{C}H\,CH_2Br$$

Propagation step

$$CH_3-\dot{C}H\,CH_2Br+HBr \longrightarrow CH_3 \cdot CH_2 \cdot CH_2Br+\dot{B}r$$

—do—

25. (a,b,c,d)



$$CH_2=CH-CH=CH_2 \xrightarrow[80°C]{HBr} \underset{80\%}{CH_3-\overset{Br}{\overset{|}{C}H}-CH=CH_2} + \underset{20\%}{CH_3-CH=CH-CH_2Br}$$

$$CH_2=CH-CH=CH_2 \xrightarrow[45°C]{HBr} \underset{15\%}{CH_3-\overset{Br}{\overset{|}{C}H}-CH=CH_2} + \underset{85\%}{CH_3-CH=CH-CH_2Br}$$

The intermediate carbocations are :

$$\underset{\text{More stable}}{CH_3-\overset{+}{C}H-CH=CH_2} \quad \text{and} \quad \underset{\text{Less stable}}{CH_3-CH=CH-\overset{+}{C}H_2}$$

The product formed by more stable carbocation is always kinetically controlled and by less stable carbocation is thermodynamically controlled.

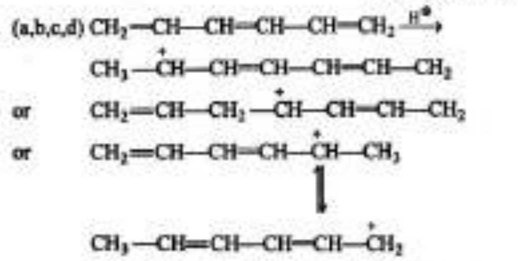
26. (a,c)

$$CH\equiv CH+CN^- \longrightarrow \overset{-}{C}N=CHCN \xrightarrow{H^+} CH_2=CHCN$$

$$CH_3OH+KOH \longrightarrow CH_3OK+H_2O$$

$$CH_3OK \rightleftharpoons CH_3O^- +K^+$$

$$CH\equiv CH+CH_3O^- \longrightarrow \overset{-}{C}H=CHOCH_3 \xrightarrow{H^+} CH_2=CHOCH_3$$



27. (a,b,c,d) $CH_2=CH-CH=CH-CH=CH_2 \xrightarrow{H^{\oplus}}$

$$CH_3-\overset{+}{C}H-CH=CH-CH=CH-CH_2$$

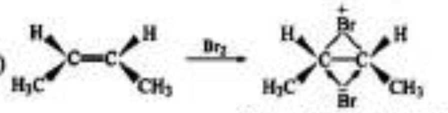
or $$CH_2=CH-CH_2-\overset{+}{C}H-CH=CH-CH_2$$

or $$CH_2=CH-CH=CH-\overset{+}{C}H-CH_3$$

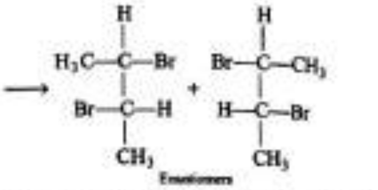
$$\updownarrow$$

$$CH_3-CH=CH-CH=CH-\overset{+}{C}H_2$$

28. (a,b,c,d)



Symmetrical bromonium ion



Enantiomers

29. (c,d) Unsymmetrical carbonyl compounds form syn and anti oximes.

$$\rangle C=O \xrightarrow{H_2NOH} \rangle C=NOH \text{ (Syn and anti oximes)}$$

30. (a,b,c,d) Follow mechanism of $\rangle C=O \longrightarrow \rangle C^+-O^-$.
Notice more the +ve charge on C^+ centre, more is its reactivity.

31. (a,d) Hemi-acetal and hemi-ketals are given in basic medium, whereas acetal and ketal in acid medium.

32. (a,b,c) Each has $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\overset{OH}{\overset{|}{C}H}-$ unit. In (d) halogen attacks on H of CH_2 as it has reactive methylene H-atoms.

33. (a,b,d) Dicarboxylic acids show decarboxylation on heating. Also, β-oxocarboxylic acids also undergo decarboxylation.

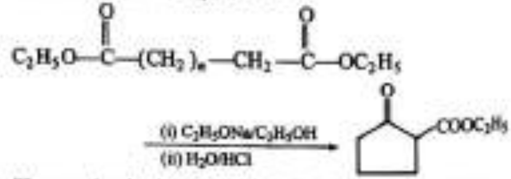
34. (a,b,c) If both the carbonyl compounds have α-H-atom, four products are formed. If one of the carbonyl compounds has an α-H-atom, two products are formed. The products formed have similar physical and chemical properties and thus their separation is difficult.

35. (a,c,d) Tollens reagent is a mild oxidant. It converts CHOH to CHO and then COOH as well as hemi-acetals are also converted to aldehyde and then —COOH.

36. (a,d) Follow tautomerism.

37. (b,c,d) Simple ketals are less stable.

38. (a,b,c) Dieckman condensation is an intramolecular condensation shown by diesters.



$$C_2H_5O-\overset{O}{\overset{\|}{C}}-(CH_2)_n-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

The reaction is given by 1, 6; 1, 7 and 1,8 dibasic esters.

39. (a,b,c,d) All are facts.

40. (a,c) α-keto aldehydes lacking with α-H-atom also show Cannizzaro reaction. Keto group is reduced and aldehyde is oxidised.

41. (a,b,c) MnO_2 oxidises only alcohols with allyl group and benzyl alcohol.

42. (b,c) In others —OH will also be reduced.

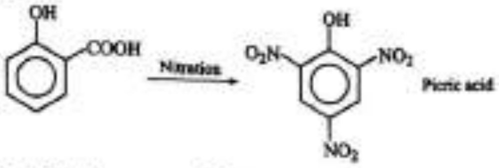
43. (a,b,c,d) Compounds having an acidic or active H-atom give alkane with Grignard reagent.

44. (a,b,c) The reaction made by hexamethylene tetraamine followed by hydrolysis is called Duff reaction.

45. (a,c,d) Stearic hindrance in (b) does not allow to give the test.

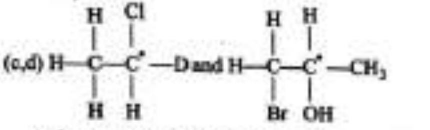
46. (a,b,d) Aryl fluoride does not give Ullmann's reaction.

47. (b,c)



48. (a,c) In (c) presence of three $-NO_2$ groups increases reactivity of Cl.

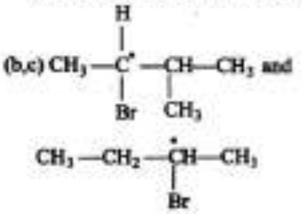
49. (c,d)



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{Cl}{\underset{H}{C^{*}}}{-}D}$ and $\mathrm{H{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{OH}{C^{*}}}{-}CH_3}$

(C^* are asymmetric carbon atoms)

50. (b,c)

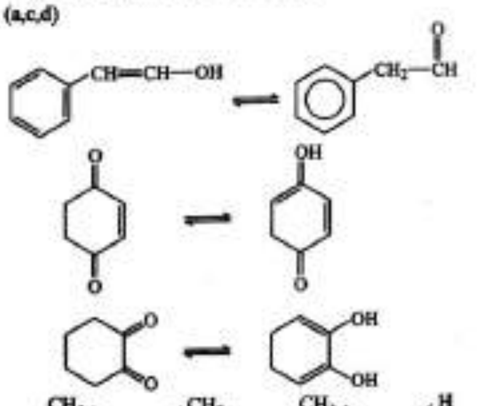


$\mathrm{CH_3{-}\overset{H}{\underset{Br}{C^{*}}}{-}\underset{CH_3}{CH}{-}CH_3}$ and

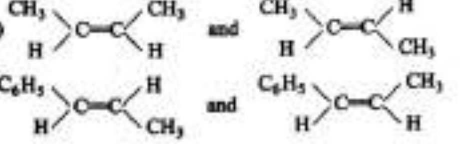
$\mathrm{CH_3{-}CH_2{-}\underset{Br}{\overset{*}{C}H}{-}CH_3}$

(C^* are asymmetric carbon atoms)

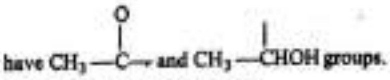
51. (a,c,d)



52. (a,c)



53. (a,d) Both have

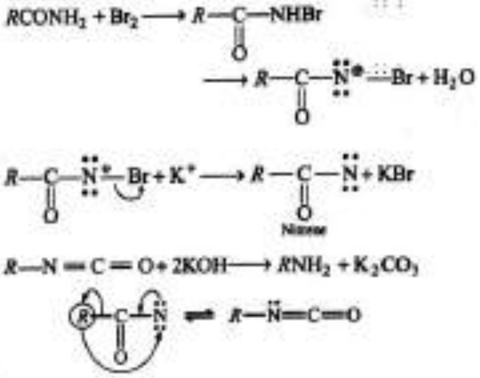


$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}}$ and $\mathrm{CH_3{-}\overset{|}{C}HOH}$ groups.

54. (a,c) This is Hoffmann bromide reaction

$$RCONH_2 + Br_2 + 4KOH_{(aq.)} \longrightarrow RNH_2 + 2KBr + 2H_2O + K_2CO_3$$

mechanism



$$RCONH_2 + Br_2 \longrightarrow R{-}\underset{O}{\underset{\|}{C}}{-}NHBr \longrightarrow R{-}\underset{O}{\underset{\|}{C}}{-}\ddot{N}^{\ominus}\cdots Br + H_2O$$

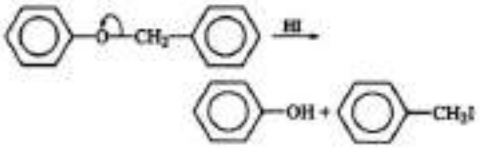
$$R{-}\underset{O}{\underset{\|}{C}}{-}\ddot{N}^{\ominus}{-}Br + K^+ \longrightarrow R{-}\underset{O}{\underset{\|}{C}}{-}\ddot{N} + KBr$$

Nitrene

$$R{-}N{=}C{=}O + 2KOH \longrightarrow RNH_2 + K_2CO_3$$

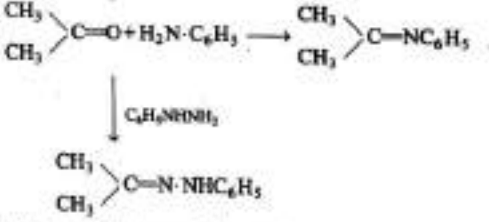
$$R{-}\underset{O}{\underset{\|}{C}}{-}\ddot{N} \rightleftharpoons R{-}\ddot{N}{=}C{=}O$$

55. (a,d)



56. (a,b,d) Benzaldehyde does not have α-H-atom.

57. (a,d)



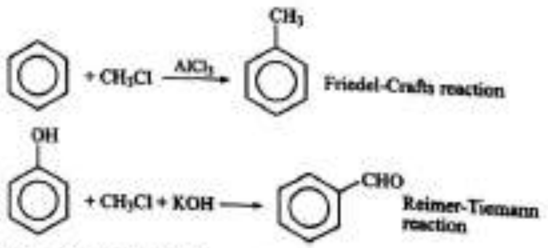
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O + H_2N{\cdot}C_6H_5 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}NC_6H_5$$

$$\downarrow C_6H_5NHNH_2$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}N{\cdot}NHC_6H_5$$

58. (a,b) Follow mechanism or Reimer-Tiemann reaction.

59. (b,d)

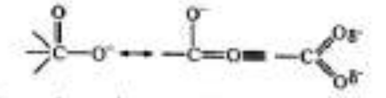


60. (b,c) $C_6H_5NH_3Cl$ gives effervescences with $NaHCO_3$ and white ppt. with $AgNO_3$.

61. (a,c) These are facts.

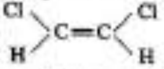
62. (a,b,c) These are the facts

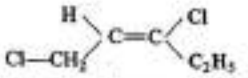
63. (a,c) Carboxylic acids are more acidic than phenol because carboxylate anion is more resonance stabilised than phenoxide ion.



$-NO_2$ gp. is an electron withdrawing and increases the acidity of phenol.

64. (b,d)

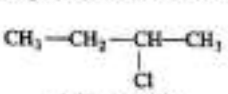




65. (a,d) *n*-butane and 2-methyl propane have two isomeric monochloro derivatives :

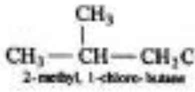
$CH_3-CH_2-CH_2-CH_2Cl$

1-chloro butane (i)



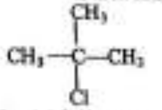
$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

2-chloro butane (ii)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2Cl$

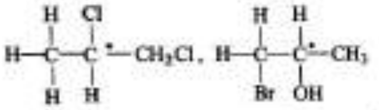
2-methyl, 1-chloro-butane



$CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

2-methyl, 2-chloropropane

66. (c,d)



$H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}^{*}-CH_2Cl, \quad H-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}^{*}-CH_3$

A chiral carbon atom or an asymmetric C-atom is that C-atom which contains four different gps at its four valencies.

67. (c,d) In saturated state, carbon forms four σ-bonds and has sp^3-hybridisation.

68. (a,d) Aniline and phenyl hydrazine both undergo condensation reaction to form hydrazones.

$$C_6H_5N\boxed{H_2+O}=C(CH_3)_2 \longrightarrow C_6H_5N=C(CH_3)_2+H_2O$$

$$C_6H_5NH\text{-}N\boxed{H_2+O}=C(CH_3)_2 \longrightarrow C_6H_5NH\cdot N=C(CH_3)_2+H_2O$$

69. (b,c,d) An aromatic molecule may have

(i) $(4n+2)\pi$ electrons (Huckel rule)
$n = 0, 1, 2, 3 ......$

(ii) Molecule should be flat *i.e.*, all the should lie in one plane.

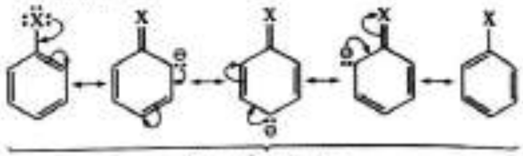
(iii) The compound must be cyclic and having a extended conjugated π system.

70. (b,d) The halogen atom in Aryl halide is comparatively less reactive towards nucleophilic substitution reaction than alkyl halide due to :

(i) Resonance stabilization

(ii) sp^2-hybridized carbon attached to the halogen.

(iii) development of partial double bond character in C—Cl bond.



Resonating structure

71. (a,d) NH_3 and dichlorodifluoro methane are used as refrigerant.

72. (a,b) Iodoform reaction is given by those compounds which contains $COCH_3$ gp. (methyl ketone), all sec. alcohols and ethyl alcohol (only *p*-alcohol).
Exceptions $CH_3CO \; CH_2COOC_2H_5$ (ethylacetoacetate), CH_3CONH_2 (acetamide), although contain $-COCH_3$ gp. yet do not give iodoform test.

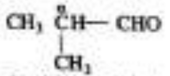
73. (a,b,d) $-NO_2$ gp. is an electron withdrawing gp. and have $-I$ and $-M$ effects, therefore decreases the electron density at *o*- and *p*- position and, electrophilic attacks at *m*-position.

74. (a,c) Aldehydes having α-H atom undergo aldol condensation.

$CH_3\overset{\alpha}{C}H_2CHO$

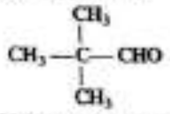
Propionaldehyde

Benzaldehyde
(no α-hydrogen atom)



$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\alpha}{C}H}}-CHO$

2-methylpropionaldehyde



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CHO$

2,2-dimethylpropionaldehyde
(no α-hydrogen atom)

75. (a,b,d) Ethyl chloride and acetyl chloride undergo nucleophilic substitution reaction with alc. KCN while benzaldehyde undergoes benzoin condensation and chlorobenzene does not react.

$$C_2H_5Cl \xrightarrow{\text{KCN (alc.)}} C_2H_5CN+KCl$$

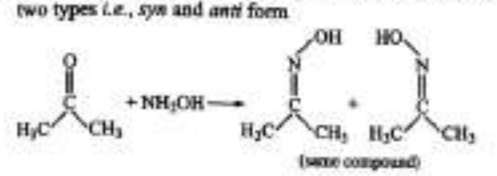
$$CH_3COCl \xrightarrow{\text{KCN (alc.)}} CH_3COCN+KCl$$

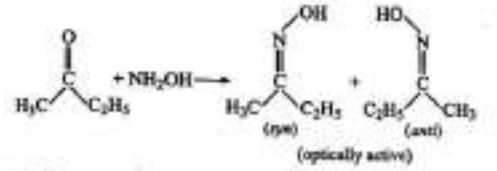
$$2C_6H_5CHO \xrightarrow{\text{KCN (alc.)}} C_6H_5CHOHCOC_6H_5$$

76. (b,d) Keto-enol tautomerism is shown by those compounds which have α-hydrogen to the CO group.

77. (a,b) The compounds containing α-Hydrogen atom undergo aldol condensation. In aldol condensation, two molecules of aldehydes or ketones combine to form the α-hydroxy aldehyde or ketone.

78. (b,c) Acetone reacts with hydroxyl amine to form oxime of two types *i.e.*, *syn* and *anti* form

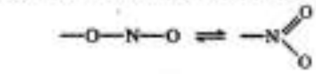




79. (c,d)

$$2C_2H_5Br + 2AgNO_2 \rightarrow \underset{\text{(Major)}}{C_2H_5NO_2} + \underset{\text{(Minor)}}{C_2H_5ONO} + AgBr$$

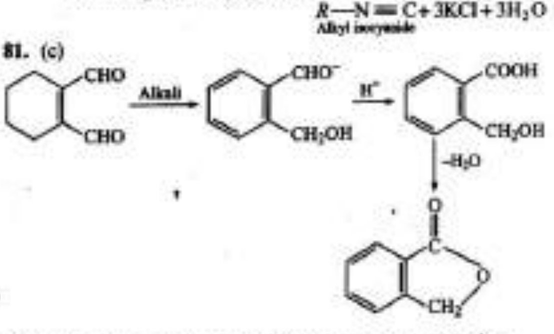
$-NO_2$ gp. exists into two tautomeric forms.



80. (b,d) Carbylamine test is given by primary amines.

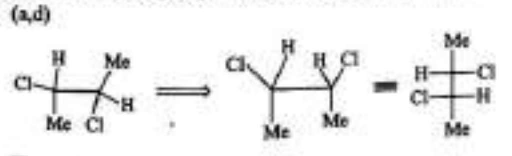
$$R—NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Alkyl isocyanide}}{R—N \equiv C} + 3KCl + 3H_2O$$

81. (c)



82. (c) It is cumene hydroperoxide rearrangement reaction.

83. (a,d)



The molecule is optically active.

The molecule passes an axis of symmetry (C_2) perpendicular to the C—C bond.

84. (b), (c), (d)

85. (a,d) The molecule has $C_{abcd}C_{(ab)_2} \cdot C_{abcd}$.

i.e., $n = 2$ (asymmetric carbon)

∴ **Optical isomer**

$$\text{Enantiomer} = 2^{n-1} = 2^{2-1} = 2$$

$$\text{meso} = 2^{\frac{2n-2}{2}} = 2^1 = 2$$

Geometrical = 2 due to one double lined

86. (a,b,c) Trimethyl amine does not have H atom on N

$$\rangle N—H + B_2H_6 \longrightarrow [BH_2(N\langle\ )_2]^+[BH_4]^-$$

87. (b,c) These are facts for given sugars.

88. (b,d) Follow text

89. (b,c) Follow mechanism.

90. (a,b) Buta-1-3-diene has sp^2-sp^2 bond and belong to conjugated system, hence such bonds posses double bond character. The molecule is planar and exists in two conformations, transoid (*s-trans*) and cisoid (*s-cis*).

Alkynes are planar.

In ketenes and allenes (even no. of double bonds) H-atoms are out of plane.

91. (c,d) If *X* is-$CONH_2$ it will be converted to $—CH_2NH_2$ only either on reduction with $Na + C_2H_5OH$ or $LiAlH_4$ by Br_2/OH^- (Hoffmann Bromamide Reaction).

$$H_2NCO—(CH_2)_4—CONH_2 \xrightarrow{Br_2/OH^-} H_2N—(CH_2)_4—NH_2$$

If *X* is $-COOMe$ it will form diol only on catalytic reduction with $Na + C_2H_5OH$ or $LiAlH_4$ (ether). If *X* is $-CN$ it will form $-CH_2NH_2$ on reduction with H_2/Ni

$$NC—(CH_2)_4—CN \xrightarrow{H_2/Ni} H_2N—CH_2(CH_2)_4CH_2—NH_2$$

All these will form condensation polymer with dicarboxylic acid.

$$H_2N—CH_2(CH_2)_4CH_2—NH_2 \xrightarrow{HOOC—(CH_2)_4COOH} \text{Polyamide}$$

$$H_2N—(CH_2)_4—NH_2 \xrightarrow{HOOC—(CH_2)_4COOH} \text{Polyamide}$$

92. (b,d)

(a) Both are soluble in NaOH, hence can not be separated by NaOH.

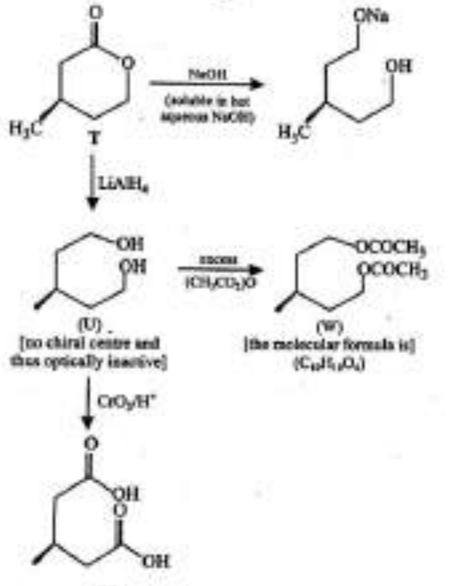
(b) Benzoic acid (C_6H_5COOH) is soluble in NaOH and $NaHCO_3$, while benzyl alcohol ($C_6H_5CH_2OH$) is not soluble in $NaHCO_3$ and thus mixtures can be separated.

(c) Benzyl alcohol ($C_6H_5CH_2OH$) and phenol (C_6H_5OH) can be separated by NaOH as only the later is soluble in NaOH. However, in $NaHCO_3$, both are insoluble. Hence, can not be separated.

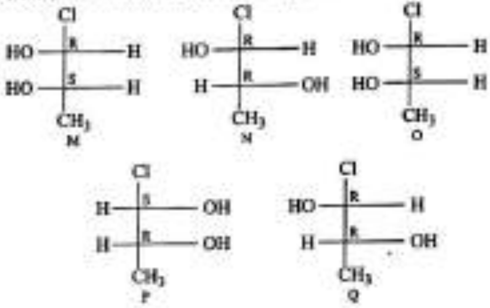
(d) α-phenyl acetic acid ($C_6H_5CH_2COOH$) is soluble in NaOH and $NaHCO_3$. Whereas benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, mixture can be separated.

93. (b,c)

Compound  and  being antiaromatic in nature and therefore unstable at room temperature.



94. (a,c,d) The scheme of reaction is given below



95. (a,b,c) The Fischer projections of M, N, O, P and Q are shown below

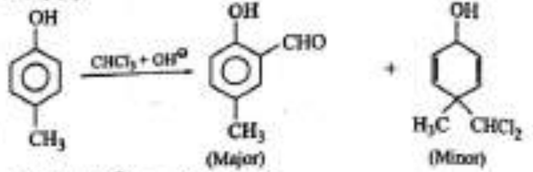
M and N are diastereoisomers

M and O are identical

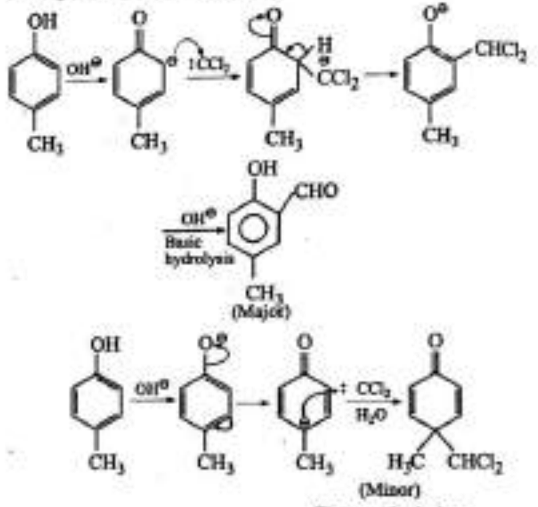
M and P are enantiomers

M and Q are diastereoisomers

96. (b,d)

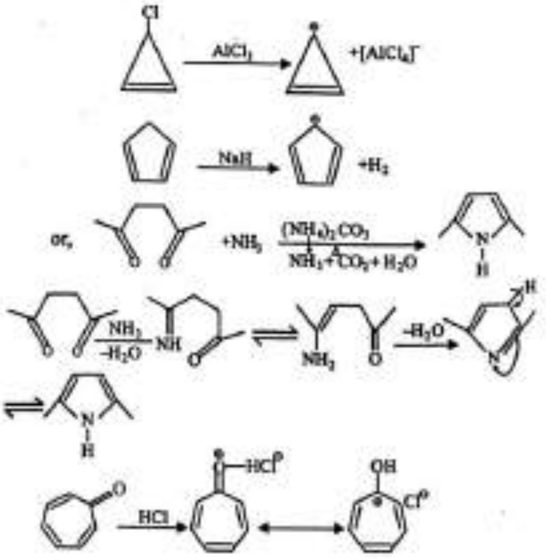


$CHCl_3 + OH^{\ominus} \longrightarrow :CCl_2 + H_2O$

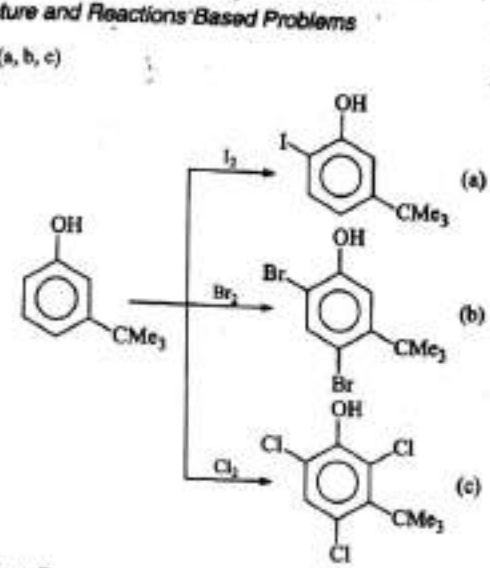


(Does not hydrolyse due to steric hindrence)

97. (a, b, c, d) All products obey Huckel rule for aromaticity.



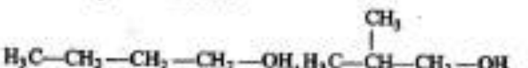
98. (a, b, c)



99. (a, c, d)

Isomeric alcohols of molecular formula, $C_4H_{10}O$ are

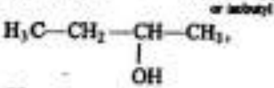
Primary or 1° alcohol



$H_3C-CH_2-CH_2-CH_2-OH$, $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-OH$

(1°) n-butanol or butan-1-ol; (1°) 2-methylpropan-1-ol or isobutyl alcohol

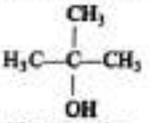
2° alcohol



$H_3C-CH_2-\underset{\underset{\displaystyle OH}{|}}{C}H-CH_3$,

(2°) sec-butyl alcohol or butan-2-ol

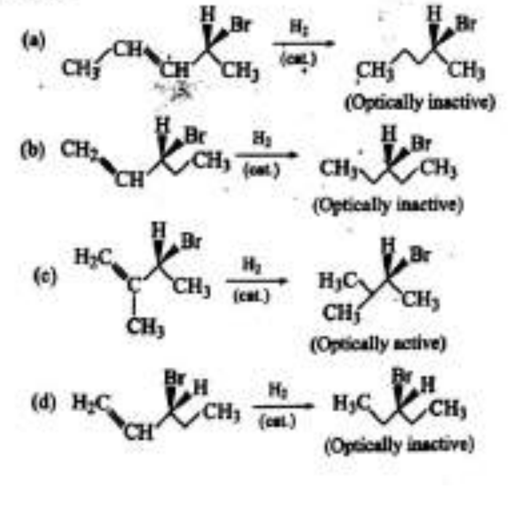
3° alcohol



$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$

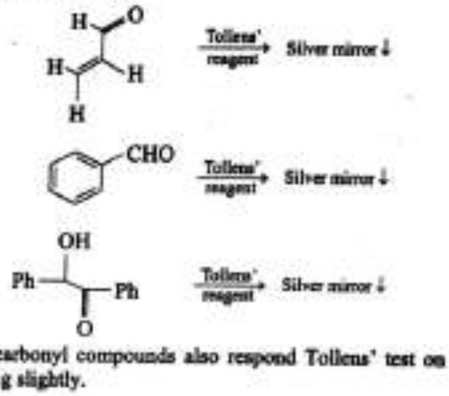
(3°) tert-butanol or 2-methylpropan-2-ol

100. (b, d)



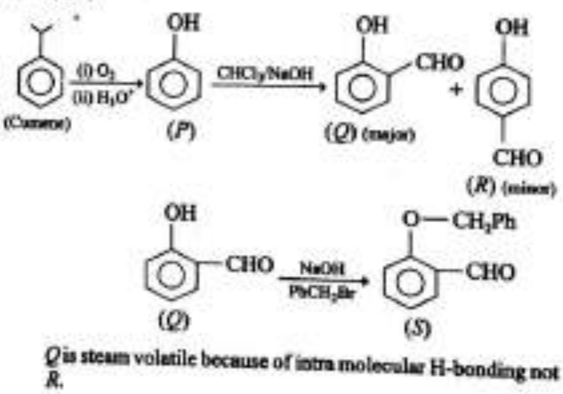
101. (a, b, c)

Aldehydes, formic acid, formic esters and α-hydroxy attached to a powerful electron withdrawing gp. such as ketons, carboxylic acid, amide, esters, cyanide show positive Tollens' test.



α, β dicarbonyl compounds also respond Tollens' test on warming slightly.

102. (b, c)

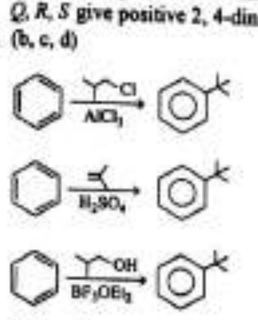


Q is steam volatile because of intra molecular H-bonding not R.

Q and R give positive test with 1% aqueous $FeCl_3$ solution.

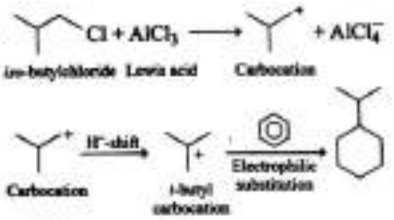
Q, R, S give positive 2, 4-dinitrophenyl hydrazine.

103. (b, c, d)

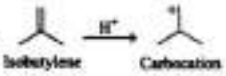


Note : Benzene neither reacts with sod. ethoxide nor with t-bromide. t-butyl bromide reacts with sodium ethoxide show E_1 and E_2 elemination to give isobutylene and ethanol. Neither of these two reacts with C_6H_6.

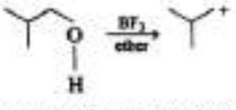
(b)



(c)



(d) BF_3(gas) dissolved in ether



OH being poor leaving gp. but due to lone pair on O, it becomes good leaving gp. and leads to carbocation.

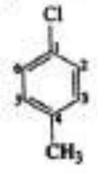
104. (c, d)

$NaBH_4/C_2H_5OH$ and Raney Ni/H_2 in T.H.F. do not reduce acid (—COOH), ester (—COOR) and epoxide

105. (b, c)

1-Chloro-4-methylbenzene

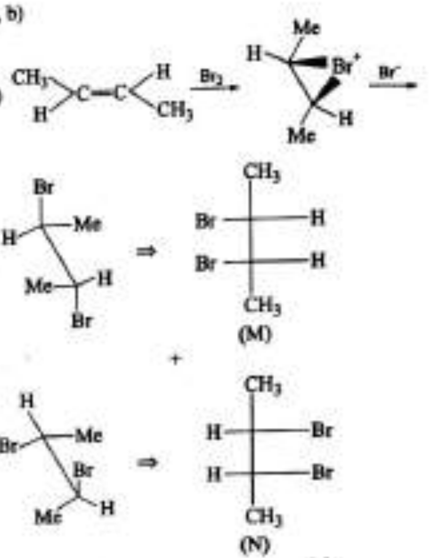
Since "Toluene" is accepted by IUPAC as a name of parent carbon chain, therefore



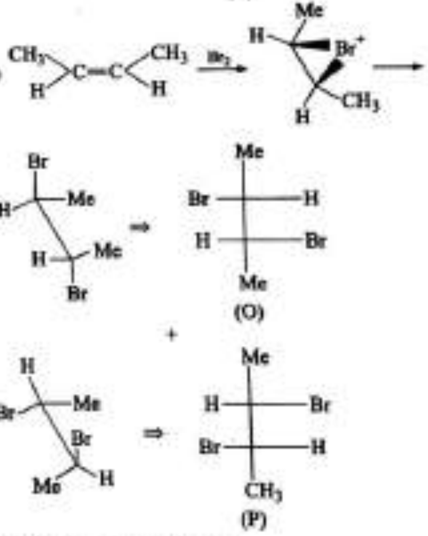
can also be named as 4-chlorotoluene.

106. (a, b)

(i)



(ii)



(O) and (P) are enantiomers

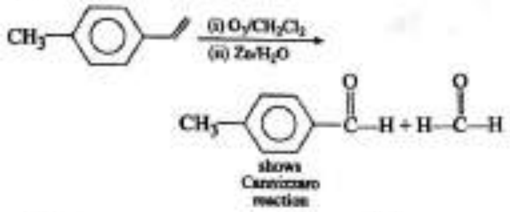
(a) (M) and (O) are distereomers of each other
(N) and (P) are distereomers of each other

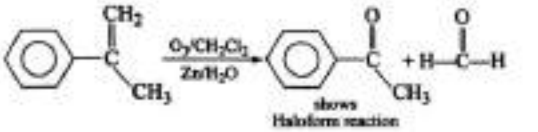
(b) Addition of Br_2 on alkene follows non-classical carbocation mechanism. It is anti or trans addition

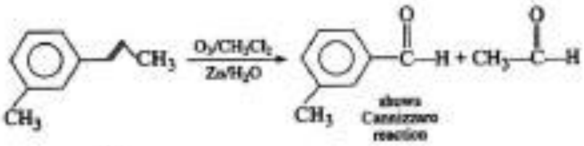
(c) (O) and (P) are enantiomers

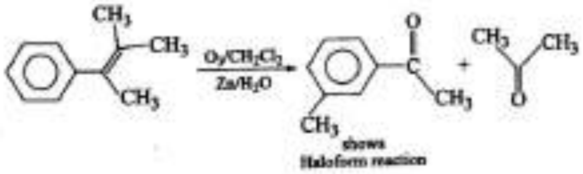
(d) (M) and (N) are identical and (O) and (P) are enantiomers
(M and O) are distereomers and (N and P) are distereomers

107. (a, c)









108. (a, c, d)

When medium is highly polar and protic

S_{N^1} **order :**

benzyl > allyl > 3° > 2° > 1° > methyl > phenyl halide

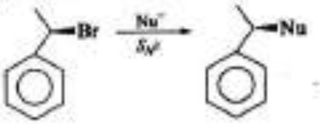
Hence options (c) is correct.

S_{N^2} **order :**

phenyl > methyl > 1° > 2° > 3° > allyl > benzyl halide

(I) and (II) will follow S_{N^2} when medium is polar aprotic and nucleophile is strong and in high concentration.

Option (d) is correct as



Inversion in case of S_{N^2}.

Option (b) is incorrect for both S_{N^1} and S_{N^2} conditions.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Organic molecules show chemical reaction on account of homolytic bond fission or heterolytic bond fission in addition to inductive effect, electromeric effect,' resonance and hyperconjugation. The usual reactions shown by organic molecules are substitution (S_N1) and (S_N2) addition (syn and anti) and elimination (E_1 and E_2) reactions along with rearrangement reactions. In addition to these, various oxidation and reduction reactions are also given. The species which attacks a +ve centre is called nucleophile and the species capable of attacking –ve centres are called electrophile.

[1] Which is not formed during homolytic or heterolytic fission of covalent bond?

(a) Free radical (b) Carbocation

(c) Carbanion (d) Bridged carbocation

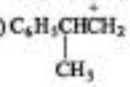
[2] The electromeric effect in a molecule occurs only of it has atleast one :

(a) σ-bond (b) lone pair

(c) π-bond (d) three centred bond

[3] The most stable carbocation among the following is :

(a) $C_6H_5^+$

(b) 
$C_6H_5\overset{+}{C}H\underset{CH_3}{\underset{|}{C}}H_2$

(c) $C_6H_5-\overset{+}{C}(CH_3)_2$ (d) $C_6H_5\overset{+}{C}H_2$

[4] During nitration of an organic compound, HNO_3 acts as :

(a) acid (b) base

(c) neutral (d) salt

[5] Dextro 2-bromobutane on treatment with NaOH(*aq*) will not give :

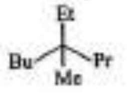
(a) racemic mixture of 2-butanol if S_N1 is obeyed

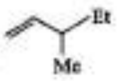
(b) laevo form of 2-butanol if S_N2 is obeyed

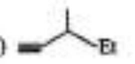
(c) dextro form of 2-butanol if S_N2 is obeyed

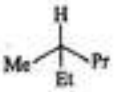
(d) 100% inversion if S_N2 is obeyed

[6] Which does not represent the simplest chiral alkane, alkene or alkyne?

(a) 

(b) 

(c) 

(d) 

[7] Which of the following is neither a nucleophile or electrophile?

(a) NO_2^+ (b) Cl^+

(c) CN^- (d) $(CH_3)_4N^+$

Comprehension 2 : Two molecules having same molecular formula but different structural formula due to migration of mobile H-atom between two polyvalent atoms is called tautomerism. The two isomers possess different functional groups and show interconversion of one into other giving rise to a dynamic equilibrium. These show such rapid interconversion that they cannot be independently isolated, *e.g.*,

$$CH_3 \cdot CHO \rightleftharpoons CH_2=CHOH$$

[1] The compound cyclohex-1-en-ol-1 can be distinguished from cyclohexanol by :

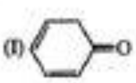
(I) NH_2OH (II) Neutral $FeCl_3$ (III) $Ag(NH_3)_2OH$

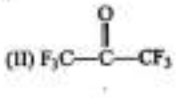
(IV) Br_2 water

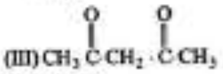
(a) I, II, IV (b) I, III

(c) II, III (d) II, IV

[2] Tautomerism is possible in :

(I) 

(II) 
$F_3C-\overset{O}{\overset{\|}{C}}-CF_3$

(III) 
$CH_3\overset{O}{\overset{\|}{C}}CH_2\cdot\overset{O}{\overset{\|}{C}}CH_3$

(IV) $CH_3CH_2NO_2$

(a) I, III, IV (b) I, II, III

(c) I, II, IV (d) II, III, IV

[3] Enolic form of acetyl acetone is stabilized by :

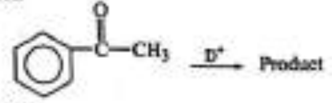
(a) van der Waals' forces

(b) intermolecular H-bonding

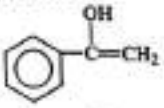
(c) intramolecular H-bonding

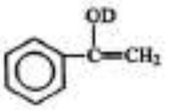
(d) dipole-dipole repulsion

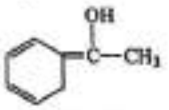
[4] In the reaction

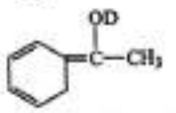


the product is :

(a) 

(b) 

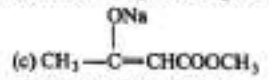
(c) 

(d) 

[5] The solubility of methyl acetoacetate in dilute NaOH solution is due to the formation of :

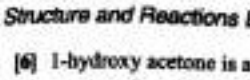
(a) $NaCH_2 \cdot CO \cdot CH_2COOCH_2Na$

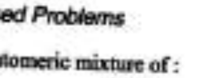
(b) $CH_3COCH_2COOCH_2Na$

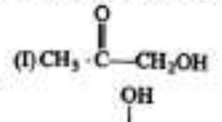
(c) 
$CH_3-\overset{ONa}{\overset{|}{C}}=CHCOOCH_3$

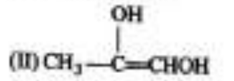
(d) $CH_3CO \cdot CH_2 \cdot COONa$

[6] 1-hydroxy acetone is a tautomeric mixture of :

(I) 
$CH_3\cdot\overset{O}{\overset{\|}{C}}-CH_2OH$

(II) 
$CH_3-\overset{OH}{\overset{|}{C}}=CHOH$

(III) 

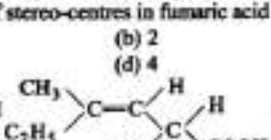
(IV) 
$CH_2=\overset{OH}{\overset{|}{C}}-CH_2OH$

(a) I, III
(b) I, IV
(c) I, II
(d) It does not show tautomerism

Comprehension 3: Organic compounds having same molecular formula and same structure formula but different spatial arrangements of atoms or groups are known as stereo-isomers. The atom in a molecule round which positions of atoms are to be changed is called stereo-centre. In geometrical isomerism, it represents for a doubly bonded atom whereas in optical isomerism it represents for a chiral centre. *cis* and *trans* are two common forms of geometrical isomerism whereas enantiomers (a pair of *d* and *l*) are common forms of optical isomers :

[1] Select the set of incorrect statements :
(a) A *cis*-isomer has lower b.pt. than *trans*-isomer
(b) A *cis*-isomer has lower m.pt. than *trans*-isomer
(c) Butan-2-ol has chiral carbon
(d) 3-methyl-3-ethyl octane is simplest chiral alkane

[2] The number of stereo-centres in fumaric acid :
(a) 1 (b) 2
(c) 3 (d) 4

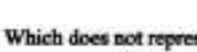
[3] The compound  shows :
(I) geometrical isomerism (II) optical isomerism
(III) stereo-isomerism (IV) none of these
(a) I, II, III (b) II
(c) I (d) IV

[4] The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane are :
(a) 2 (b) 3
(c) 4 (d) 1

[5] The number of structural and configurational isomers of a bromocompound C_5H_9Br formed by the addition of HBr on 2-pentyne respectively are :
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

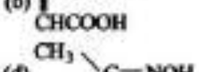
[6] Total number of isomers shown by C_4H_8 are :
(a) 3 (b) 4
(c) 5 (d) 6

[7] Which does not represent geometrical isomers?

(a) 

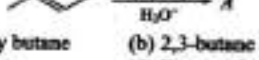
(b) 
$\begin{matrix}CHCOOH\\ \|\\ CHCOOH\end{matrix}$

(c) $CH_3CH=NOH$

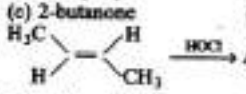
(d) 
${CH_3 \atop CH_3}\!>C=NOH$

Comprehension 4: The carbon-carbon double bond in a molecule is capable of decolorizing Br_2/CCl_4 following free radical mechanism. The decolorization of Br_2/water solution however shows electrophilic addition. The addition of bromine to cyclopentene provides evidence for bromonium ion immediate in bromine addition. It follows ionic mechanism. When cyclopentene reacts with bromine in presence of CCl_4 anti addition occurs and gives *trans*-isomer so addition of halogen to an alkene is a stereospecific reaction. *cis*-alkene on addition with halogen gives *meso* products and *trans* alkene on addition gives racemic mixture.

[1] In the reaction given below *A* is :



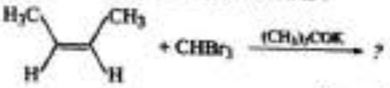
(a) 2,3-epoxy butane (b) 2,3-butane diol
(c) 2-butanone (d) Epoxy ethane

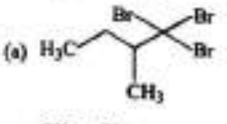
[2]  A Intermediate forms are :

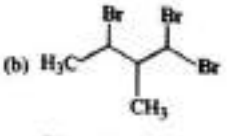
(a) hydroxonium ion (b) chloronium ion
(c) hydronium ion (d) none of these

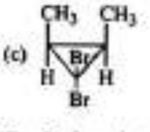
[3] *Trans*-2-butene on reacting with Br_2 in CCl_4 forms mainly :
(a) ± 2,3-dibromobutane (b) + 2,3-dibromobutane
(c) −2,3-dibromobutane (d) *Meso*-2,3-dibromobutane

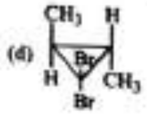
[4] The product obtained in the reaction is :



(a) 

(b) 

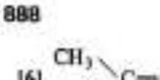
(c) 

(d) 

[5] The final product in

 II, is :

(a) *Meso*-2,3-butane diol (b) 2-butanol
(c) ±2,3-butandiol (d) 2-butanone

[6]  $(CH_3)_2C{=}C(CH_3)_2$ on passing through 5% Br_2/CCl_4 which seems to be correct :

(a) No colour change in Br_2/CCl_4 solution

(b) Addition product as 2,3-dibromo-2,3-dimethyl butane

(c) Colour of Br_2/CCl_4 is discharged

(d) The reaction occurs through electrophilic addition

[7] Which of the following statements are correct?

(1) Addition of Br_2 on 2,3-dimethyl butene is free radical addition in presence of H_2O

(2) Addition of Br_2 on ethene in presence of NaCl(*aq*) gives only 1,2-dibromo ethane

(3) Addition of Br_2 on alkene occurs at more faster rate in presence of polar or ionising medium

(4) Addition of Br_2 on alkene in a vessel coated with steric acid occurs at faster rate than in a bottle coated with wax

(a) 1, 2 (b) 1, 2, 4

(c) 2, 3, 4 (d) 3, 4

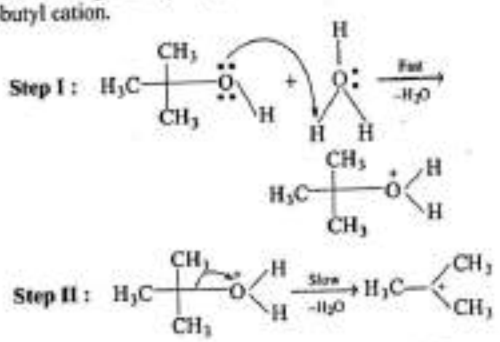
Comprehension 5: The dehydration of alcohols and the conversion of alcohols to alkyl halides by treatment of hydrogen halides are similar in two important ways suggesting the formation of carbocation as key intermediate.

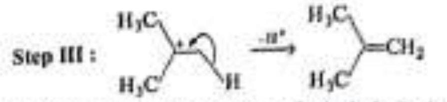
(a) Both reactions are protonated by acids.

(b) The reactivity of alcohols decrease in the order, tertiary > secondary > primary due to the formation of stable carbocations, which is stabilized by hyperconjugation and +*I* effect. The dehydration of alcohol follows three steps mechanism for acid-base catalysed dehydration of least stable tertiary butyl alcohol, *i.e.*,

$$(CH_3)_3COH \xrightarrow[\Delta]{H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

In step I, protonation (acid catalysed) of *tert*-butyl alcohol takes place. In step II, dissociation of *tert*-butyloxenium ion takes place followed by formation of carbocation. Alkene is formed in step III by deprotonation (base catalysed) of *tert*-butyl cation.





Another important reaction of alcohols is iodoform reaction given by ethanol (in primary alcohols) and are secondary alcohols having 2-ol nature. Such alcohols give yellow ppt. of CHI_3 with NaOH and I_2 solution.

[1] Why dehydration of vinyl alcohols is not difficult?

(a) Due to high enthalpy of vinylic —C—OH bond

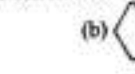
(b) Due to unstable nature of =C—OH both by tautomerism

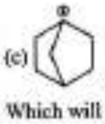
(c) Carbocation never forms in case of vinyl alcohol

(d) Both (a) and (b) are correct

[2] Which carbocation will not form an intermediate?

(a) $(C_6H_5)_3\overset{+}{C}$

(b) 

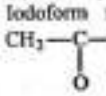
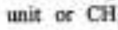
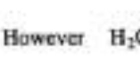
(c) 

(d) $CH_3{=}\overset{+}{C}H$

[3] Which will give iodoform test?

(a) 2-methylpropan-2-ol (b) Ethyl acetoacetate

(c) 2-methylbutan-2-ol (d) 3-methylpentan-2-ol

[4] Iodoform reaction is given by molecules having  $CH_3{-}\underset{\|}{\underset{O}{C}}{-}$ unit or  $CH_3{-}\underset{|}{C}HOH$ unit attached to carbon or H-atom. However  $H_2C(COR)_2$ and $CH_3\cdot CO\cdot CH_2COOC_2H_5$ does not give iodoform reaction because :

(a) I_2 reacts at active H-atom

(b) I_2 reacts at α-methyl group

(c) I_2 does not react with these molecule

(d) Hydrolysis of iodide substituted molecule does not occur

[5] The reagent used to distinguish 1-cycloethanol and 2-cycloethanol is :

(a) Soda lime (b) NaOI + H_2O

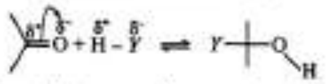
(c) Acidified $KMnO_4$ (d) (*Aq.*) $FeCl_3$

[6] An alcohol on iodoform reaction give iodoform and sodium salt of unsaturated acid containing 3 carbon atoms. The alcohol is :

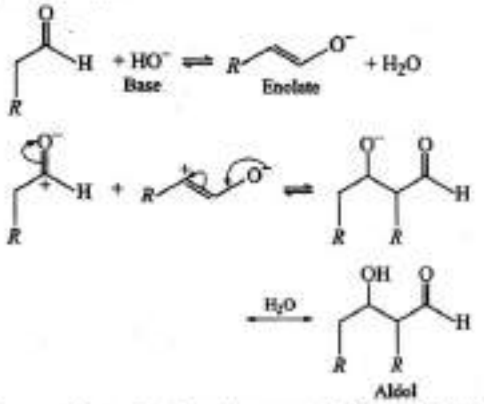
(a) But-3-en-2-ol (b) Prop-2-en-2-ol

(c) Pent-3-en-2-ol (d) 3-methyl-but-3-en-2-ol

Comprehension 6: Aldehydes and ketones are polar molecule. Nucleophiles attack on carbonyl group (>C=O) at carbon (positively charged) and electrophiles are attacked by oxygen. The characteristic reaction of aldehyde and ketone is nucleophilic addition to the carbon of carbonyl group.

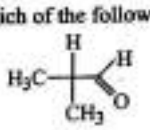


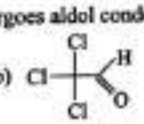
Aldehydes and ketones undergo condensation only when they consist α-hydrogen atom. The reaction takes place in presence of dilute alkali and one aldehyde molecule is partially converted to its enolate anion by the base. The enolate ion undergoes nucleophilic addition to the carbonyl group. The alkoxide formed in nucleophilic addition step, abstracts a proton from the solvent to give aldol, which consists aldehydic and hydroxyl group.

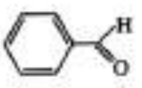


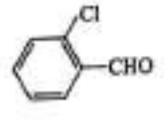
The reactivity of carbonyl compounds for nucleophilic addition reaction is inversely proportional to +*I* effect. In absence of α-H atom, the aldehydes undergo Cannizzaro's reaction.

[1] Which of the following undergoes aldol condensation?

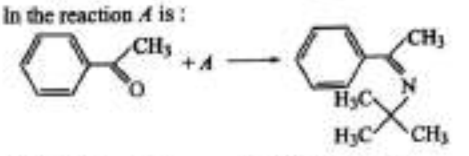
(a) 

(b) 

(c) 

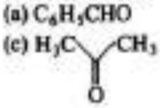
(d) 

[2] In the reaction *A* is :



(a) $(CH_3)_2—NH$
(b) $(CH_3)_3—N$
(c) $(CH_3)_3C—NH_2$
(d) none of these

[3] Which one is most reactive for addition of alcohol on carbonyl group?

(a) C_6H_5CHO
(b) HCHO
(c) 
(d) $CH_3 \cdot CHO$

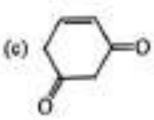
[4] How many aldol products can form when 2-butanone and propanaldehyde reacts in presence of dilute base?

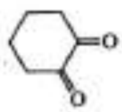
(a) 4
(b) 5
(c) 6
(d) 7

[5] Tautomerism is not exhibited by :

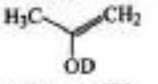
(a) 

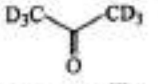
(b) 

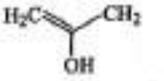
(c) 

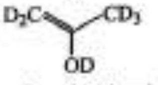
(d) 

[6] The enol form of acetone after treatment with D_2O gives:

(a) 

(b) 

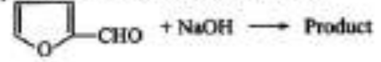
(c) 

(d) 

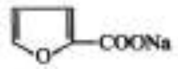
[7] Which does not undergo intermolecular Cannizzaro's reaction?

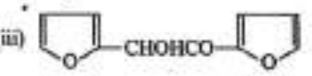
(a) *m*-chloro benzaldehyde
(b) 2-methyl propanal
(c) Glyoxalic acid
(d) Glyoxal

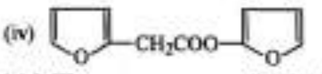
[8] The product formed in the reaction are :



(i) 

(ii) 

(iii) 

(iv) 

(a) I, III
(b) II, III
(c) III, IV
(d) I, II

Comprehension 7 : Organic compounds having —COOH group are called carboxylic acid. An organic compound having —OH group and —COOH group both, are called hydroxy acid. Molecules with two carboxylic groups are dibasic and those having 3 carboxy group are tribasic acid. A dibasic acid having two —COOH group on adjacent carbon atoms looses H_2O to form inner anhydride. Hydroxy acids behave both as acids and alcohols and the hydroxyl and carboxyl groups do not interfere with each other when they are far apart. The heating of hydroxy acids however gives different products depending upon the nature of α-, β- or γ-hydroxy substituted acids.

[1] Which are correct for citric acid?

(I) It forms three series of salts
(II) It is α-hydroxy acid
(III) It is β-hydroxy acid
(IV) On heating to 150°C it gives aconitic acid
(V) It contains two —OH group

(a) I, II, IV, V (b) I, II, III, IV
(c) I, II, IV (d) I, III, IV

[2] α-hydroxy acids on heating forms :

(a) Lactides (b) Lactones
(c) Unsaturated acids (d) Either of these

[3] Which one is not correct for tartaric acid?

(I) It is an unsaturated acid
(II) It has two —OH group and two —COOH group
(III) It exist in four forms
(IV) It gives pyruvic acid on heating
(V) On heating it forms anhydride

(a) II, IV (b) II, III, IV
(c) I, II, V (d) II, V

[4] Which of the following does not forms its anhydride?

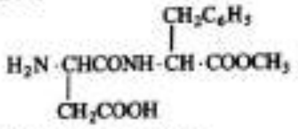
(I) Maleic acid (II) Tartaric acid
(III) Citric acid (IV) Fumaric acid
(V)Malic acid (VI) Malonic acid

(a) II, III, IV, VI (b) II, III, IV, V
(c) I, II, III, IV (d) III, IV, V, VI

[5] Which one is not correct for fumaric and maleic acid?

(a) Both are dibasic acid
(b) $\mathrm{p}K_{a_1}$ for maleic acid is lesser than $\mathrm{p}K_{a_1}$ of fumaric acid
(c) $\mathrm{p}K_{a_2}$ for maleic acid is greater than $\mathrm{p}K_{a_2}$ for fumaric acid
(d) $\mathrm{p}K_{a_1}$ of maleic acid is more than fumaric acid

Comprehension 8 : Aspartame is an artificial sweetener having peptide bond in its structure given below :



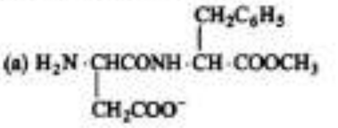
$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COOH}{|}}{C}HCONH\text{-}\overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOCH_3}$$

[1] It contains the functional groups :

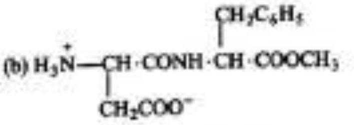
(I) Amino (II) Carboxylic (III) Ester (IV) Amide
(V) Benzyl

(a) I, II, III, IV, V (b) I, II, III, IV
(c) I, II, III (d) I, II, IV, V

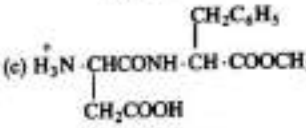
[2] Its zwitter ion structure is :

(a) 

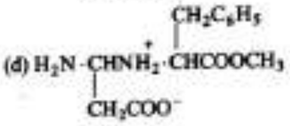
$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COO^-}{|}}{C}HCONH\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOCH_3}$$

(b) 

$$\mathrm{H_3\overset{+}{N}—\underset{\underset{\displaystyle CH_2COO^-}{|}}{C}H\cdot CONH\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOCH_3}$$

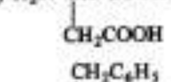
(c) 

$$\mathrm{\overset{+}{H}_3N\cdot \underset{\underset{\displaystyle CH_2COOH}{|}}{C}HCONH\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOCH_3}$$

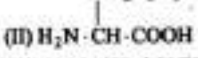
(d) 

$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COO^-}{|}}{C}HN\overset{+}{H}_2\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}HCOOCH_3}$$

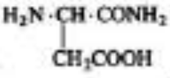
[3] Aspartame on hydrolysis forms two amino acids :

(I) 

$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COOH}{|}}{C}H\cdot COOH}$$

(II) 

$$\mathrm{H_2N\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOH}$$

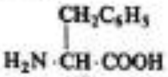
(III) 

$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COOH}{|}}{C}H\cdot CONH_2}$$

(IV) 

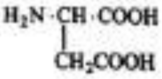
$$\mathrm{H_2N\cdot CHCOHN\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOH}$$

(a) I, II (b) III, IV
(c) I, III (d) II, IV

[4] Which is correct for 

$$\mathrm{H_2N\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOH}$$

(I) and



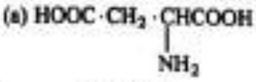
$$\mathrm{H_2N\cdot \underset{\underset{\displaystyle CH_2COOH}{|}}{C}H\cdot COOH}$$

(II)

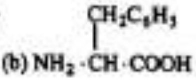
(1) (I) is less hydrophobic
(2) (I) is more hydrophobic
(3) $C_6H_5\cdot CH_2^-$ is more hydrophobic than CH_2COOH
(4) $C_6H_5—CH_2—$ is less hydrophobic than CH_2COOH

(a) 2, 3 (b) 1, 4
(c) 2, 4 (d) 1, 3

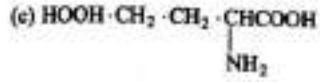
[5] Aspartic acid has the structure :

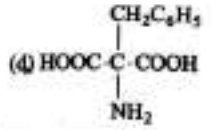
(a) 

$$\mathrm{HOOC\cdot CH_2\cdot \underset{\underset{\displaystyle NH_2}{|}}{C}HCOOH}$$

(b) 

$$\mathrm{NH_2\cdot \overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}H\cdot COOH}$$

(c) 
$HOOH \cdot CH_2 \cdot CH_2 \cdot \underset{\underset{NH_2}{|}}{C}HCOOH$

(d) 
$HOOC \cdot \overset{\overset{CH_2C_6H_5}{|}}{\underset{\underset{NH_2}{|}}{C}} \cdot COOH$

Comprehension 9: The term arene is used to benzene and its homologues. The term aromatic refers for the organic compounds which obey Huckel rule, *i.e.*, all aromatic compounds must possess π electrons equal to $(4n+2)$ where n is any positive integer. Due to aromatic nature benzene and its homologues show electrophilic substitution reactions producing *o*- and *p*-substituted derivatives or *m*-substituted derivatives. The orientation (new incoming group's substitution) in benzene nucleus is explained in terms of directive influence of the groups.

[1] Side chain of a nucleus can be oxidised to —COOH group only when it has atleast one :

(a) Vinylic H
(b) Benzylic H
(c) Allylic H
(d) Olefinic H

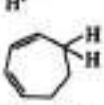
[2] The general formula for arenes having monocyclic nature where y represents number of 6-membered rings is :

(a) C_nH_{2n-6y}
(b) C_nH_{2n-8y}
(c) C_nH_{2n-4y}
(d) C_nH_{2n-5y}

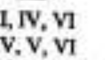
[3] Which of the following are aromatic in nature?

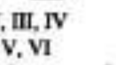
(I) 

(II) 

(III) 

(IV) 

(V) 

(VI) 

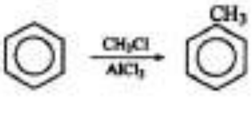
(a) II, III, IV, VI
(b) I, II, III, IV
(c) III, IV, V, VI
(d) IV, V, VI

[4] Which of the following are *m*-directing groups?

(I) $—NH_3^+$
(II) $—NH_2$ in acid
(III) $—CCl_3$
(IV) $—COO^-$
(V) —NC
(VI) —CN

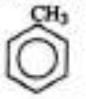
(a) I, II, III, VI
(b) IV, V, VI
(c) III, IV, V
(d) III, IV, VI

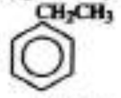
[5] Which of the following statements regarding S_E reaction in C_6H_6 is wrong?

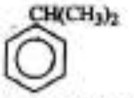


(a) $AlCl_3$ acts as Lewis acid
(b) $AlCl_3$ acts to produce free radical
(c) $AlCl_3$ acts to produce electrophile
(d) $AlCl_3$ acts as halogen carrier

[6] Oxidation of which arene homologues does not produce benzoic acid with acidic $KMnO_4$ gives respectively :

(a) 

(b) 

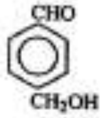
(c) 

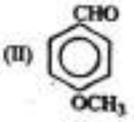
(d) 

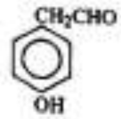
Comprehension 10: Five isomeric para-disubstituted aromatic compounds (*A*) to (*E*) with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds :

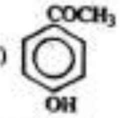
(i) Both (*A*) and (*B*) form a silver mirror with Tollen's reagent; also, (*B*) gives a positive test with $FeCl_3$ solution but (*A*) not.
(ii) (*C*) gives positive iodoform test.
(iii) (*D*) is readily extracted in aqueous $NaHCO_3$ solution.
(iv) (*E*) on acid hydrolysis gives 1,4-dihydroxybenzene.

[1] The compound (*A*) is :

(I) 

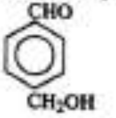
(II) 

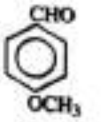
(III) 

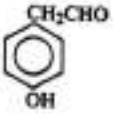
(IV) 

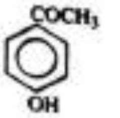
(a) I, II, III
(b) I, II, III, IV
(c) I, II
(d) I, IV

[2] The compound (*B*) is :

(a) 

(b) 

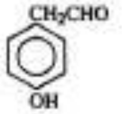
(c) 

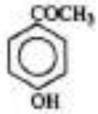
(d) 

[3] The compound (C) is :

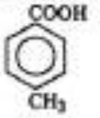
(a) 

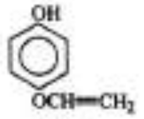
(b) 

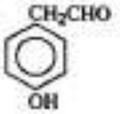
(c) 

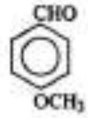
(d) 

[4] The compound (D) is :

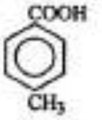
(a) 

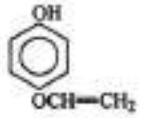
(b) 

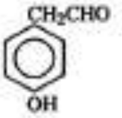
(c) 

(d) 

[5] The compound (E) is :

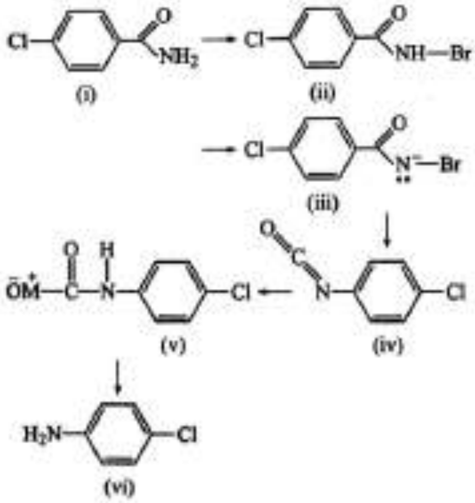
(a) 

(b) 

(c) 

(d) 

Comprehension 11: $RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this reaction, $RCONHBr$ is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction. (IIT 2006)

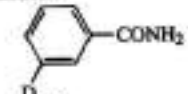
[1] How can the conversion of (i) to (ii) be brought about?

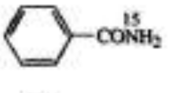
(a) KBr
(b) KBr + CH_3ONa
(c) KBr + KOH
(d) Br_2 + KOH

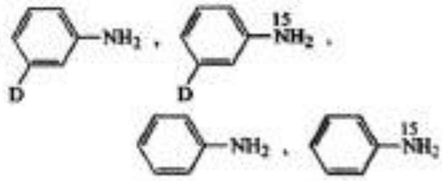
[2] Which is the rate determining step in Hofmann bromamide degradation?

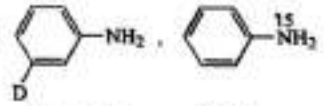
(a) Formation of (i)
(b) Formation of (ii)
(c) Formation of (iii)
(d) Formation of (iv)

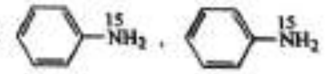
[3] What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?

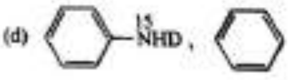

(i)


(ii)

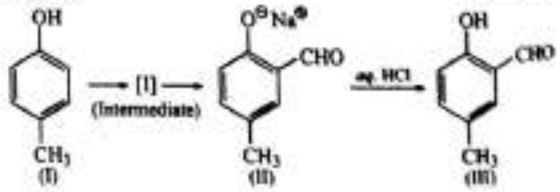
(a) 

(b) 

(c) 

(d) 

Comprehension 12 : Riemer-Tiemann reaction introduces an aldehyde group, into the aromatic ring of phenol, ortho to the hydroxyl group. The reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below. (IIT 2007)



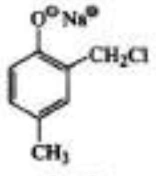
[1] Which one of the following reagents is used in the above reaction?

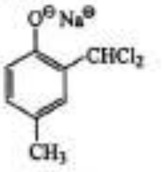
(a) *aq*. NaOH + CH_3Cl (b) *aq*. NaOH + CH_2Cl_2
(c) *aq*. NaOH + $CHCl_3$ (d) *aq*. NaOH + CCl_4

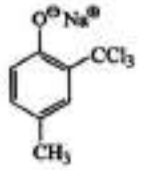
[2] The electrophile in this reaction is :

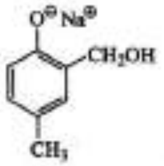
(a) $\ddot{:}CHCl$ (b) $^{+}CHCl_2$
(c) $\ddot{:}CCl_2$ (d) $\ddot{:}CCl_3$

[3] The structure of the intermediate I is :

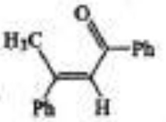
(a) 

(b) 

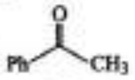
(c) 

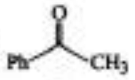
(d) 

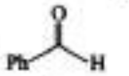
Comprehension 13: A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of I leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**. **(IIT 2008)**

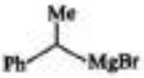
M = 

[1] Compound **H** is formed by the reaction of :

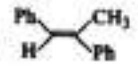
(a)  + PhMgBr

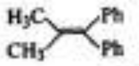
(b)  + $PhCH_2MgBr$

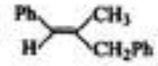
(c)  + $PhCH_2MgBr$

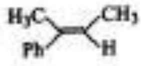
(d)  + 

[2] The structure of compound I is :

(a) 

(b) 

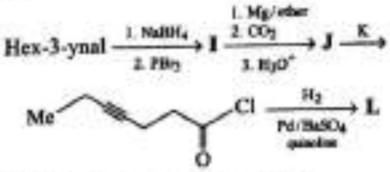
(c) 

(d) 

[3] The structure of compounds **J**, **K** and **L**, respectively, are :

(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$
(b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$
(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$
(d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

Comprehension 14 : In the following reaction sequence, products, **I**, **J** and **L** are formed, **K** represents a reagent.



(IIT 2008)

[1] The structure of the product **I** is :

(a) 

(b) 

(c) 

(d) 

[2] The structure of compounds **J** and **K**, respectively, are :

(a)  and $SOCl_2$

(b)  and SO_2Cl_2

(c)  and $SOCl_2$

(d)  and CH_3SO_2Cl

[3] The structure of product **L** is :

(a) 

(b) 

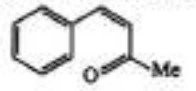
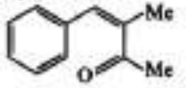
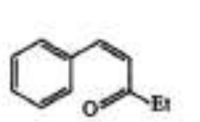
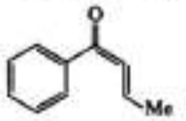
(c) 

(d) 

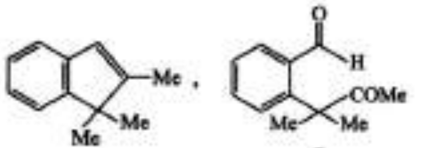
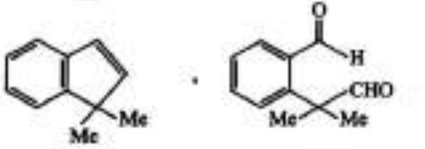
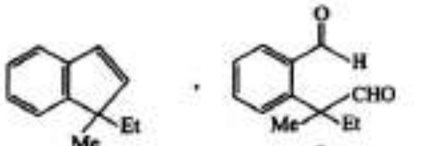
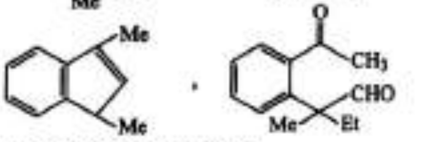
Comprehension 15: A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

$P \xrightarrow[\text{2. } H^+,\ H_2O \quad \text{3. } H_2SO_4,\ \Delta]{\text{1. MeMgBr}} Q \xrightarrow[\text{2. Zn, } H_2O]{\text{1. } O_3} R \xrightarrow[\text{2. } \Delta]{\text{1. } OH^-} S$ (IIT 2009)

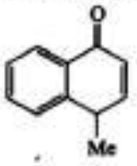
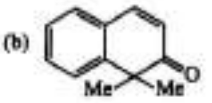
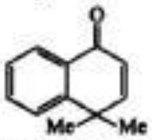
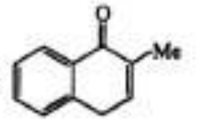
[1] The structure of the carbonyl compound **P** is :

(a)

(b)

(c)

(d)


[2] The structure of the products **Q** and **R**, respectively, are :

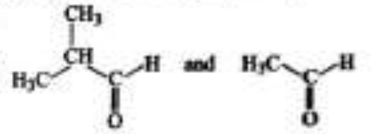
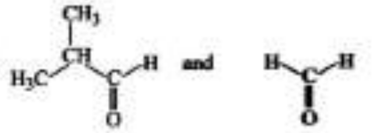
(a)

(b)

(c)

(d)


[3] The structure of the product **S** is :

(a)

(b)

(c)

(d)


Comprehension 16: Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below : (IIT 2010)

[1] The compounds *P* and *Q* respectively are :

(a)

(b)

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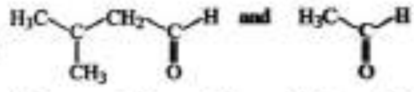
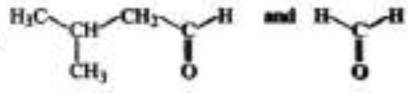
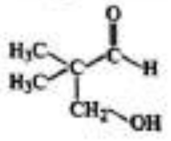
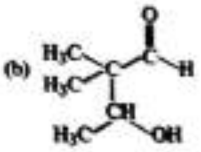
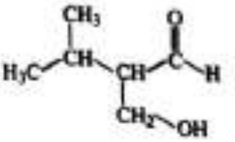
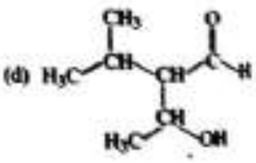
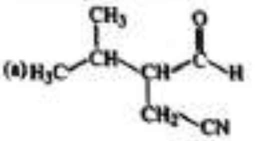
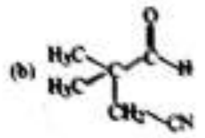
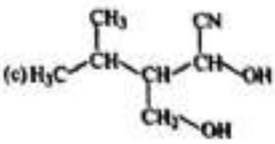
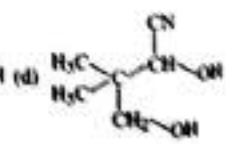

(d)


[2] The compound *R* is :

(a)

(b)

(c)

(d)


[3] The compound *S* is :

(a)

(b)

(c)

(d)


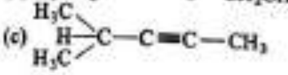
Comprehension 17 : An acyclic hydrocarbon *P*, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which *Q* is an intermediate organic compound. **(IIT 2011)**

$$\underset{(C_6H_{10})}{P} \xrightarrow[\text{(ii) NaBH}_4\text{/ethanol} \quad \text{(iii) dil. acid}]{\text{(i) dil. H}_2\text{SO}_4\text{/HgSO}_4} Q \xrightarrow[\text{(ii) O}_3 \quad \text{(iii) Zn/H}_2\text{O}]{\text{(i) conc. H}_2\text{SO}_4 \text{ (catalytic amount) } (-\text{H}_2\text{O})} 2CH_3COCH_3$$

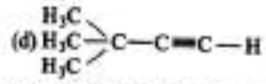
[1] The structure of compound *P* is :

(a) $CH_3CH_2CH_2CH_2—C{\equiv}C—H$

(b) $H_3CH_2C—C{\equiv}C—CH_2CH_3$

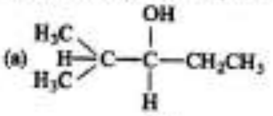
(c) 

$(H_3C)_2CH—C{\equiv}C—CH_3$

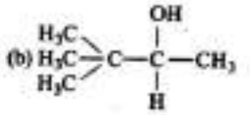
(d) 

$(H_3C)_3C—C{\equiv}C—H$

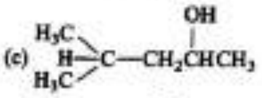
[2] The structure of the compound *Q* is :

(a) 

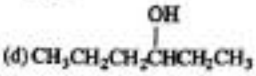
$(H_3C)_2CH—CH(OH)—CH_2CH_3$

(b) 

$(H_3C)_3C—CH(OH)—CH_3$

(c) 

$(H_3C)_2CH—CH_2CH(OH)CH_3$

(d) 

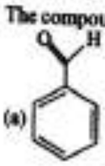
$CH_3CH_2CH_2CH(OH)CH_2CH_3$

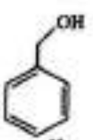
Comprehension 18 : In the following reaction sequence, the compound *J* is an intermediate :

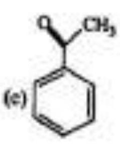
$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\text{(ii) SOCl}_2 \quad \text{(iii) anhyd. AlCl}_3]{\text{(i) H}_2\text{, Pd/C}} K$$

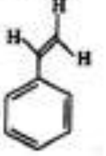
J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and a positive Baeyer's test. **(IIT 2012)**

[1] The compound *I* is :

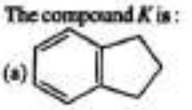
(a) 

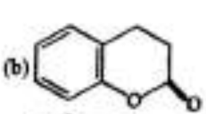
(b) 

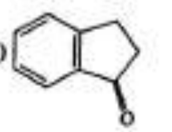
(c) 

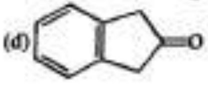
(d) 

[2] The compound *K* is :

(a) 

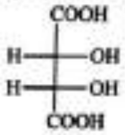
(b) 

(c) 

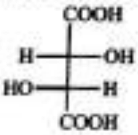
(d) 

Comprehension 19 : *P* and *Q* are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2 / H_2O. On heating, *P* forms the cyclic anhydride.

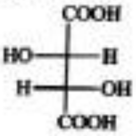
Upon treatment with dilute alkaline $KMnO_4$, *P* as well as *Q* could produce one or more than one from *S*, *T* and *U*.



(*S*)



(*T*)

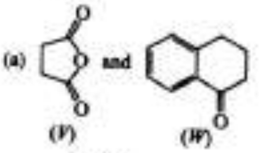


(*U*)

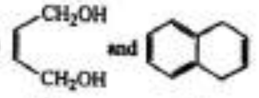
[JEE (Advanced) II 2013]

[1] In the following reaction sequences *V* and *W* are, respectively

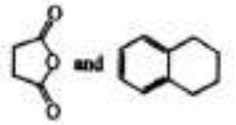
$$Q \xrightarrow[\Delta]{H_2/Ni} V$$

(a) 

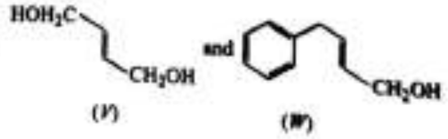
(*V*) (*W*)

(b) 

(*V*) (*W*)

(c) 

(*V*) (*W*)

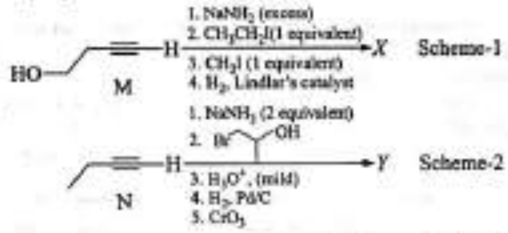
(d) 

(*V*) (*W*)

[2] Compounds formed from P and Q are, respectively : **[JEE (Advanced) II 2013]**

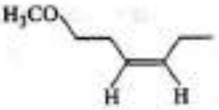
(a) Optically active S and optically active pair (T, U)
(b) Optically inactive S and optically inactive pair (T, U)
(c) Optically active pair (T, U) and optically active S
(d) Optically inactive pair (T, U) and optically inactive S

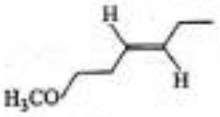
Comprehension 20 : Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.

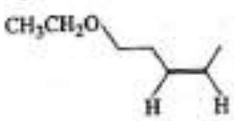


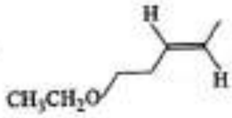
[JEE (Advanced) II 2014]

[1] The product X is :

(a)


(b)


(c)


(d)


[2] The correct statement with respect to product Y is :

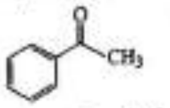
(a) It gives a positive Tollens test and is a functional isomer of X.
(b) It gives a positive Tollens test and is a geometrical isomer of X.
(c) It gives a positive iodoform test and is a functional isomer of X.
(d) It gives a positive iodoform test and is a geometrical isomer of X.

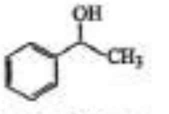
Comprehension 21 : In the following reaction

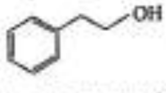
$$\begin{tikzcd}
C_8H_6 \arrow[r, "Pd\text{-}BaSO_4", "H_2"'] \arrow[d, "H_2O"', "HgSO_4,\ H_2SO_4"'] & C_8H_8 \arrow[r, "(i)\ B_2H_6", "(ii)\ H_2O_2,\ NaOH,\ H_2O"'] & X \\
C_8H_8O \arrow[r, "(i)\ EtMgBr,\ H_2O", "(ii)\ H^+,\ heat"'] & Y &
\end{tikzcd}$$

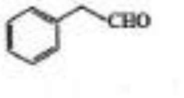
[JEE (Advanced) II 2015]

[1] Compound X is :

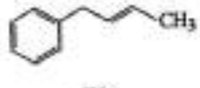
(a)


(b)


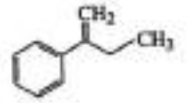
(c)


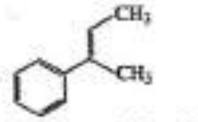
(d)


[2] The major compound Y is :

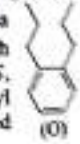
(a)


(b)


(c)


(d)


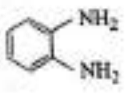
Comprehension 22 : Treatment of compound O with $KMnO_4 / H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with $Br_2/NaOH$ produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.

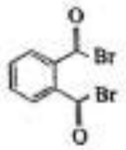


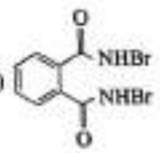
(O)

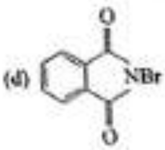
[JEE (Advanced) II 2016]

[1] The compound R is :

(a)


(b)


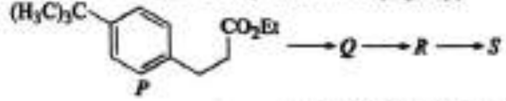
(c)


(d)


[2] The compound T is :

(a) glycine
(b) alanine
(c) valine
(d) serine

Comprehension 23 : The reaction of compound *P* with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives *Q*. The compound *Q* on treatment with H_2SO_4 at 0°C gives *R*. The reaction of *R* with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces comound *S*. [Et in compound *P* is ethyl group].



P

[JEE (Advanced) II 2017]

[1] The reactions, *Q* to *R* and *R* to *S*, are :

(a) Dehydration and Friedel-Crafts acylation

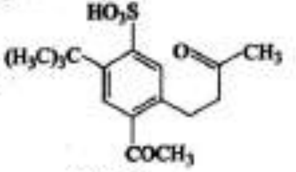
(b) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation

(c) Aromatic sulfonation and Friedel-Crafts acylation

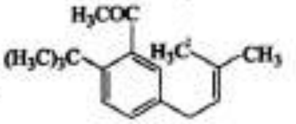
(d) Friedel-Crafts alkylation and Friedel-Crafts acylation

[2] The product *S* is :

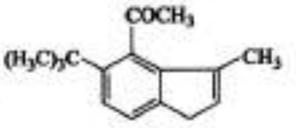
(A)



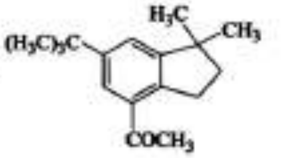
(B)



(C)



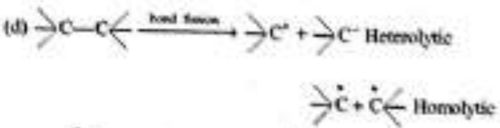
(D)



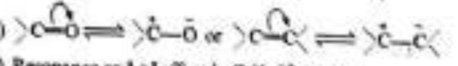
SOLUTIONS

Comprehension 1

[1] (d)



[2] (c)

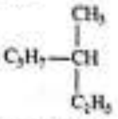


[3] (c) Resonance and +*I* effect in $C_6H_5C^+(CH_3)_2$

[4] (b) $\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow NO_2^+ + HSO_4^- + H_3\dot{O}$

[5] (c) This is against the characteristics of S_N2

[6] (a) The simplest alkane with chirality is

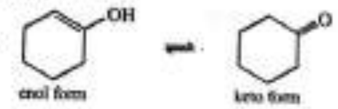


$C_3H_7-\underset{C_2H_5}{\overset{CH_3}{CH}}$

[7] (d) It can neither accept electron pair nor can donate.

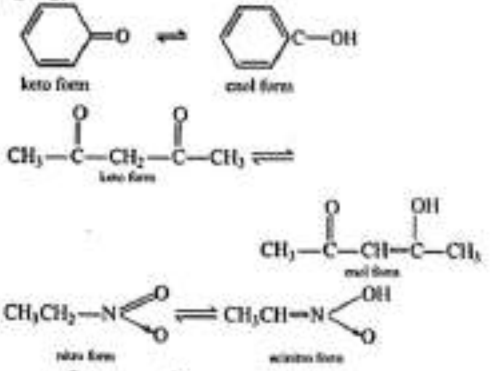
Comprehension 2

[1] (a)

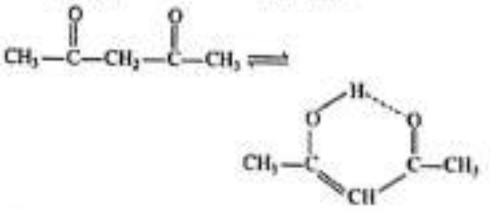


$FeCl_3(aq)$ gives +ve test with enol form; NH_2OH gives +ve test with keto form. Br_2 water shows decolorisation due to C═C.

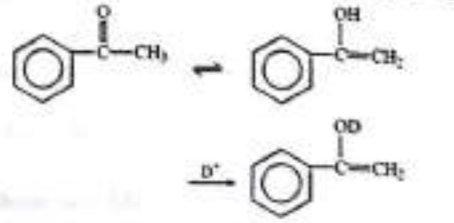
[2] (a)



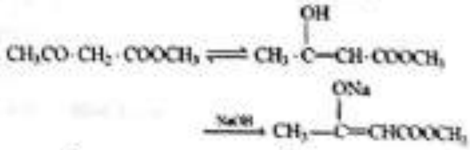
[3] (c)



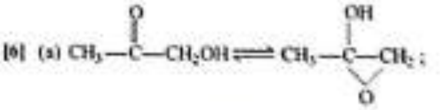
[4] (b)



[5] (c) Enol form reacts with Na to form sodium salt.



[6] (a)

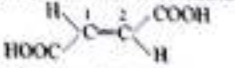


It is ring chain tautomerism.

Comprehension 3

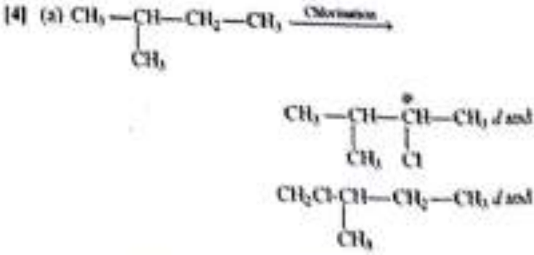
[1] (d) *cis* being usually more polar and thus high b.pt. Also *trans*-shows more asymmetry in close packing, thus low m.pt. 3-methyl hexane is simplest chiral alkane.

[2] (b) An atom in a molecule whose any two groups when interchanged produces stereoisomers is called stereocentre.



[3] (a) It has C═C and one chiral centre.

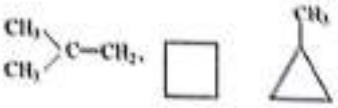
[4] (a)



[5] (b) $CH_3\cdot C{\equiv}CH-CH_2\cdot CH_3 \xrightarrow{HBr} CH_3\cdot CH_2-CHBr\cdot CH_2\cdot CH_3$

It has *cis* and *trans* form. The other four are structural isomerism by allocating Br at carbon 1,2,4 and 5.

[6] (d) $CH_3\cdot CH_2\cdot CH{=}CH_2$, $\underset{\text{cis and trans}}{CH_3CH{=}CH\cdot CH_3}$,

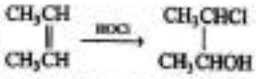


[7] (d) Acetone oxime has two similar gp round doubly bonded carbon.

Comprehension 4

[1] (a)

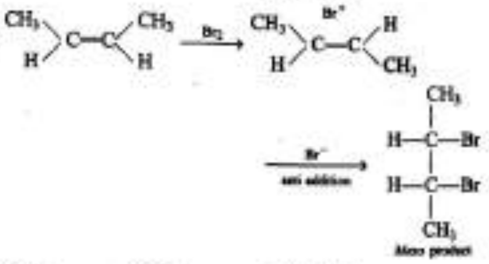
[2] (b)



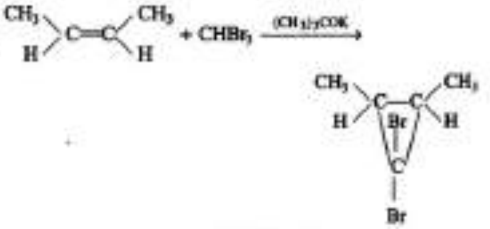
$$CH_3CH{=}CHCH_3 \xrightarrow{HOCl} CH_3CHCl{-}CH_3CHOH$$

$$HOCl + H^+ \rightleftharpoons ClOH_2^+ \rightleftharpoons \underset{\text{Chloronium ion}}{Cl^+} + H_2O$$

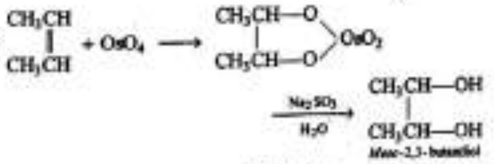
[3] (d)



[4] (c)

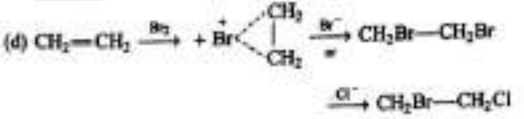


[5] (a)



[6] (a) The given alkene has no olefinic H-atom and thus no reaction.

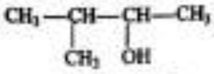
[7] (d)



Comprehension 5

[1] (d) These are facts.

[2] (c) Rest all will form carbocation.

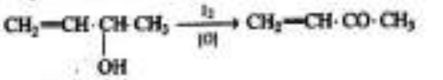
[3] (d)  $CH_3{-}\underset{CH_3}{CH}{-}\underset{OH}{CH}{-}CH_3$ has $CH_3{-}\underset{|}{C}HOH$ unit responsible for iodoform reaction.

[4] (a) Both have $H_2C\langle$ group attached to electron withdrawing groups and thus H-atom of $\rangle CH_2$ become reactive and such a $H_2C\langle$ group is called reactive methylene gp.

$$\rangle CH_2 + I_2 \longrightarrow \rangle CI_2 \xrightarrow{OH^-} \rangle C(OH)_2 \longrightarrow \rangle C{=}O$$

[5] (b) 1-cycloethanol will give iodoform reaction.

[6] (a)



$$\underset{\text{But-3-en-2-ol}}{CH_2{=}CH{\cdot}\underset{OH}{CH}{\cdot}CH_3} \xrightarrow[{[O]}]{I_2} CH_2{=}CH{\cdot}CO{\cdot}CH_3$$

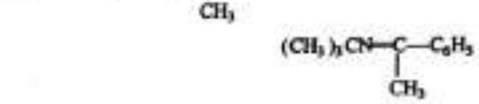
$$CH_2{=}CHCOCH_3 \xrightarrow{I_2} CH_2{=}CH{\cdot}CO{\cdot}CI_3$$

$$CH_2{=}CHCOCI_3 \xrightarrow{NaOH} CH_2{=}CHCOONa + CHI_3$$

Comprehension 6

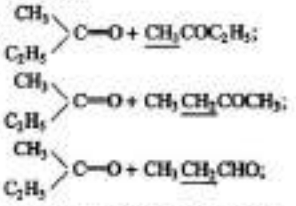
[1] (a) Rest all do not have α-H-atom.

[2] (c)



[3] (a) C_6H_5 give rise to $-I$ effect and thus nucleophilic addition is favoured.

[4] (c)



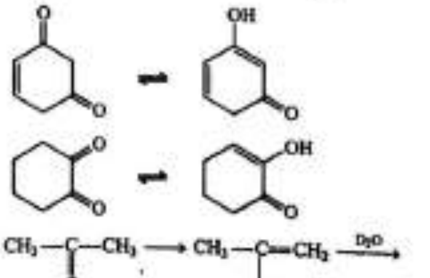
$CH_3CH_2CH{=}O + CH_3\overline{\underline{CH_2}}CHO;$

$CH_3CH_2CH{=}O + \underline{CH_3}\overline{COC}_2H_5;$

$CH_3CH_2CH{=}O + \overline{CH_3}\,\underline{CH_2}COCH_3;$

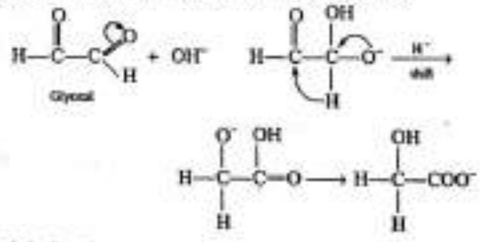
— indicates α-H-atoms

[5] (b)



[6] (a)

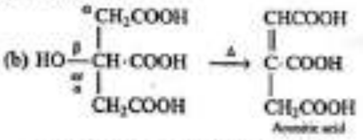
[7] (d) Rest all show intermolecular Cannizzaro reaction.



[8] (d) It is Cannizzaro reaction.

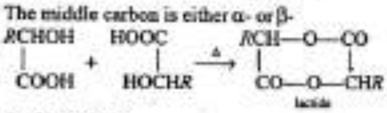
Comprehension 7

[1] (b)

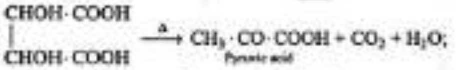

$$\mathrm{HO\overset{\beta}{\underset{\alpha}{-}}\overset{^{\alpha}CH_2COOH}{\underset{CH_2COOH}{CH}}\cdot COOH \xrightarrow{\Delta} \overset{CHCOOH}{\underset{\underset{\text{Aconitic acid}}{CH_2COOH}}{C}}\cdot COOH}$$

The middle carbon is either α- or β-

[2] (a)


$$\mathrm{\underset{COOH}{RCHOH} + \underset{HOCHR}{HOOC} \xrightarrow{\Delta} \underset{\text{lactide}}{\underset{CO{-}O{-}CHR}{RCH{-}O{-}CO}}}$$

[3] (b)

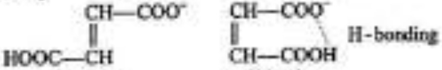

$$\mathrm{\underset{CHOH\cdot COOH}{CHOH\cdot COOH} \xrightarrow{\Delta} \underset{\text{Pyruvic acid}}{CH_3\cdot CO\cdot COOH} + CO_2 + H_2O;}$$

D-, *L*-, *DL*- and *meso* forms are isolated.

[4] (a) Rest all forms anhydrides.

[5] (d)

	Maleic	Fumaric
pK_{a_1}	1.92	3.02
pK_{a_2}	6.23	4.38

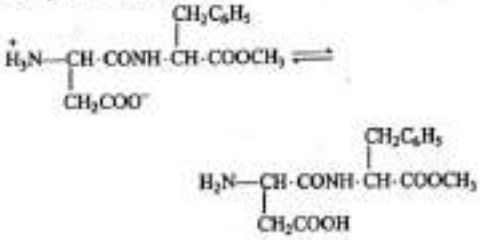


$$\mathrm{\underset{\text{Fumarate ion}}{\overset{CH{-}COO^-}{HOOC{-}CH}} \qquad \underset{\text{Maleate ion, Less dissociation}}{\overset{CH{-}COO^-}{CH{-}COOH}}}$$

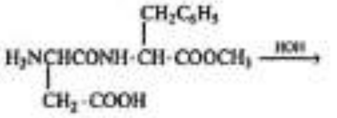
Comprehension 8

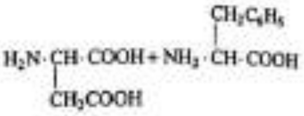
[1] (b) Benzyl is not functional gp.

[2] (b)


$$\mathrm{\overset{+}{H_3N}{-}\underset{CH_2COO^-}{CH}\cdot CONH\cdot\overset{CH_2C_6H_5}{CH}\cdot COOCH_3 \rightleftharpoons H_2N{-}\underset{CH_2COOH}{CH}\cdot CONH\cdot\overset{CH_2C_6H_5}{CH}\cdot COOCH_3}$$

[3] (a)


$$\mathrm{H_3N\underset{CH_2\cdot COOH}{CH}CONH\cdot\overset{CH_2C_6H_5}{CH}\cdot COOCH_3 \xrightarrow{HOH}}$$

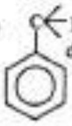

$$\mathrm{H_2N\cdot\underset{CH_2COOH}{CH}\cdot COOH + NH_2\cdot\overset{CH_2C_6H_5}{CH}\cdot COOH}$$

[4] (a) $C_6H_5\cdot CH_2$— is more hydrophobic

[5] (a) Aspartic acid is 2-amino butan-dioic acid

Comprehension 9

[1] (b)



Benzylic carbon; H-atom attached on carbon joined directly to an aromatic ring.

Side chain must have at least one H or C (benzylic carbon)

[2] (a) $y = 1$ for monocyclic, thus, C_nH_{2n-6}.

[3] (a) I has 4π electrons, II has 6π electrons, III has 2π electrons, IV has 6π electrons, V has 6π electrons but delocalised over six carbon atom and not over entire ring. VI has 6π electrons and localised over entire cyclic system.

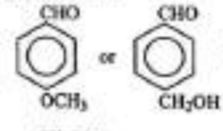
[4] (a) A positive charge makes the last gp *m*-directing whereas a –ve charge makes a gp *o*- and *p*-directing. In CCl_3, follow Hammick Illing worth rule.

[5] (b) $\underset{\text{Acid}}{AlCl_3} + CH_3Cl \longrightarrow [AlCl_4]^- + CH_3^+$

[6] (d) Side chain in *t*-butyl benzene does not have benzylic H-atom

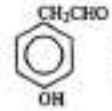
Comprehension 10

[1] (c)



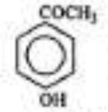
Presence of —CHO group and thus reduces Tollen's reagent.

[2] (c)



Presence of —CHO group and thus reduces Tollen's reagent. Phenolic group gives positive test with $FeCl_3$ (aq.).

[3] (d)

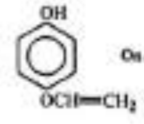


Presence of methyl ketone group and thus gives positive iodoform test.

[4] (a)

Presence of carboxylic group and thus forms sodium salt of acid.

[5] (b)



On acid hydrolysis gives 1, 4-dihydroxy benzene.

Comprehension 11

[1] (d) Hofmann bromamide reaction takes place with Br_2 + KOH.

[2] (d) Also read mechanism of reaction.

[3] (b) —do—

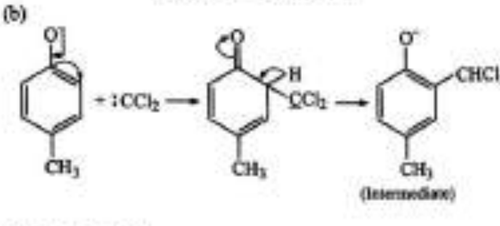
Comprehension 12

[1] (c) The reagent used in the given Reimer-Tiemann reaction is *aq.* NaOH + $CHCl_3$.

[2] (c) The electrophile in the given reaction is $:CCl_2$ generated from $CHCl_3$ by *aq.* NaOH.

$$CHCl_3 + OH \rightleftharpoons CCl_3 + H_2O$$
$$CCl_3 \rightleftharpoons :CCl_2 + Cl$$

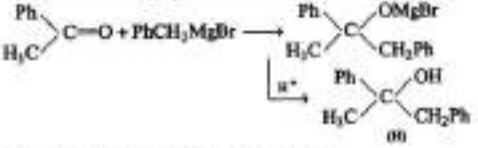
[3] (b)



(Intermediate)

Comprehension 13

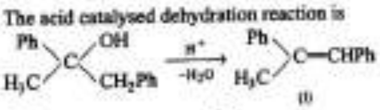
[1] (b) A tertiary alcohol (**H**) which can undergo acid catalysed dehydration will be formed when the ketone $PhCOCH_3$ reacts with $PhCH_2MgBr$. The reaction is



$$(Ph)(H_3C)C{=}O + PhCH_2MgBr \longrightarrow (Ph)(H_3C)C(OMgBr)(CH_2Ph) \xrightarrow{H^+} (Ph)(H_3C)C(OH)(CH_2Ph)$$

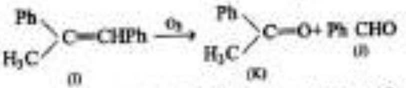
(H)

[2] (a) The acid catalysed dehydration reaction is



$$(Ph)(H_3C)C(OH)(CH_2Ph) \xrightarrow[-H_2O]{H^+} (Ph)(H_3C)C{=}CHPh$$

(I)



[3] (d)

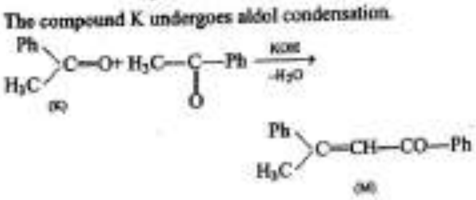
$$(Ph)(H_3C)C{=}CHPh \xrightarrow{O_3} (Ph)(H_3C)C{=}O + Ph\,CHO$$

(I) (K) (J)

The compound **J** is PhCHO. It undergoes Cannizzaro reaction.

$$2PhCHO \xrightarrow[H_2O]{KOH} PhCH_2OH + \underset{(L)}{PhCOO^-K^+}$$

The compound K undergoes aldol condensation.

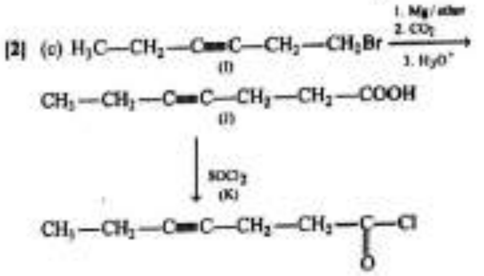


$$\underset{(K)}{(Ph)(H_3C)C{=}O} + H_3C{-}\underset{\underset{O}{\|}}{C}{-}Ph \xrightarrow[-H_2O]{KOH} \underset{(M)}{(Ph)(H_3C)C{=}CH{-}CO{-}Ph}$$

Comprehension 14

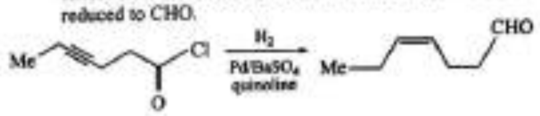
[1] (d) $H_3C{-}CH_2{-}\underset{\text{Hex-3-ynal}}{C{\equiv}C}{-}CH_2{-}CHO \xrightarrow[2.\ PBr_3]{1.\ NaBH_4} H_3C{-}CH_2{-}\underset{(I)}{C{\equiv}C}{-}CH_2{-}CH_2Br$

[2] (c)



$$H_3C{-}CH_2{-}\underset{(I)}{C{\equiv}C}{-}CH_2{-}CH_2Br \xrightarrow[3.\ H_3O^+]{1.\ Mg/ether \quad 2.\ CO_2} CH_3{-}CH_2{-}\underset{(J)}{C{\equiv}C}{-}CH_2{-}CH_2{-}COOH$$
$$\xrightarrow[(K)]{SOCl_2} CH_3{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}Cl$$

[3] (c) The use of Lindlar catalyst leads to *syn* addition. This causes the formation *cis* isomer. Besides this, —COCl is reduced to CHO.

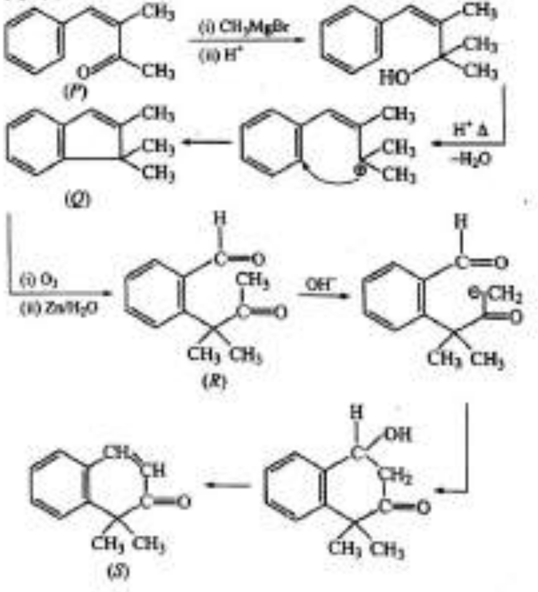


Comprehension 15

[1] (b)

[2] (a)

[3] (b)

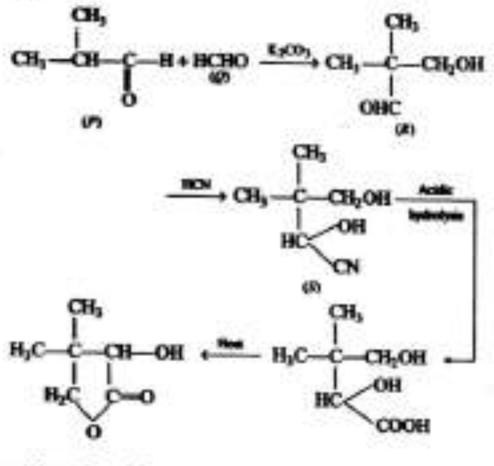


Comprehension 16

[1] (b)

[2] (a)

[3] (d)

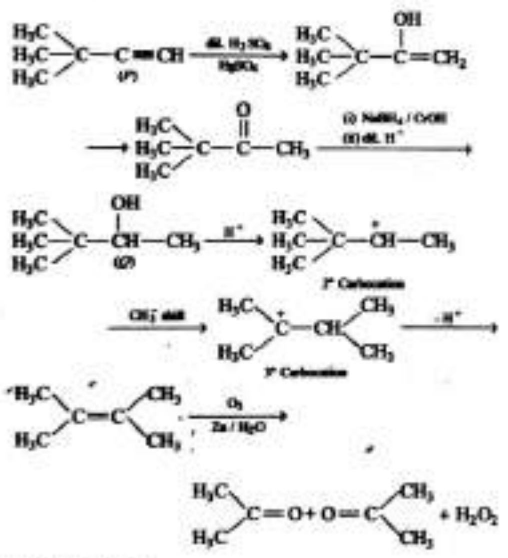


Comprehension 17

[1] (d)

[2] (b)

Explanation :



Comprehension 18

[1] (a)

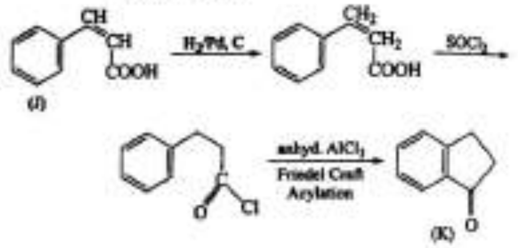
[2] (c)

Explanation :

$\underset{(I)}{Ph\text{—}CHO} \xrightarrow[\text{CH}_3\text{COONa}]{(\text{CH}_3\text{CO})_2\text{O}}$ (Perkin condensation)

$\underset{\text{(Cinnamic Acid)}}{\underset{(J)}{Ph\text{—}CH{=}CH\text{—}COOH}} \xrightarrow{NaHCO_3}$ (Effervescences due to presence of COOH gp.)

$\xrightarrow[\text{(Bayer's reagent)}]{\text{1\% cold, alk. KMnO}_4}$ (Positive test for unsaturation)



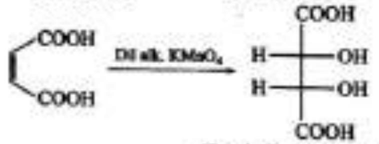
Comprehension 19

[1] (a)

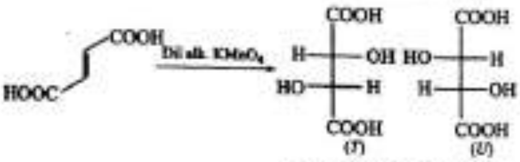
$C_4H_4O_4$ is a dicarboxylic acid and thus it may be HOOC—CH=CH—COOH

The two isomers are :

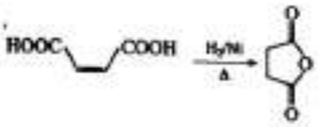
Maleic acid Fumaric acid



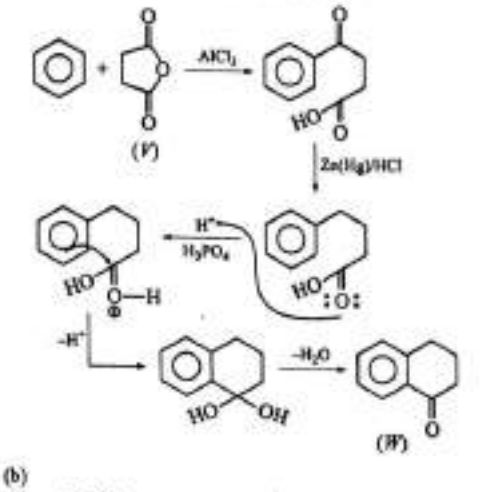
(*S* optically inactive as it is meso form of tartaric acid)



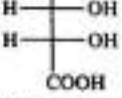
(optically active compounds but racemic mixture is optically inactive)



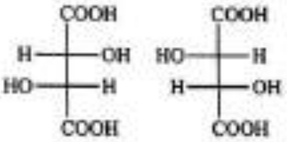
(V)



[2] (b)



(S is optically inactive as it is meso form of tartaric acid having symmetry)



(T) (U)

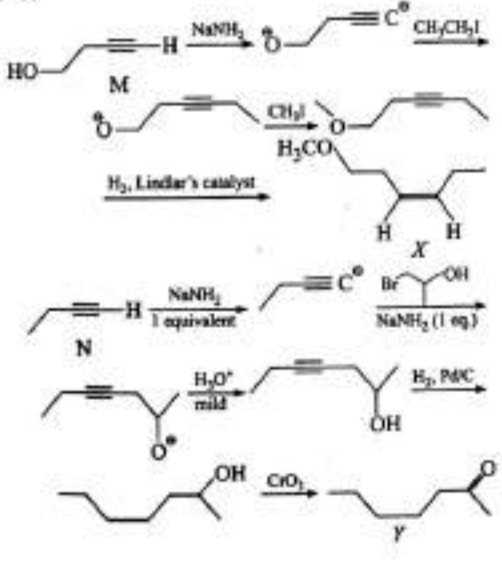
(optically active) (optically active)

Racemic mixture is optically inactive

Comprehension 20

[1] (a)

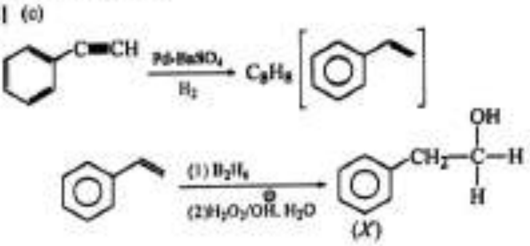
[2] (c)



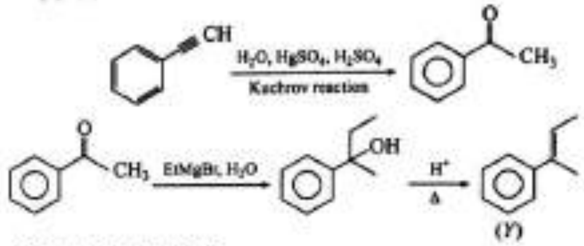
X and *Y* are functional isomers of each other and *Y* gives iodoform test.

Comprehension 21

[1] (c)

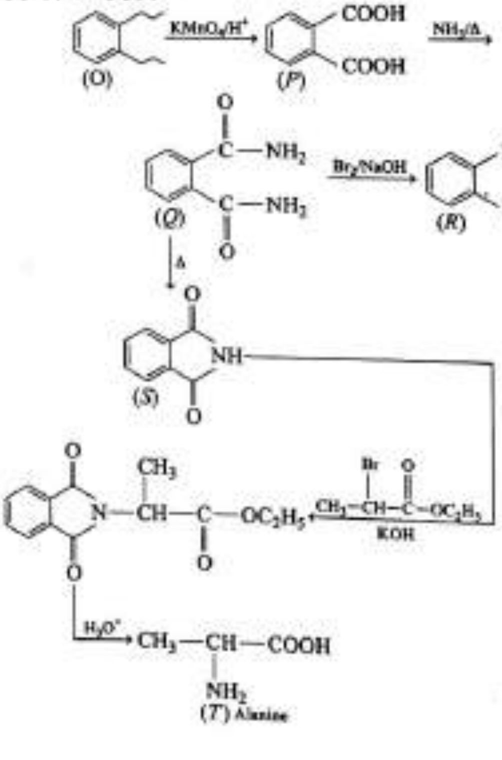


[2] (d)



Comprehension 22

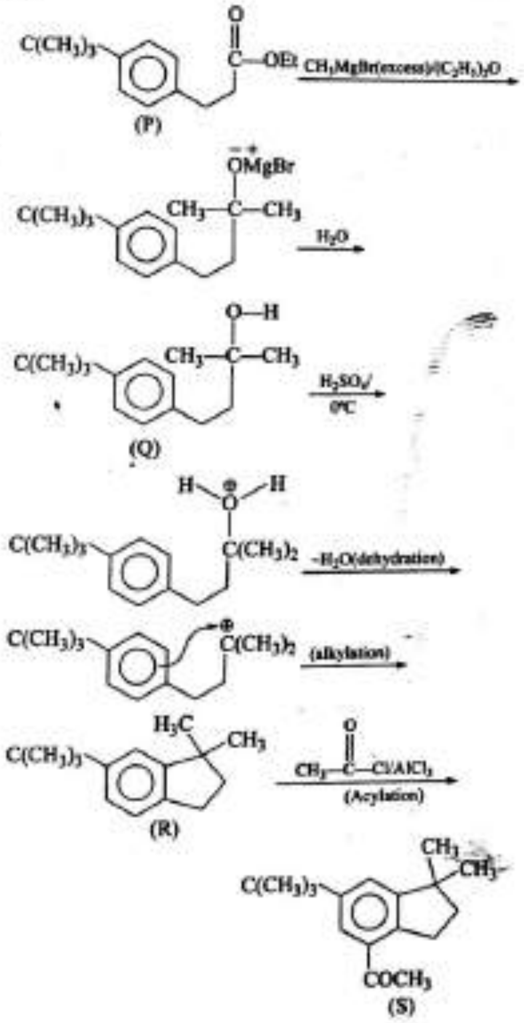
[1] (a) and [2] (b)



Comprehension 23

[1] (b)

[2] (d)



In each sub question below, a statement **S** and an explanation **E** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question.

(a) S is correct but **E** is wrong.
(b) S is wrong but **E** is correct.
(c) Both S and E are correct and **E** is correct explanation of **S.**
(d) Both S and E are correct but **E** is not correct explanation of S.

1. S : Solubility of *n*-alcohol in water decreases with increases in molar mass.
E : The hydrophobic nature of alkyl chain increases.

2. S : The yield in organic reactions are 100%.
E : The organic reactions take place along with side reaction.

3. S : Ethane is much less reactive than ethene.
E : Bond angles in ethane are less than those in ethene.

4. S : 2, 3-dimethyl but-2-ene decolourize Br_2 water.
E : 2, 3- dimethyl but-2-ene is an unsaturated compound.

5. S : C_6H_6 does not decolourize Br_2 water.
E : All the six carbon atoms have delocalized π-electrons.

6. S : C_6H_5Cl on treating with NaOH does not show replacement of Cl atom by OH.
E : The resonance in chlorobenzene stabilizes the molecule.

7. S : Nitrobenzoic acid is more acidic than benzoic acid.
E : Presence of electron repelling group decreases the acidic character in molecule.

8. S : *p*-dimethoxybenzene is polar.
E : The different orientations of methoxy group in ring results in to produce dipole.

9. S : H atoms of ethyne are acidic in nature.
E : The *sp*-hybridization of carbon atoms makes C atoms more electronegative.

10. S : Acetate ion is more basic than formate ion.
E : The *+IE* methyl group in acetate ion intensifies electron density on oxygen atom.

11. S : C_2H_5I is more reactive than C_2H_5Cl.
E : I being less electronegative than Cl.

12. S : 1-butene on reaction with HBr in the presence of per oxide produces 1-bromobutane.
E : It involves the formation of primary radical.

13. S : Phenol is more reactive than benzene towards electrophilic substitution reaction.
E : In the case of phenol, the intermediate carbocation is more resonance stabilised.

14. S : Ethyl acetoacetate gives reddish violet colour with $FeCl_3(aq)$.
E : Ethyl acetoacetate shows keto-enol isomerism.

15. S : Acetate ion is more basic than methoxide ion.
E : Acetate ion is resonance stabilised.

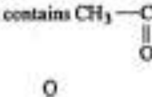
16. S : The unpaired electron of CH_3 free radical occupies *p*-orbital.
E : $\dot{C}H_3$ possesses sp^2 hybridisation.

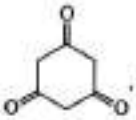
17. S : Acetic acid does not undergo haloform reaction.
E : Acetic acid has no α-hydrogen.

18. S : Benzo nitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
E : Cyanide (CN^-) is a strong nucleophile.

19. S : Addition of Br_2 to 1-butene gives two optical isomers.
E : The product contains one asymmetric carbon atom.

20. S : $CH_3COCH_2COOC_2H_5$ will give iodoform test.
E : It contains $CH_3-\underset{\underset{O}{\|}}{C}-$ unit linked to carbon atom.



21. S :  , will show tautomerism.
E : It contains α-hydrogen atom near keto group.

22. S : Addition of Br_2 on maleic acid gives *d* and *l* isomers of product.
E : The addition of Br_2 on maleic acid follow anti addition.

23. S : Benzaldehyde forms two oximes on reacting with NH_2OH.
E : The two oximes are formed due to geometrical isomerism arised in product.

24. S : Aniline does not undergo Friedel-Craft's reaction.
E : $-NH_2$ gp. of aniline reacts with $AlCl_3$ (Lewis acid) to give acid-base reaction.

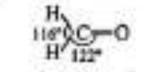
25. S : Cannizzaro's reaction is a disproportionation reaction.
E : One molecule of aldehyde is oxidised on the cost of other.

26. S : All enzymes are proteins but all proteins are not enzymes.
E : Enzymes are biocatalyst and possess a stable configuration having active sites.

27. S : Borazole is less reactive than benzene.
E : Both borazole and benzene have same structure (three π bonds) but borazole has polar bonds.

28. S : Addition of H_2 in presence of catalyst on *trans*-2, 3-diphenyl but-2-ene gives *meso* form of 2, 3-diphenyl butane.
E : Addition of H_2 in presence of catalyst is *syn*-addition and the product formed is racemic mixture.

29. **S :** HCHO has sp^2-hybridised carbon and the following geometry :



E : The bond angles are changed due to multiple bond-bond pair repulsion.

30. **S :** Tertiary butyl benzene on oxidation gives benzoic acid.

E : A side chain containing benzylic hydrogen atom is oxidised to —COOH group.

31. **S :** Ethanol is more viscous than glycerol.

E : Both possess H-bonding.

32. **S :** The presence of Ag^+ ion enhances the solubility of alkenes in water.

E : Ag^+ co-ordinates with the alkene by *p-d* π bonding giving an ion and thus solubility increases.

33. **S :** The central carbon-carbon bond in 1, 3-butadiene is shorter than *n*-butane.

E : In butadiene the central bond has sp^2-sp^2 nature whereas in butane it is sp^3-sp^3.

34. **S :** 2, 3-dichloropentene has four stereoisomers.

E : It contains two chiral carbon atoms.

35. **S :** Chlorine deactivates the C_6H_6 ring for S_E reaction yet it is *o*-, *p*-directing.

E : —*M* effect is greater than −*I* effect in chlorobenzene.

36. **S :** S_N2 reactions take place through transition state formation.

E : Primary carbocation is more stable than secondary carbocation.

37. **S :** Addition of bromine on *trans*-2-butene yields *meso*-2, 3-dibromobutane.

E : Br_2 shows electrophilic addition.

38. **S :** $CH{\equiv}C{-}CH_2{-}CH{=}CH_2$ adds up HBr to give
$CH{\equiv}C{-}CH_2CHBr{\cdot}CH_3$ while
$CH{\equiv}C{-}CH{=}CH_2$ adds up HBr to give
$CH_2{=}CBrCH{=}CH_2$.

E : An isolated double bond is more reactive than triple bond but in later case conjugate molecule is formed.

39. **S :** A mixture of HNO_3 and H_2SO_4 is used for the nitration of benzene.

E : H_2SO_4 works as an acid and HNO_3 as a base to produce NO_2^+ ion.

40. **S :** Cyclohexane floats over water.

E : Cyclohexane always has boat like structure.

41. **S :** Iodination of alkane is carried out in presence of iodic acid.

E : Iodine is an oxidizing agent.

42. **S :** Reaction of *tert.* butyl chloride with Na gives 2,2,3,3-tetramethyl butane.

E : *Tert.* butyl chloride on Wurtz reaction gives alkene.

43. **S :** A small amount of ethanol is added to $CHCl_3$ bottles.

E : It acts as negative catalyst for the oxidation of $CHCl_3$ to $COCl_2$.

44. **S :** The *p*-isomer of dichlorobenzene has higher m.p. than *o*-and *m*-isomer.

E : *p*-isomer is symmetrical and thus shows more closely packed structure.

45. **S :** *n*-butyl chloride has lower b.p. than *n*-butyl bromide.

E : The b.p. increases with increase in molar mass.

46. **S :** CHI_3 gives a precipitate with $AgNO_3$ solution on heating but $CHCl_3$ not.

E : C—I bond is quite weak as compared to C—Cl bond.

47. **S :** Alcohols cannot be dried by $CaCl_2$.

E : $CaCl_2$ forms solvated molecules with alcohols.

48. **S :** Methanol is stronger acid than water.

E : All alcohols are stronger acid than water.

49. **S :** Acid catalysed dehydration of *t*-butanol is faster than *n*-butanol.

E : The order of stability of carbocation is 3° > 2° > 1°.

50. **S :** Acetone forms one oxime whereas acetophenone forms two oximes.

E : In acetophenone *syn* and *anti* form of geometrical isomers are possible.

51. **S :** The boiling point of nitro-alkanes is higher than their corresponding alkyl nitrites.

E : Nitro-alkanes show strong dipole-dipole interaction.

52. **S :** Acylation of aniline increases the reactivity of C_6H_6 ring.

E : Acylation of aniline decreases the electron density at C_6H_6 ring.

53. **S :** Sulphanilic acid is insoluble in water and organic solvents.

E : Sulphanilic acid is typical dipolar salt.

54. **S :** Nitromethane and acinitromethane are tautomers to each other.

E : Migration of H atom from α-C atom to electronegative atom which is bonded with multiple bond develops this phenomenon.

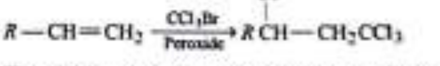
55. **S :** Alcohols give only substitution products with HX and not elimination product.

E : $\overline{X}$ is a very weak base which cannot abstract proton from alcohol.

56. **S :** Salicyldehyde is less soluble in water than *p*-hydroxy benzaldehyde.

E : The former shows intermolecular H-bonding.

57. **S :**



$$R{-}CH{=}CH_2 \xrightarrow[\text{Peroxide}]{CCl_3Br} R\overset{\overset{\displaystyle Br}{|}}{C}H{-}CH_2CCl_3$$

E : The addition obey free radical addition on alkenes in presence of peroxide.

58. **S :** 2,3-dimethyl but-2-ene is more stable than but-2-ene.

E : 2,3-dimethyl but-2-ene possesses 12 α-hydrogen atoms whereas but-2-ene possesses only 6 α-hydrogen atoms and therefore former shows more pronounced hyperconjugation.

59. S : Hydroxyl amine NH_2OH gives positive Lassaigne's test for nitrogen.

E : The formation of NaCN during preparation of sodium extract will give positive Lassaigne's test for nitrogen.

60. S : RI is more reactive than RCl towards S_N reaction.

E : The rate of reaction for S_N1 or S_N2 mechanism is $RI > RCl$.

61. S : Chloral hydrate $CCl_3CH(OH)_2$ is a stable molecule.

E : An organic compound having two —OH gps. on one carbon atom is unstable.

62. S : Addition of KCN solution to carbonyl compounds decreases the pH of solution.

E : KCN in aqueous solution forms a basic solution due to hydrolysis of CN^-. The nucleophilic addition on carbonyl and brings in a decrease in H^+ ions or an increase in OH^- ions.

63. S : In strongly acidic medium, aniline becomes less reactive towards electrophilic reagent.

E : $—NH_2$ group is *o*-and *p*-directing.

64. S : *Trans*-2-chloro propene has higher dipole moment than *cis*-2-chloro propene.

E : The resultant vector sum of all the vectors in *trans*-2-chloro propene is more than *cis*-2-chloro propene.

65. S : Aryl halides undergo nucleophilic substitution with ease.

E : The carbon halogen bond in aryl halides has partial double bond character.

66. S : Benzene removes butter stain from a table cloth.

E : Butter has an affinity towards benzene.

67. S : β-keto carboxylic acids lose CO_2 when heated to about 370 K.

E : An enol is first formed by loss of CO_2, but it readily tautomerize to give more stable ketone.

68. S : S_N2 reactions of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

E : S_N2 reactions always proceed with inversion of configuration.

69. S : 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.

E : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism whereas 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

70. S : *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

E : Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer.

71. S : Dimethyl sulphide is commonly used for the reduction of an ozonide of compound.

E : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

72. S : Ethyl alcohol reacts with HI to give ethyl iodide but it does not react with HCN.

E : HI being a strong acid and thus donate a proton to ethyl alcohol and thus $Et\,OH_2^+$ is formed readily. OH_2^+ being good leaving group and thus reaction $Et\,OH_2^+ + I^- \rightarrow EtI + H_2O$ occurs. HCN being weak acid does not form $CH_3OH_2^+$.

73. S : Phenyl group is known to exert negative inductive effect but each phenyl ring in biphenyl $(C_6H_5—C_6H_5)$ is more reactive than benzene towards S_E reaction.

E : In biphenyl one of the phenyl group acts as electron donor and the other electron acceptor.

74. S : Enol form of $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$ is less stable than enol form of CH_3COCH_3.

E : H-bonding in enol form of CH_3COCH_3 is stronger than that of enol form of $CH_3 \cdot COCH_2COCH_3$.

75. S : A carboxylic acid on treatment with ammonia gives amide at room temperature.

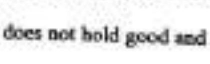
E : Carboxylic acids do not undergo nucleophilic substitutions under basic conditions.

76. S : Energy of resonance hybrid is equal to the average of energies of all canonical forms.

E : Resonance hybrid can not be presented by a single structure.

77. S : Pent-2-one and pent-3-one are position isomers.

E : Keto group is divalent group.

78. S : Cyclooctane using the structure  is cyclic and have conjugated 8 π-electron system but not an aromatic compound.

E : $(4n+2)\pi$ electron rule does not hold good and ring is not planar.

79. S : Optically active 2-iodobutane on treatment with NaI in acetone undergoes recemisation.

E : Reaction involves multiple walden inversion and the product contains mixture of dextro and laevo forms.

80. S : Presence of nitro group at ortho or para position increases the reactivity of haloarenes towards S_N reaction.

E : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

81. S : Hydrolysis of (−)-2-bromooctane proceeds with inversion of configuration.

E : The reaction proceeds through the formation of a carbocation.

82. S : *o*-Nitrophenol is less soluble in water than *m*- and *p*-isomers.

E : *m*- and *p*- nitrophenol exist as associated liquid.

83. S : The α-H atom in carbonyl compounds is less acidic.

E : The anion formed after the loss of α-H atom is resonance stabilized.

84. S : Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.

E : Bromine addition to an alkene is an electrophilic addition. **(IIT 2001)**

85. S : In strongly acidic solution aniline becomes more reactive towards electrophilic reagents.

E : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. **(IIT 2006)**

86. S : Glucose gives a reddish-brown precipitate with Fehling's solution.

E : Reaction of glucose with Fehling's solution gives CuO and gluconic acid. **(IIT 2007)**

87. S : *p*-hydroxy benzoic acid has a lower boiling point than *o*-hydroxy benzoic acid.

E : *o*-hydroxy benzoic acid has intramolecular hydrogen bonding. **(IIT 2007)**

88. S : Molecules that are not superimposable on their mirror images are chiral.

E : All chiral molecules have chiral centres. **(IIT 2007)**

89. S : Aniline on reaction with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

E : The colour of the compound formed in the reaction of aniline with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation. **(IIT 2008)**

90. S : Bromobenzene upon reaction with Br_2 / Fe gives 1,4-dibromobenzene as the major product.

E : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **(IIT 2008)**

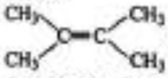
ANSWERS (Statement Explanation Problems)

1. (c) The solubility of alcohols in water is due to H-bonding. As the molar mass of alcohol increases, the increase in hydrophobic nature of alkyl gp. results in decrease in solubility.

2. (b) The yield of organic reactions is not 100% because they take place with side reactions.

3. (d) Ethene is more reactive than ethane due to the presence of π-bond.

4. (b)



does not decolourise Br_2 water as it does not contain olefinic H atom, *i.e.*, all the olefinic H atoms are substituted by $—CH_3$ gp. No doubt it is an unsaturated compound.

5. (c) C_6H_6 does not decolourise Br_2 water because of resonance stabilization due to delocalisation of π-electrons.

6. (c) The given statement is true because of given explanation.

7. (d) Presence of electron attracting gp (here $—NO_2$) give rise to an increase in acidic character of benzoic acid.

8. (c) *p*-dimethoxybenzene is

a polar molecule because of different orientations of methoxy groups.

9. (c) Ethyne is acidic in nature due to given explanation.

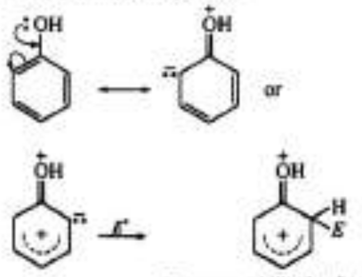
10. (c) $CH_3 \rightarrow \underset{\underset{O}{\|}}{C} \rightarrow \overline{O}$ (The negative charge is intensified and thus basic character is more in CH_3COO^- than $HCOO^-$).

11. (d) C_2H_5I is more reactive than C_2H_5Cl due to lower bond energy of C—I bond than C—Cl bond.

12. (a) Addition of HBr in alkene in presence of peroxide takes place *via* free radical mechanism (secondary free radical).

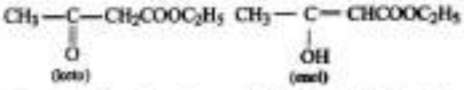
13. (c) Presence of *o*-and *p*-directing group (except halogens) activates ring for S_E reactions.

Thus, both the reason and assertion are correct and reason is an explanation for assertion.



The more stabilized carbocation and thus facilitate attack of electrophile

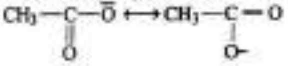
14. (c)



$$\underset{\text{(keto)}}{CH_3—\underset{\underset{O}{\|}}{C}—CH_2COOC_2H_5} \quad \underset{\text{(enol)}}{CH_3—\underset{\underset{OH}{|}}{C}=CHCOOC_2H_5}$$

The enolic form gives characteristic test with $FeCl_3(aq.)$

15. (b)



$$CH_3—\underset{\underset{O}{\|}}{C}—\overline{O} \longleftrightarrow CH_3—\underset{\underset{O^-}{|}}{C}=O$$

$CH_3—\overline{O}$, No resonance.

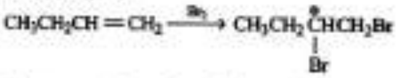
Also CH_3OH is less acidic than CH_3COOH ; thus CH_3COO^- is less basic than CH_3O^-. Stronger is acid, weaker is conjugate base.

16. (c) Explanation is correct reason for statement.

17. (a) Compounds having $CH_3—\underset{\underset{O}{\|}}{C}—$ unit linked with C or H show haloform reaction. $CH_3—\underset{\underset{O}{\|}}{C}—OH$ has 3α-hydrogen atom but not above structure.

18. (b) No doubt CN^- is stronger nucleophile than Cl^-, but chlorine atom in chlorobenzene is firmly attached to ring due to resonance.

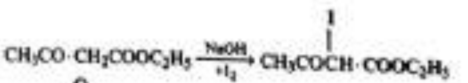
19. (c)



$$CH_3CH_2CH=CH_2 \xrightarrow{Br_2} CH_3CH_2\underset{\underset{Br}{|}}{\overset{*}{C}}HCH_2Br$$

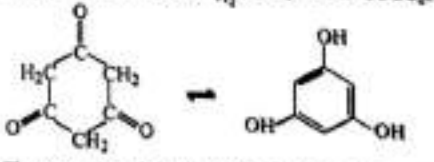
* is asymmetric carbon and thus optical isomerism.

20. (b) $CH_3—\underset{\underset{O}{\|}}{C}—CH_2COOC_2H_5$ does not give iodoform test inspite of $CH_3—\underset{\underset{O}{\|}}{C}—$ unit linked to atom because halogen reacts at acidic H atom in place of CH_3 unit of $CH_3—\underset{\underset{O}{\|}}{C}—$

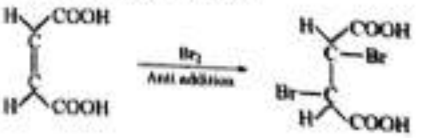


$$CH_3CO \cdot CH_2COOC_2H_5 \xrightarrow[+I_2]{NaOH} CH_3CO\overset{\overset{I}{|}}{C}H \cdot COOC_2H_5$$

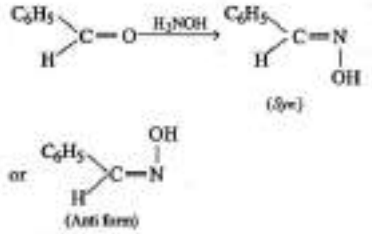
21. (c)



22. (c) The term *anti*-addition represents for the addition of Br_2 *trans*-position to available sites.



23. (c)



24. (c) Aniline is Lewis base and thus consumes $AlCl_3$ which therefore cannot provide electrophile to develop Friedel-Craft's reaction.

25. (c) In Cannizzaro's reaction,

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

26. (c) Explanation is correct reason for statement.

27. (b) Explanation is correct and suggest that borazole is more reactive.

28. (b) Explanation is correct and thus assertion is wrong.

29. (c) Explanation is correct reason for statement.

30. (b) Tertiary butyl benzene has no benzylic hydrogen atom.

31. (b) Glycerol is more viscous than ethanol due to more extensive H-bonding.

32. (c) Explanation is correct reason for statement.

33. (c) Explanation is correct reason for statement.

34. (c) Explanation is correct reason for statement.

35. (c) Explanation is correct reason for statement.

36. (a) S_N1 reaction takes place with carbocation formation whereas S_N2 reactions proceed with transient state. Primary carbocation is less stable than secondary carbocation.

37. (d) Addition of Br_2 on *trans*-2-butene gives *meso*-2, 3-dibromobutane following *anti*-addition, which is however electrophilic one.

38. (c) Explanation is correct reason for statement.

39. (c) $2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

40. (a) Cyclohexane is higher than water and has boat as well as chair structures.

41. (c) Explanation is correct reason for statement.

42. (b) $(CH_3)_3CBr \xrightarrow{Na} (CH_3)_2C{=}CH_2$

43. (c) Explanation is correct reason for statement.

44. (c) Explanation is correct reason for statement.

45. (c) Explanation is correct reason for statement.

46. (c) Explanation is correct reason for statement.

47. (c) Explanation is correct reason for statement.

48. (a) CH_3OH is stronger acid than water and rest all alcohols are weaker acids.

49. (c) Explanation is correct reason for statement.

50. (c) Explanation is correct reason for statement.

51. (c) Explanation is correct reason for statement.

52. (b) $-NHCOCH_3$ has lesser activating nature than $-NH_2$ group.

53. (c) Explanation is correct reason for statement.

54. (c) Explanation is correct reason for statement.

55. (c) Explanation is correct reason for statement.

56. (a) Salicyldehyde shows intramolecular H-bonding.

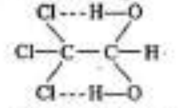
57. (c) Explanation is correct reason for statement.

58. (c) The phenomenon of displacement of electrons by conjugative mechanism involving σ and π-electron is called hyperconjugation. It is arised when alkyl groups having atleast one H atom on the α-carbon atom attached to an unsaturated carbon atom are able to release electrons due to delocalisation of σ and π bond. It is more pronounced if α-H atom are more in number. Thus, stability of alkenes has been explained in terms of hyper conjugation.

59. (b) Organic compounds (NH_2OH is inorganic) *i.e.*, compound of carbon also having nitrogen on fusion forms NaCN which gives violet colour during Lassaigne's test.

60. (c) The rate of reaction for alkyl halide is $RI > RBr > RCl > RF$ whether it obeys S_N1 or S_N2 mechanism due to steric hindrance of alkyl group.

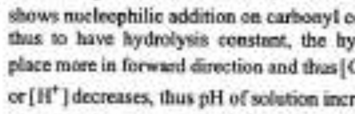
61. (d) Chloral hydrate is stable inspite of two OH gps on one carbon atom due to H-bonding



62. (b) $KCN + H_2O \rightleftharpoons KOH + HCN$; the HCN formed now shows nucleophilic addition on carbonyl compounds and thus to have hydrolysis constant, the hydrolysis takes place more in forward direction and thus $[OH^-]$ increases or $[H^+]$ decreases, thus pH of solution increases.

63. (d) In presence of acid $-NH_2$ gp. forms $-NH_3^+$, *i.e.*, anilium ion and shows *m*-directing nature. Thus, ring is deactivated for S_E reactions.

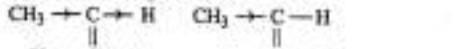
64. (c)



65. (b) In aryl halides the halo atoms decrease the electron density on benzene ring. But due to mesomeric effect it donates the electron pair to the benzene ring, therefore C—Cl bond gets partial double bond character.

66. (d) Both are correct. Benzene being non polar dissolves oils which are weak polar.

67. (d) Both correct. In this reaction ketones are directly formed.



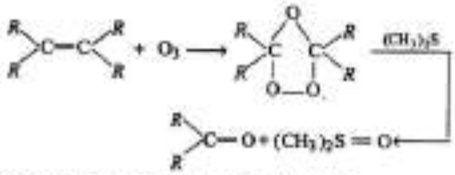
$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2\cdot COOH \xrightarrow{\Delta} CH_3CH_2COCH_3$$

68. (b) Halogen atom of aryl halids cannot be replaced by $-OH$ due to partial double bond character of C—Cl bond.

69. (d) As compared to chlorobenzene, the intermediate carbon ion resulting from 4-nitrochlorobenzene is stabilized by $-R$ effect of the $-NO_2$ gp.

70. (c) Both statement and reason are correct, and statement is an explanation of assertion.

71. (c) It is fact.



72. (c) Explanation is correct reason for statement.

73. (a) Both phenyl gps in biphenyl are of same nature.

74. (a) H-bonding in each forms provides stability.

75. (b) $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{150-200} RCONH_2$

76. (b) Canonical forms do not have real existence and thus energy can not be obtained.

77. (b) Pent-2-one and pent-3-one are metamers.

78. (c) Explanation is correct reason for statement.

79. (c) —do—

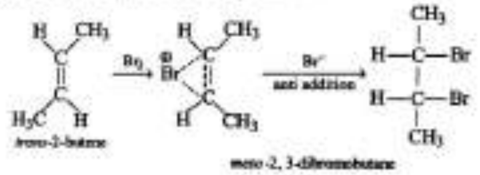
80. (c) —do—

81. (a) The reaction follows S_N1 mechanism.

82. (d) *o*-nitrophenol shows intramolecular H-bonding *m*- and *p*-isomers show intermolecular H-bonding.

83. (b) More is the stability of anion formed after loss of α-H atom by ketones, more is acidic nature of α-H atom.

84. (d) It is an *anti* addition of Br_2 to alkene.



85. (b) $C_6H_5NH_2 + H^+ \longrightarrow C_6H_5NH_3^+$

86. (a) Cu_2O is formed.

87. (b) *p*-hydroxy benzoic acid has higher b.pt. than ortho benzoic acid.

88. (a) 2, 3-pentadiene has no chiral carbon but chiral molecule.

89. (b) Red dye is formed.

90. (a) Bromo group is *ortho*-and *para*-directing. Mesomeric effect is more dominant than the inductive effect.

MATCHING TYPE PROBLEMS

Type I Only One Match Possible

1.

List-A	List-B
(a) Nitrobenzene to hydrazobenzene	1. Sn/HCl
(b) Nitrobenzene to azoxybenzene	2. CH_3OH/CH_3ONa
(c) Nitrobenzene to aniline	3. Zn/NH_4Cl
(d) Nitrobenzene to phenyl hydroxyl amine	4. Zn/KOH

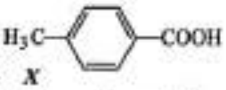
2.

List-A	List-B
(a) Heating glycerol with conc. H_2SO_4	1. Glyoxal as one of the products
(b) Hydrogenation of carbon	2. 2-hydroxy ethanoic acid
(c) Action of glyoxal with NaOH	3. Synthetic petrol
(d) Reductive ozonolysis of ethyne	4. Acrolein

3. (IIT 2007)

List-A	List-B
(A) Cellulose	(p) Natural polymer
(B) Nylon 6,6	(q) Synthetic polymer
(C) Protein	(r) Amide linkage
(D) Sucrose	(s) Glucoside linkage

4. (IIT 2003)

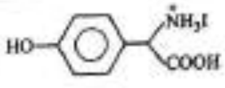
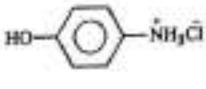
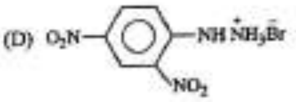
Acid	K_a
(A) Benzoic acid	(p) 6.4×10^{-5}
(B) 	(q) 30.6×10^{-5}
(C) 	(r) 10.2×10^{-5}
(D) 	(s) 3.3×10^{-5}
(E) 	(t) 4.2×10^{-5}

5.

X	Y
(A) Williamson's synthesis	(p) *tert*-alcohol
(B) Neutral $FeCl_3$ test	(q) Ether
(C) Lucas test	(r) Phenol

TYPE II More Than One Match Are Possible

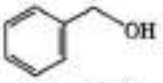
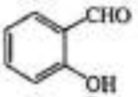
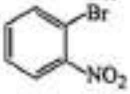
6. (IIT 2006)

Column-I	Column-II
(A) $H_2N—\overset{+}{N}H_3\overset{-}{Cl}$	(p) Sodium fusion extract of the compound gives prussion blue colour with $FeSO_4$
(B) 	(q) Gives positive $FeCl_3$ test
(C) 	(r) Gives white ppt with $AgNO_3$
(D) 	(s) Reacts with aldehyde to form corresponding hydrazone derivative

7. Match the compounds/ions in Column I with their properties/reactions in Column II. (IIT 2007)

Column-I	Column-II
(A) C_6H_5CHO	(p) gives precipitate with 2, 4-dinitrophenylhydrazine
(B) $CH_3C \equiv CH$	(q) gives precipitate with $AgNO_3$
(C) CN^-	(r) is a nucleophile
(D) I^-	(s) is involved in cyanohydrin formation

8. (IIT 2009)

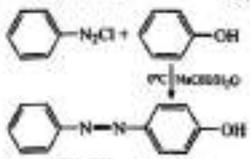
Column-I	Column-II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(s) Esterification with acetic anhydride
	(t) Dehydrogenation

9. (IIT 2009)

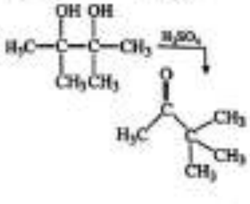
Column-I	Column-II
(A) $CH_3CH_2CH_2CN$	(p) Reduction with Pd–C H_2
(B) $CH_3CH_2OCOCH_3$	(q) Reduction with $SnCl_2$/HCl
(C) $CH_3—CH=CH—CH_2OH$	(r) Development of foul smell on treatment with chloroform and alcoholic KOH
(D) $CH_3CH_2CH_2CH_2NH_2$	(s) Reduction with diisobutyl-aluminium hydride (DIBAL-H)
	(t) Alkaline hydrolysis

10. **Column-I** **Column-II** **(IIT 2010)**

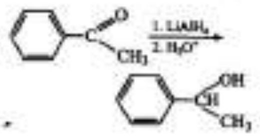
(A)



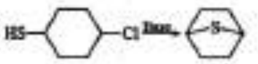
(B)



(C)



(D)



(p) Racemic mixture

(q) Addition reaction

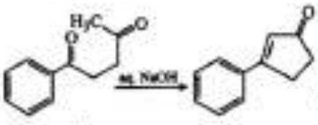
(r) Substitution reaction

(s) Coupling reaction

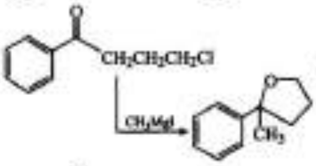
(t) Carbocation intermediate

11. **Column-I** **Column-II** **(IIT 2011)**

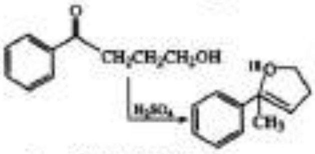
(A)



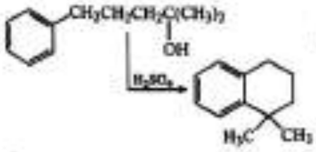
(B)



(C)



(D)



(p) Nucleophilic substitution

(q) Electrophilic substitution

(r) Dehydration

(s) Nucleophilic addition

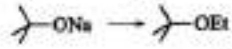
(t) Carbanion

12. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists :

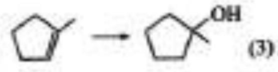
List I **List II**

(P)

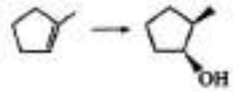
(Q)



(R)



(S)



(1) (i) $Hg(OAc)_2$; (ii) $NaBH_4$

(2) NaOEt

(3) Et—Br

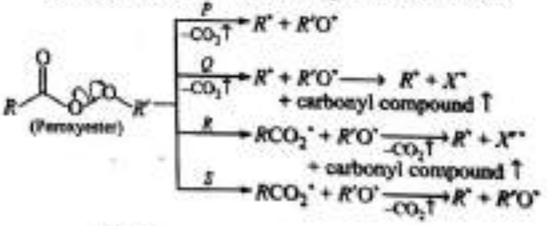
(4) (i) BH_3; (ii) $H_2O_2/NaOH$

[JEE (Advanced) II 2013]

Codes:

	P	*Q*	*R*	*S*
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

13. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists.



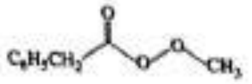
List- I **List-II**

P. Pathway *P*

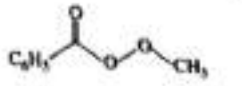
Q. Pathway *Q*

R. Pathway *R*

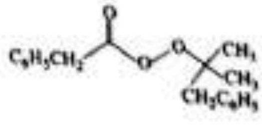
1.



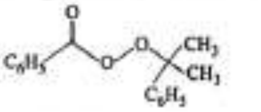
2.



3.



S. Pathway *S* 4.



[JEE (Advanced) II 2014]

Codes:

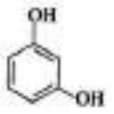
	P	*Q*	*R*	*S*
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

14. Match the four starting materials (P, Q, R, S) given in List-I with the corresponding reaction schemes (I, II, III, IV) provided in List-II and select the correct answer using the code given below the lists.

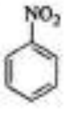
List-I **List-II**

P.  1. Scheme I

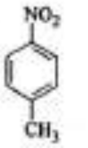
$$? \xrightarrow[\text{(iv) } NH_3]{\text{(i) } KMnO_4, HO^-, \text{ heat (ii) } H^+, H_2O \text{ (iii) } SOCl_2} C_7H_6N_2O_3$$

Q.  2. Scheme II

$$? \xrightarrow[\text{(v) dil. } H_2SO_4, \text{ Heat (vi) } HO^-]{\text{(i) Sn/HCl (ii) } CH_3COCl \text{ (iii) conc. } H_2SO_4 \text{ (iv) } HNO_3} C_6H_6N_2O_2$$

R.  3. Scheme III

$$? \xrightarrow[\text{(iii) } H_2S.NH_3 \text{ (iv) } NaNO_2, H_2SO_4 \text{ (v) hydrolysis}]{\text{(i) red hot iron, 873 K (ii) fuming } HNO_3, H_2SO_4, \text{ Heat}} C_6H_5NO_3$$

S.  4. Scheme IV

$$? \xrightarrow[\text{(iii) dil. } H_2SO_4, \text{ Heat}]{\text{(i) conc. } H_2SO_4, 60^\circ C \text{ (ii) conc. } HNO_3, \text{ conc. } H_2SO_4} C_6H_5NO_4$$

[JEE (Advanced) II 2014]

Codes:

	P	*Q*	*R*	*S*
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

Q. 15, 16 and 17 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contains starting materials, reaction conditions, and type of reactions, respectively.

Column-1	Column-2	Column-3
(I) Toluene	(i) NaOH/Br_2	(P) Condensation
(II) Acetophenone	(ii) $Br_2/h\nu$	(Q) Carboxylation
(III) Benzaldehyde	(iii) $(CH_3CO)_2O$/ CH_3COOK	(R) Substitution
(IV) Phenol	(iv) NaOH/CO_2	(S) Haloform

15. For the synthesis of benzoic acid, the only correct combination is :

(a) (III) (iv) (R) (b) (IV) (ii) (P)
(c) (I) (iv) (Q) (d) (II) (i) (S)

16. The only correct combination in which the reaction proceeds through radical mechanism is :

(a) (I) (ii) (R) (b) (II) (iii) (R)
(c) (III) (ii) (P) (d) (IV) (i) (Q)

17. The only correct combination that gives two different carboxylic acids is :

(a) (IV) (iii) (Q) (b) (III) (iii) (P)
(c) (II) (iv) (R) (d) (I) (i) (S)

ANSWERS

1. a – 4; b – 2; c – 1; d – 3
2. a – 4; b – 3; c – 2; d – 1
3. A – p; B – q; C – r; D – s
4. A – p; B – q; C – r; D – s; E – t
5. A – q; B – s; C – p.
6. A – r, s; B – p, q; C – p, q, r; D – p, s
7. A – p, s; B – q; C – q, r, s; D – q, r
8. A – p, q, t; B – p, s, t; C – r, s; D – p
9. A – p, q, s, t; B – s, t; C – p; D – r
10. A – r, s, t; B – t; C – p, q; D – r
11. A – r, s, t; B – p, s; C – r, s; D – q, r
12. (a) P – 2, Q – 3, R – 1, S – 4
13. (a) P – 1, Q – 3, R – 4, S – 2
14. (c) P – 3, Q – 4, R – 2, S – 1
15. (d) (II), (i), (S)
16. (a) (I), (ii), (R)
17. (b) (III), (iii), (P)