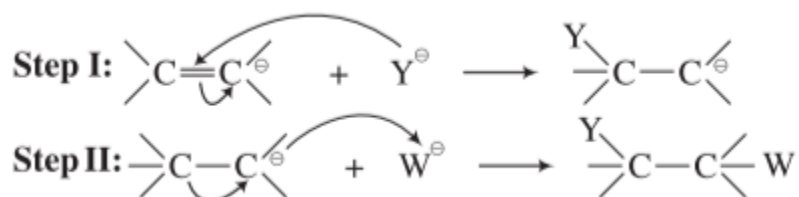


Aldehydes, Ketones and Carboxylic Acids

Case Study Based Questions

Case Study 1

Nucleophilic addition reactions are encountered in compounds having polar functional groups ($C=O$, $C=N$, $C=S$). In the first step, a nucleophile with its pair of electrons attacks the carbon atom of a double or triple bond, forming a carbanion. It is followed by a second step in which this carbanion reacts with a positive species.

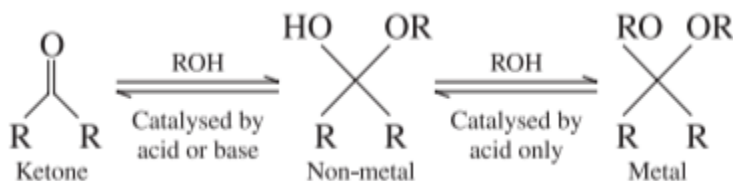


When the olefin contains a good leaving group (as defined for nucleophilic substitution), substitution is a side reaction. (i.e. a nucleophilic substitution at a vinylic substrate). Addition of HCN to carbonyl group and addition of alcohol to carbonyl group is a nucleophilic addition reaction.

Addition of HCN to carbonyl group: In this reaction cyanide ion (CN^-) acts as a nucleophile which attacks the carbon of carbonyl group, the carbon-oxygen double bond breaks followed by capture of proton and a cyanohydrin is formed.



Addition of alcohol to carbonyl compounds: Aldehydes and ketones react with one mole of alcohol to form hemiacetal or hemiketal, respectively. Reaction with second mole of alcohol gives acetal or ketal. In this reaction, the alcohol with lone pair of electrons of oxygen atom acts as a nucleophile.

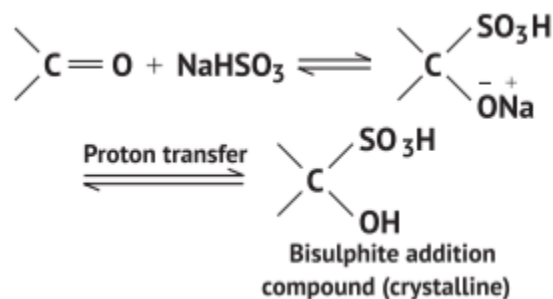


Read the given passage carefully and give the answer of the following questions:

Q1. Identify the example in which both nucleophilic addition and nucleophilic addition elimination reaction occur respectively in the carbonyl compound.

- Reduction to alcohols
- Addition of sodium sulphide
- Tollen's test
- Reaction with alcohols

Q2. Consider the following reaction:



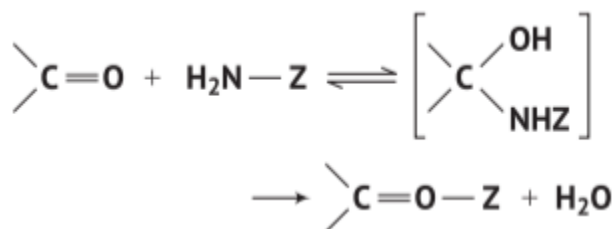
In the given reaction, equilibrium lies largely to the right hand side for most aldehydes and the left for most ketones due to:

- electronic reasons
- steric reasons
- bonding reasons
- Both a. and b.

Q3. Which of the following alternative is correct for the treatment of ketones with ethylene glycol in the presence of dry HCL?

- The product obtained is ethylene glycol hemi-ketal
- In this reaction, electrophilicity of carbonyl carbon decreases
- HCL protonates the oxygen of the carbonyl group
- The product thus obtained is cyanohydrin

Q4. Consider the following reaction:



Which of the following statements is/are true about the above reactions?

- a. H_2NZ tends to add to the carbon of carbonyl group of aldehydes and ketones
- b. The reaction is reversible and catalysed by acid
- c. The equilibrium favours the product formation due to rapid dehydration of the intermediate
- d. All of the above

Answers

- 1. (d) Reaction with alcohols
- 2. (b) steric reasons
- 3. (c) HCL protonates the oxygen of the carbonyl group
- 4. (c) The equilibrium favours the product formation due to rapid dehydration of the intermediate

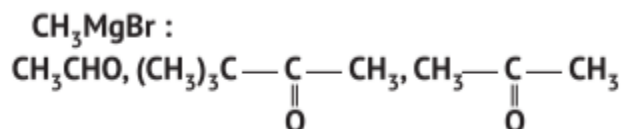
Case Study 2

The carbon-oxygen double bond is polarised in aldehydes and ketones due to higher electronegativity of oxygen relative to carbon. Therefore, they undergo nucleophilic addition reactions with a number of nucleophiles such as HCN, NaHSO, alcohols, ammonia derivatives and Grignard reagents. Aldehydes are easily oxidised by mild oxidising agents as compared to ketones. The carbonyl group of carboxylic acid does not give reactions of aldehydes and ketones. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols. Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

Q1. Write the name of the product when an aldehyde reacts with excess alcohol in presence of dry HCL.

Q2. Why carboxylic acid is a stronger acid than phenol?

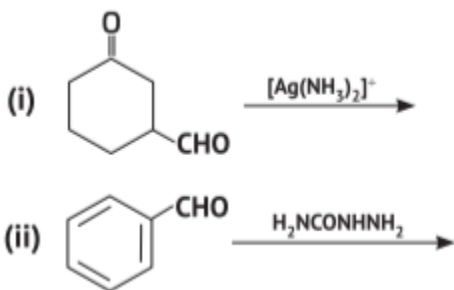
Q3. (i) Arrange the following compounds in increasing order of their reactivity towards



(ii) Write a chemical test to distinguish between propanal and propanone.

OR

Write the main product in the following:

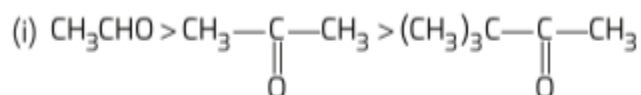


Answers

1. An aldehyde react with excess alcohol in the presence of dry HCL to yield alkoxy alcohol intermediate known as hemiacetals which further reacts with one more molecule of alcohol to give a gem-dialkoxy compound known as acetal.

2. Carboxylic acid is a stronger acid than phenol because the negative charge in carboxylate anion is more spread out compared to the phenoxide ion as there are two electronegative O-atoms in carboxylic anion compared to one in phenoxide ion. In the resonance structures of carboxylate anion, the negative charge is present on the O-atoms while in resonance of phenoxide ion, negative charge is also present on electropositive carbon atom which leads to less stability of phenoxide ion than carboxylate anion.

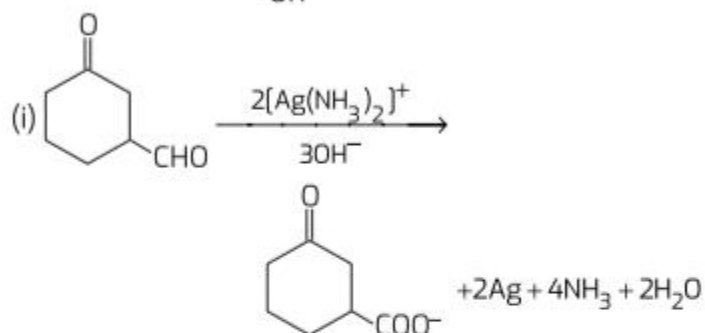
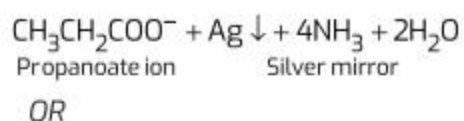
3.



Aldehydes are more reactive than ketones towards Grignard reagents due to less steric hindrance. Grignard reagents attack if the bulkiness is low.

(ii) Propanal and propanone can be distinguished by the Tollen's test. Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But propanone being a ketone does not

reduce Tollen's reagent.



The main product obtained is silver mirror due to the formation of silver metal.



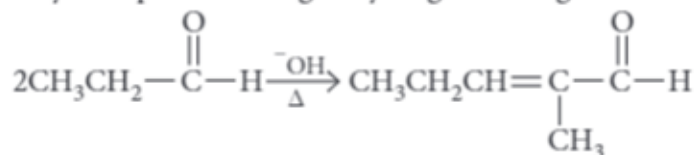
The main product obtained is Benzaldehyde semicarbazone.

Solutions for Questions 3 to 12 are Given Below

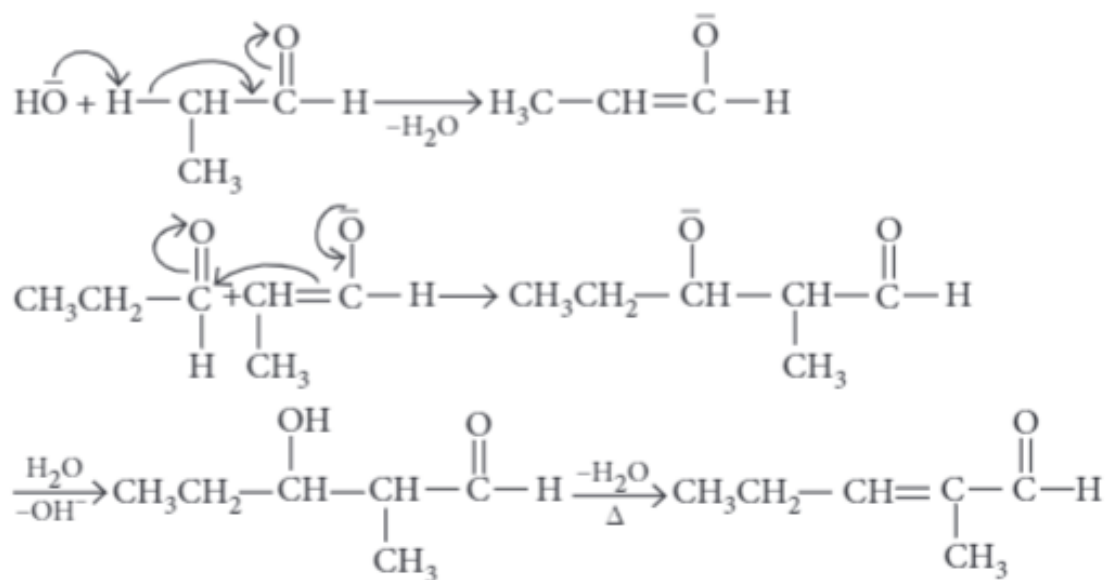
Case Study 3

Read the passage given below and answer the following questions :

The addition reaction of enol or enolate to the carbonyl functional group of aldehyde or ketone is known as aldol addition. The β -hydroxyaldehyde or β -hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction. Carbonyl compound having α -hydrogen undergoes aldol condensation reaction.



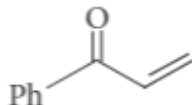
Mechanism :



The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Condensation reaction is the reverse of which of the following reaction?
 - (a) Lock and key hypothesis
 - (b) Oxidation
 - (c) Hydrolysis
 - (d) Glycogen formation
- (ii) Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?
 - (a) $\text{CH}_3\text{CH}=\text{CHCHO}$
 - (b) $\text{CH}_3\text{CH}=\text{CHCOCH}_3$
 - (c) $(\text{CH}_3)_2\text{C}=\text{CHCHO}$
 - (d) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$

(iii) Which combination of carbonyl compounds gives phenyl vinyl ketone by an aldol condensation?



- (a) Acetophenone and Formaldehyde (b) Acetophenone and acetaldehyde
(c) Benzaldehyde and acetaldehyde (d) Benzaldehyde and acetone

(iv) Which of the following will undergo aldol condensation?

- (a) HCHO (b) $\text{CH}_3\text{CH}_2\text{OH}$ (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$

OR

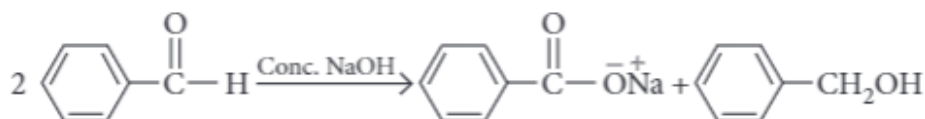
Which of the following does not undergo aldol condensation ?

- (a) CH_3CHO (b) $\text{CH}_3\text{CH}_2\text{CHO}$ (c) CH_3COCH_3 (d) $\text{C}_6\text{H}_5\text{CHO}$

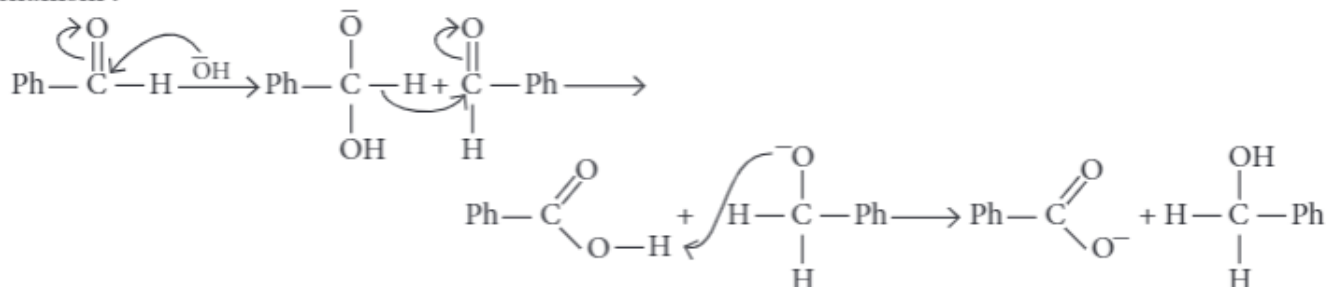
Case Study 4

Read the passage given below and answer the following questions :

When an aldehyde with no α -hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction.



Mechanism :



The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate (b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol.
- (ii) Which of the following compounds will undergo Cannizzaro reaction?
(a) CH_3CHO (b) CH_3COCH_3
(c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$
- (iii) Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is
(a) 2, 2, 2-trichloroethanol (b) trichloromethanol
(c) 2, 2, 2-trichloropropanol (d) chloroform.

OR

In Cannizzaro reaction given below :

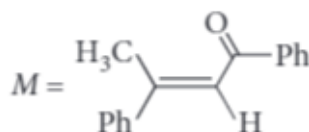


- (a) the attack OH^- at the carboxyl group
 (b) the transfer of hydride to the carbonyl group
 (c) the abstraction of proton from the carboxylic group
 (d) the deprotonation of PhCH_2OH .
- (iv) Which of the following reaction will not result in the formation of carbon-carbon bonds?
 (a) Cannizzaro reaction
 (b) Wurtz reaction
 (c) Reimer-Tiemann reaction
 (d) Friedel-Crafts' acylation

Case Study 5

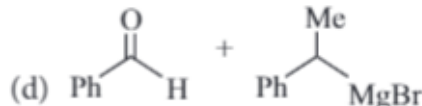
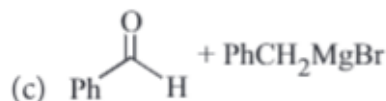
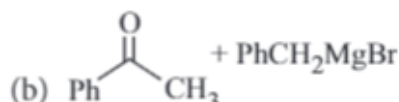
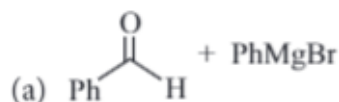
Read the passage given below and answer the following questions :

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*.



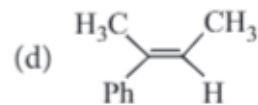
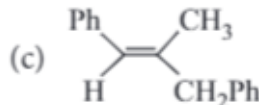
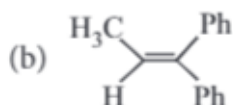
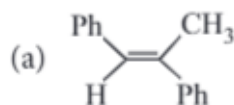
The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Compound *H* is formed by the reaction of



OR

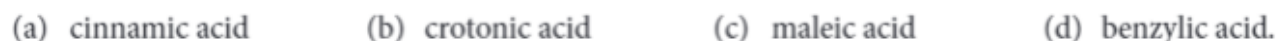
The structure of compound *I* is



- (ii) The structures of compound *J*, *K* and *L*, respectively, are



- (iii) When (*J*) is treated with acetic anhydride, in the presence of corresponding salt of an acid, the product obtained is



- (iv) Which of the following statements is correct for compound (*K*)?

- (a) It reacts with alkaline KMnO_4 followed by acidic hydrolysis and forms benzoic acid.
 (b) It reacts with iodine and NaOH to form triiodomethane.
 (c) It is prepared by the reaction of benzene with benzoyl chloride in presence of anhydrous aluminium chloride.
 (d) It reacts with freshly prepared ammoniacal silver nitrate solution.

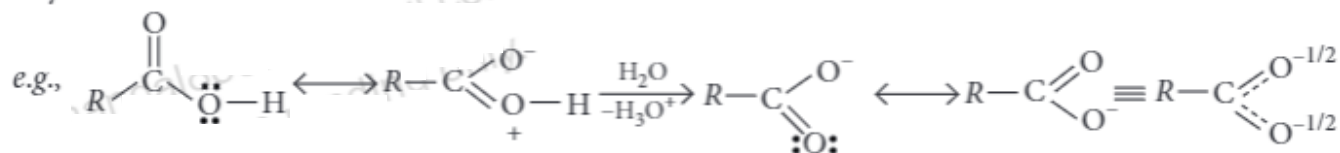
Case Study 6

Read the passage given below and answer the following questions :

Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.



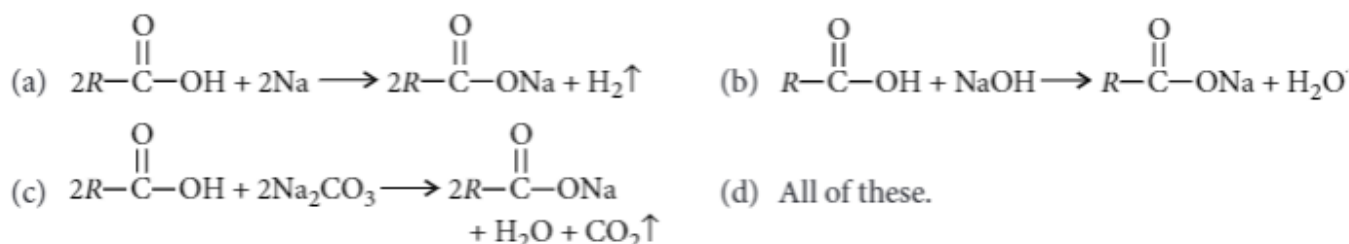
The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising the conjugate base.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following reactions is showing the acidic property of carboxylic acid?

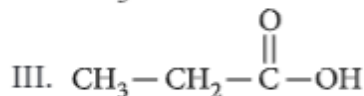
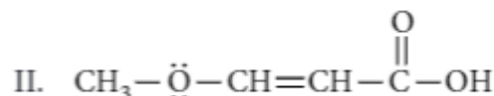
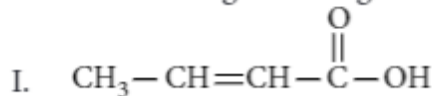


(ii) Which one of the following is the correct order of acidic strength?

- (a) $\text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{HCOOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (b) $\text{CH}_3\text{COOH} > \text{HCOOH} > \text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
 (c) $\text{HCOOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (d) $\text{CF}_3\text{COOH} > \text{CH}_3\text{COOH} > \text{HCOOH} > \text{CHCl}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

OR

The acidic strength of the given compounds follows the order :

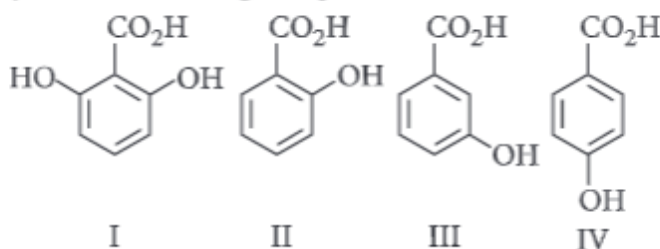


- (a) $\text{II} > \text{III} > \text{I}$ (b) $\text{III} > \text{II} > \text{I}$ (c) $\text{II} > \text{I} > \text{III}$ (d) $\text{I} > \text{II} > \text{III}$

(iii) Which of the following acids has the smallest dissociation constant?

- (a) $\text{CH}_3\text{CHF}\text{COOH}$ (b) $\text{FCH}_2\text{CH}_2\text{COOH}$ (c) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CHBr}\text{COOH}$

(iv) The correct order of acidity for the following compounds is

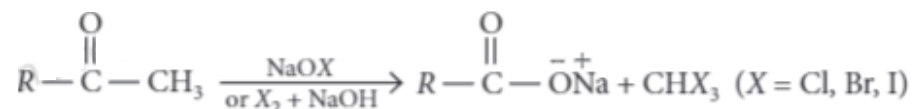


- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{III} > \text{I} > \text{II} > \text{IV}$ (c) $\text{III} > \text{IV} > \text{II} > \text{I}$ (d) $\text{I} > \text{III} > \text{IV} > \text{II}$

Case Study 7

Read the passage given below and answer the following questions :

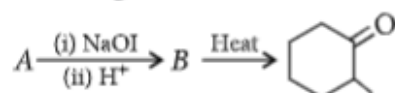
Aldehydes and ketones having acetyl group $\left(\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}- \right)$ are oxidised by sodium hypohalate (NaOX) or halogen and alkali ($\text{X}_2 + \text{OH}^-$) to corresponding sodium salt having one carbon atoms less than the carbonyl compound and give a haloform.



Sodium hypoiodite (NaOI) when treated with compounds containing $\text{CH}_3\text{CO}-$ group gives yellow precipitate of iodoform. Haloform reaction does not affect a carbon-carbon double bond present in the compound.

The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Which of the following compounds will give positive iodoform test?
- (a) Isopropyl alcohol (b) Propionaldehyde
(c) Ethylphenyl ketone (d) Benzyl alcohol
- (ii) Which of the following compounds is not formed in iodoform reaction of acetone?
- (a) $\text{CH}_3\text{COCH}_2\text{I}$ (b) $\text{ICH}_2\text{COCH}_2\text{I}$
(c) $\text{CH}_3\text{COCHI}_2$ (d) CH_3COCI_3
- (iii) For the given set of reactions,

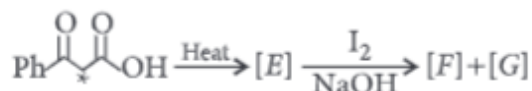
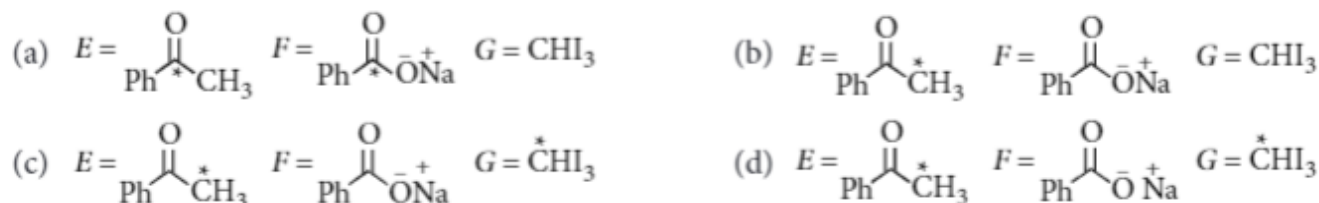


starting compound A corresponds to



OR

In the following reaction sequence, the correct structures of E, F and G are

(* implies ^{13}C labelled carbon)

- (iv) An organic compound 'A' has the molecular formula C_3H_6O . It undergoes iodoform test. When saturated with HCl it gives 'B' of molecular formula $C_9H_{14}O$. 'A' and 'B' respectively are
- (a) propanal and mesityl oxide (b) propanone and mesityl oxide
(c) propanone and 2,6-dimethyl-2,5-hepta-dien-4-one (d) propanone and propionaldehyde.

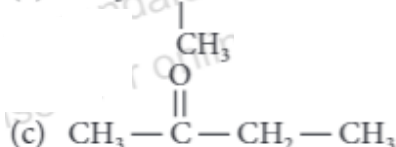
Case Study 8

Read the passage given below and answer the following questions :

(A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O . Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive iodoform test. Isomers (A) and (B) on reduction with $Zn(Hg)/conc. HCl$ give the same product (D).

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound A is



(d) none of these.

OR

Compound (C) is

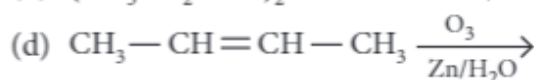
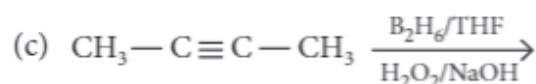
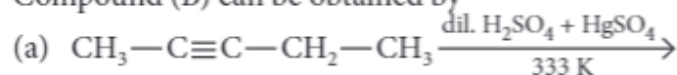
(a) *iso*-butyraldehyde

(b) butyraldehyde

(c) crotonaldehyde

(d) acrolein.

(ii) Compound (B) can be obtained by



(iii) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

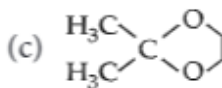
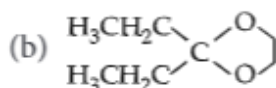
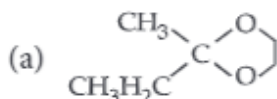
(a) A

(b) B

(c) C

(d) All are equally reactive

(iv) What will be the product when (B) reacts with ethylene glycol in presence of HCl gas?



(d) None of these.

Case Study 9

Read the passage given below and answer the following questions :

Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$ as well as catalytic hydrogenation. The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with $Zn-Hg$ and conc. HCl (Clemmensen reduction) or with hydrazine followed by $NaOH$ or KOH in highly boiling solvent such as ethylene glycol (Wolff-Kishner reduction).

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with HNO_3 , $KMnO_4$, $K_2Cr_2O_7$ etc. Even mild oxidising agents mainly Tollens' reagent and Fehling's solution also oxidise aldehydes. Ketones are generally oxidised under vigorous conditions *i.e.*, strong oxidising agents and at elevated temperatures, to give mixture of carboxylic acids having lesser number of C-atoms than the parent ketone.

The following questions are multiple choice questions. Choose the most appropriate answer :

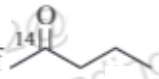
(i) Which of the following cannot be made by reduction of ketone or aldehyde with $NaBH_4$ in methanol?

(a) 1-Butanol

(b) 2-Butanol

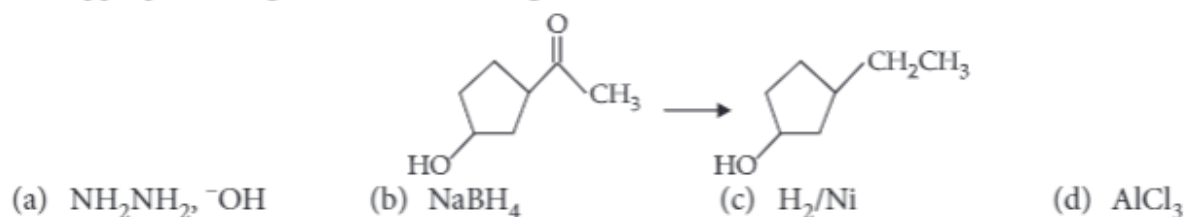
(c) 2-Methyl-1-propanol

(d) 2-Methyl-2-propanol

- (ii) The carbonyl compound producing an optically active product by reaction with LiAlH_4 is
 (a) propanone (b) butanone (c) 3-pentanone (d) benzophenone.
- (iii) A substance $\text{C}_4\text{H}_{10}\text{O}(X)$ yields on oxidation a compound $\text{C}_4\text{H}_8\text{O}$ which gives an oxime and a positive iodoform test. The substance X on treatment with conc. H_2SO_4 gives C_4H_8 . The structure of the compound (X) is
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (c) $(\text{CH}_3)_3\text{COH}$ (d) $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$
- (iv) In the oxidation of  by acidified $\text{K}_2\text{Cr}_2\text{O}_7$, the products are
 (a) $\text{CH}_3-\overset{14}{\text{C}}(\text{O})-\text{OH}$ and $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $\text{CH}_3(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and $\overset{14}{\text{CH}_3}\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{HCOOH}$ (d) none of these.

OR

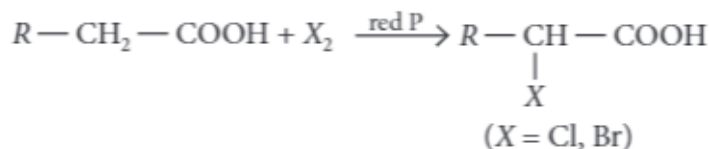
The appropriate reagent for the following transformation is



Case Study 10

Read the passage given below and answer the following questions :

Carboxylic acids having an α -hydrogen atom when treated with chlorine or bromine in the presence of small amount of red phosphorus gives α -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



When sodium salt of carboxylic acid is heated with soda lime it loses carbon dioxide and gives hydrocarbon with less number of C-atoms.



In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.
- (i) **Assertion :** $(\text{CH}_3)_3\text{CCOOH}$ does not give H.V.Z reaction.
Reason : $(\text{CH}_3)_3\text{CCOOH}$ does not have α -hydrogen atom.

(ii) **Assertion** : H.V.Z. reaction involves the treatment of carboxylic acids having α -hydrogens with Cl_2 or Br_2 in presence of small amount of red phosphorus.

Reason : Phosphorus reacts with halogens to form phosphorus trihalides.

OR

Assertion : Propionic acid with Br_2/P yields $\text{CH}_3\text{Br} + \text{CHBr} - \text{COOH}$.

Reason : Propionic acid has two α -hydrogen atoms.

(iii) **Assertion** : $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$ undergoes decarboxylation easily than $\text{C}_6\text{H}_5\text{COCOCH}_3$.

Reason : $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$ is a β -keto acid.

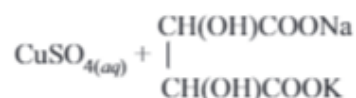
(iv) **Assertion** : On heating 3-methylbutanoic acid with soda lime, isobutane is obtained.

Reason : Soda lime is a mixture of $\text{NaOH} + \text{CaO}$ in the ratio 3 : 1.

Case Study 11

Read the passage given below and answer the following questions :

Fehling's reagent : Fehling's reagent is a mixture of two solutions. Fehling's solution A is aqueous copper sulphate solution. Fehling's solution B is alkaline sodium potassium tartarate (Rochelle salt).



It is a mild oxidising agent. It is weaker than Tollens' reagent. It oxidises only aliphatic aldehydes to carboxylate ions and itself gets reduced to reddish brown precipitate of cuprous oxide.

Aromatic aldehydes do not respond to Fehling's test. This reaction is used for the test of aliphatic aldehydes known as Fehling's reagent test.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion** : Fehling's solution can be used to distinguish between acetaldehyde and acetone.

Reason : Fehling's reagent is a mixture of two solutions.

(ii) **Assertion** : Aromatic aldehydes can be distinguished from aliphatic aldehydes by Fehling's solution.

Reason : Aromatic aldehydes reduce Fehling's solution, but aliphatic aldehydes do not.

OR

Assertion : Fehling's solution oxidises acetaldehyde to acetic acid but not benzaldehyde to benzoic acid.

Reason : The C — H bond of — CHO group in benzaldehyde is stronger than in acetaldehyde.

(iii) **Assertion** : CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ cannot be distinguished chemically by Fehling's solution.

Reason : CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ can be distinguished by iodoform test.

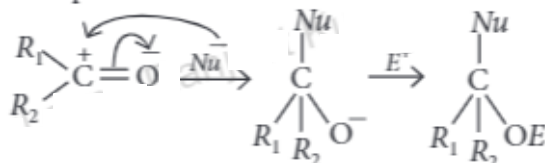
(iv) **Assertion** : Formaldehyde, when heated with Fehling's reagent produces a reddish brown ppt. of Cu.

Reason : Fehling's reagent oxidises formaldehyde to formate ion.

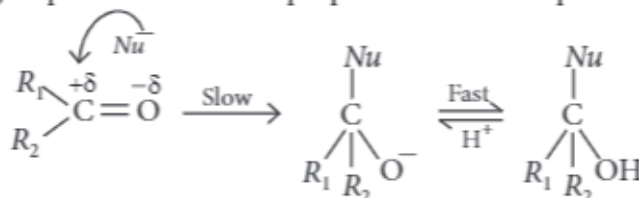
Case Study 12

Read the passage given below and answer the following questions :

Aldehydes and ketones undergo nucleophilic addition reactions.



Carbonyl carbon is electron deficient hence acts as an electrophile. Nucleophile attacks on the electrophilic carbon atom of the carbonyl group from a direction perpendicular to the plane of the molecule.



In this process, hybridisation of carbon atom changes from sp^2 to sp^3 and a tetrahedral alkoxide ion is formed as intermediate. This intermediate captures proton from the reaction medium to give the neutral product. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

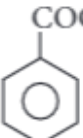
- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Benzaldehyde is more reactive than ethanal towards nucleophilic attack.

Reason : The overall effect of $-I$ and $+R$ effect of phenyl group decreases the electron density on the carbon atom of $>\text{C}=\text{O}$ group in benzaldehyde.

(ii) **Assertion :** $(\text{CH}_3)_3\text{CCOC}(\text{CH}_3)_3$ and acetone can be distinguished by the reaction with NaHSO_3 .

Reason : HSO_3^- is the nucleophile in bisulphite addition.

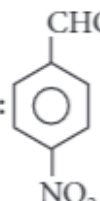
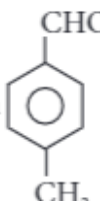
(iii) **Assertion :** Ease of nucleophilic addition of the compounds  (I), CH_3CHO (II) and CH_3COCH_3 (III) is $\text{I} > \text{II} > \text{III}$.

Reason : Aldehydes and ketones undergo nucleophilic addition reactions.

OR

Assertion : The formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN . This reaction is catalysed by a base.

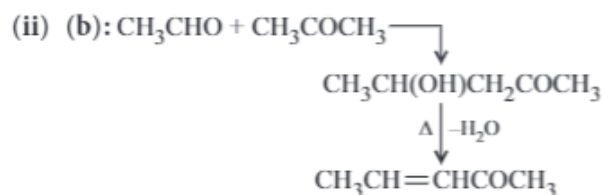
Reason : Base generates CN^- ion which is a stronger nucleophile.

(iv) **Assertion :**  is more reactive towards nucleophilic addition reaction than .

Reason : Reactivity of carbonyl group is due to electrophilic nature of carbonyl carbon.

HINTS & EXPLANATIONS

3. (i) (c): Condensation reaction is the reverse of hydrolysis, which splits a chemical entity into two parts through the action of the polar water molecule.



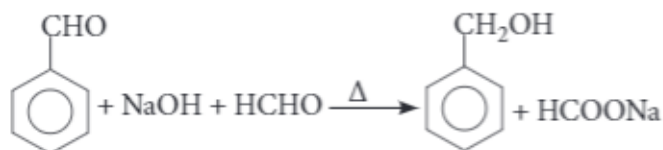
(iii) (a)

(iv) (d)

OR

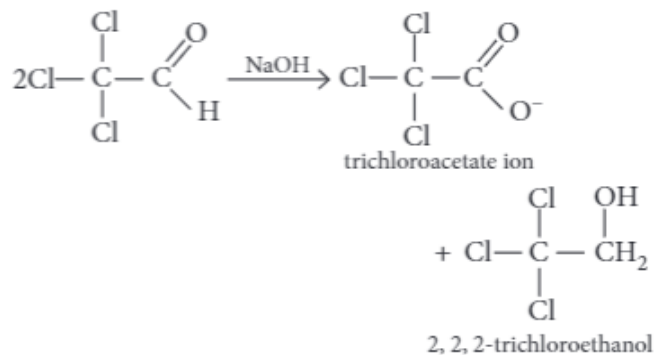
(d) : Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) with no α -hydrogen cannot undergo aldol condensation.

4. (i) (a): It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any α -hydrogen).



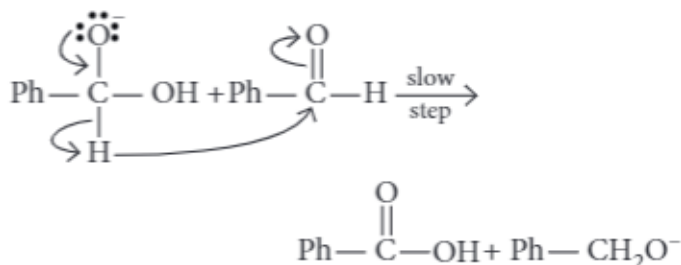
(ii) (c)

(iii) (a): The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



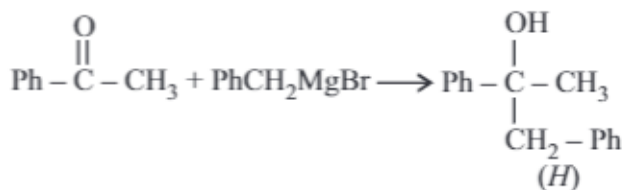
OR

(b) : Hydride transfer is the slowest step.

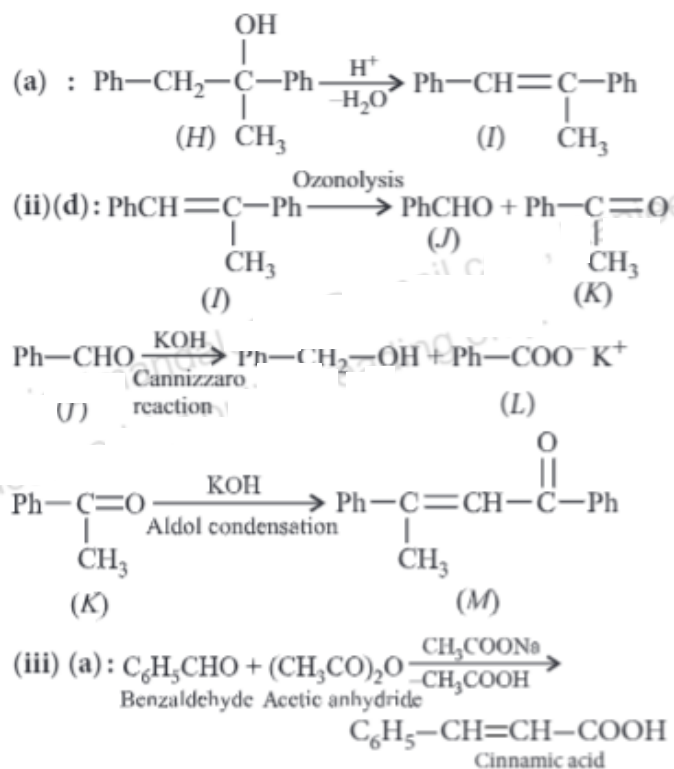


(iv) (a): C—C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C—C bond.

5. (i) (b) :



OR



(iv) (b)

6. (i) (d): All the reactions are showing the acidic properties of carboxylic acid. Carboxylic acid forms the sodium salts with all *i.e.*, alkali metals, NaOH and Na_2CO_3 etc. and removes the acidic proton from the carboxylic acid.

(ii) (a): In general, greater the $+I$ effect of the group attached to the carboxyl group, lesser will be the acidic strength and greater the $-I$ effect of the group, greater will be acidic strength. As number of halogen atoms and electronegativity of halogen atom increases, acidic strength increases.

Thus, correct order of acidic strength is



OR

(d)

(iii) (c): Stronger $-I$ group attached closer to $-\text{COOH}$ makes the acid stronger, *i.e.*, acid has the larger dissociation constant. $-\text{Br}$ shows poor ($-I$) effect and also far away from $-\text{COOH}$ group *i.e.*, option (c) has smallest dissociation constant.

(iv) (a): Due to *ortho*-effect, (I) and (II) are stronger acids than (III) and (IV). Due to two *ortho*-hydroxyl groups in (I), it is stronger acid than (II). (III) is a

stronger acid than (IV) because at *m*-position, $-\text{OH}$ group cannot exert its $+R$ effect but can only exert its $-I$ effect while at *p*-position, $-\text{OH}$ group exerts its strong $+R$ effect.

Thus, the correct order of acidity is:



7. (i) (a): Iodoform test is given by the organic

compounds having $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ or $\text{CH}_3-\underset{\text{OH}}{\underset{|}{\text{CH}}}-$ group.

$\text{CH}_3-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{OH}$: Isopropyl alcohol

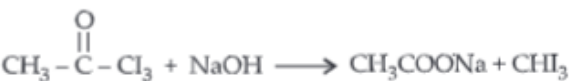
$\text{CH}_3\text{CH}_2\text{CHO}$: Propionaldehyde

$\text{C}_2\text{H}_5-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{C}_6\text{H}_5$: Ethylphenyl ketone

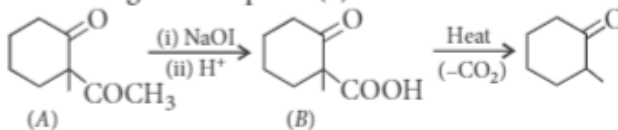
$\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$: Benzyl alcohol

Therefore, isopropyl alcohol will give positive iodoform test.

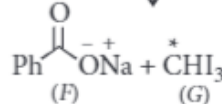
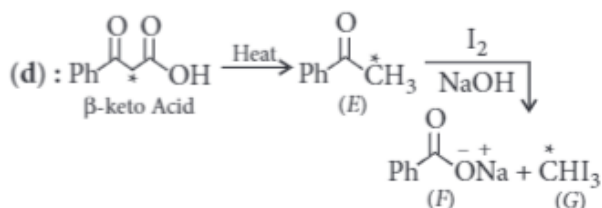
(ii) (b): Iodoform reaction of acetone occurs in following steps:



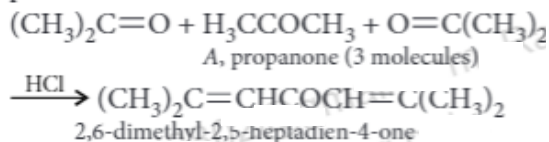
(iii) (c): Given reagents indicate the presence of $-\text{COCH}_3$ group in the starting compound A. Further, since the $-\text{COOH}$ group introduced in B due to iodoform reaction is absent in the final product, B should be a β -keto acid. Hence, A should have structure given in option (c).



OR

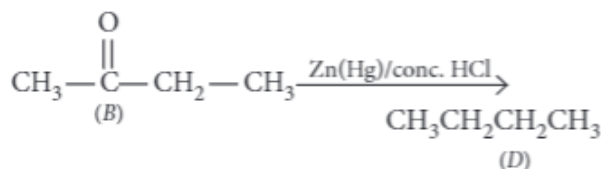
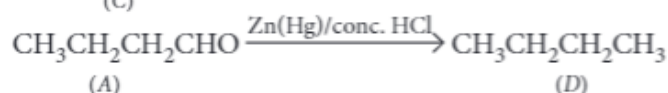
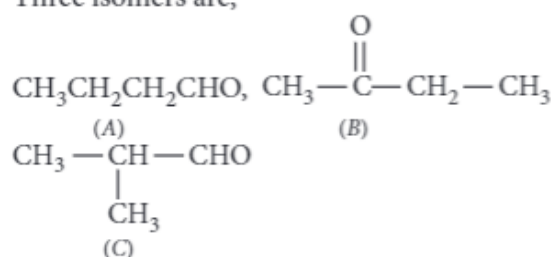


(iv) (c): Since compound A (C_3H_6O) undergoes iodoform test, it must be CH_3COCH_3 (propanone). Further, the compound 'B' obtained from 'A' has three times more the number of carbon atoms as in 'A' (propanone), 'B' must be phorone, i.e., 2,6-dimethyl-2,5-heptadien-4-one.



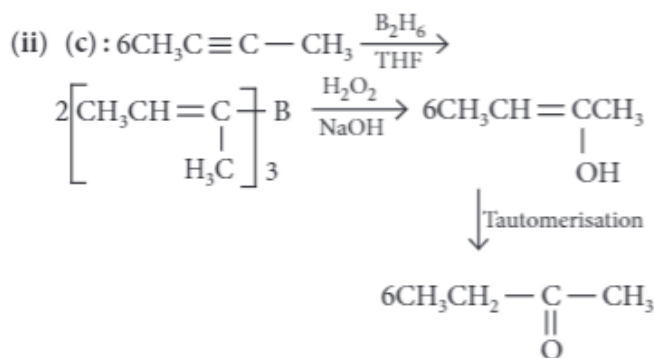
8. (i) (b): As (A) and (C) gives positive Tollens' test thus these two should be aldehydes while (B) should be a ketone (does not give Tollen's test) with $-\overset{\overset{O}{\parallel}}{C}-CH_3$ group (as it gives positive iodoform test).

Three isomers are,



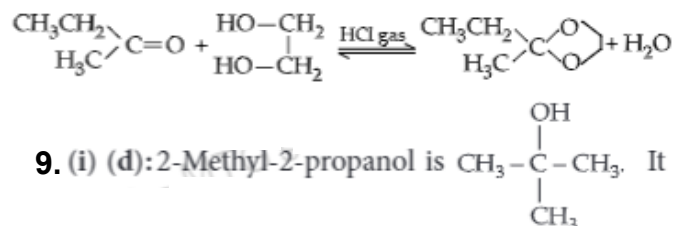
OR

(d)

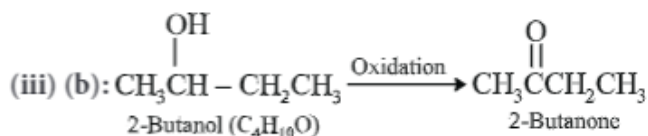
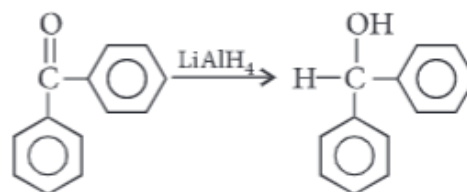
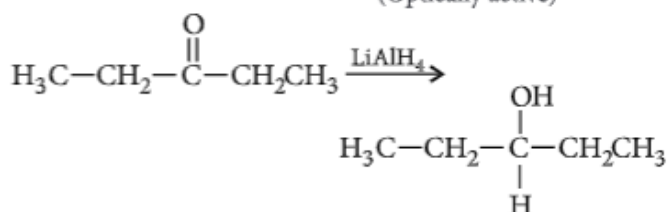
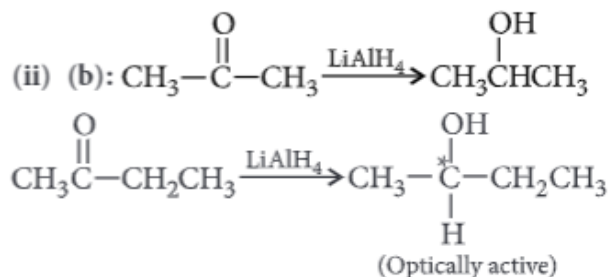


(iii) (b): (B) is least reactive among the three isomers towards addition of HCN. Aldehydes are more reactive than ketones towards nucleophilic addition reactions.

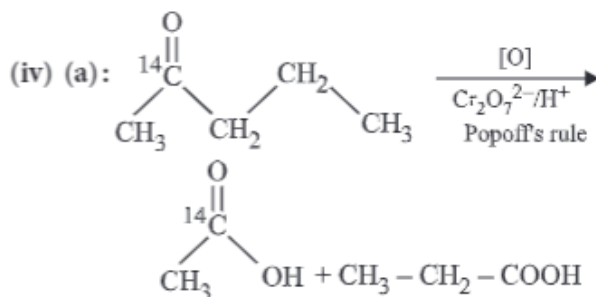
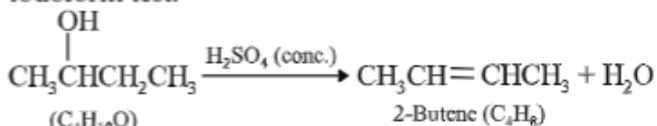
(iv) (a): When butanone reacts with ethylene glycol in presence of HCl, it forms a ketal.



cannot be obtained by reduction of an aldehyde or ketone with $NaBH_4$.



2-Butanone forms oxime on reaction with hydroxylamine (NH_2OH) and also gives positive iodoform test.



OR

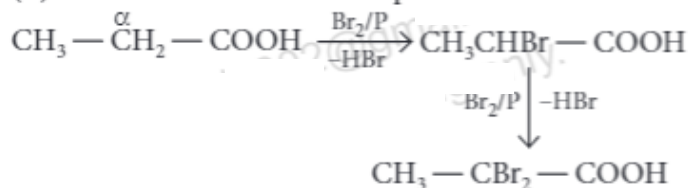
(a): This reaction is Wolff-Kishner reduction. The reagents used for this reduction are NH_2NH_2/KOH .

10. (i) (a)

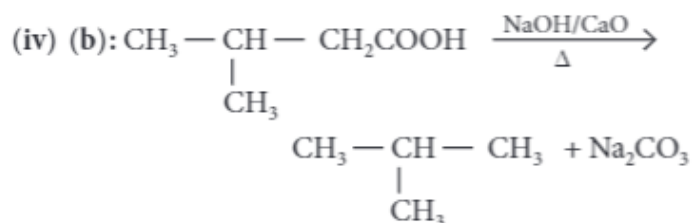
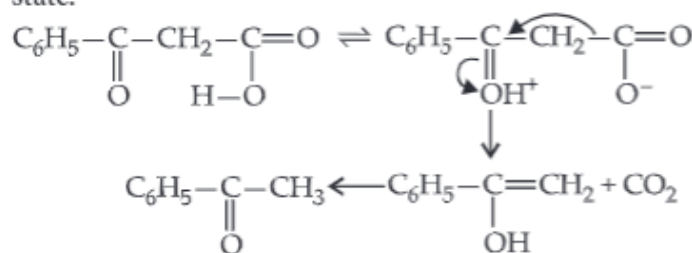
(ii) (c): Phosphorus converts a little of the acid into acid chloride which is more reactive than the parent carboxylic acid. Thus, it is the acid chloride, not the acid itself, that undergoes chlorination at the α -carbon.

OR

(d): Bromination occurs at α -positions.



(iii) (a): β -ketoacids are unstable acids. They readily undergo decarboxylation through a cyclic transition state.



11. (i) (b): All aliphatic aldehydes give red ppt. with Fehling's solution, but ketones do not reduce Fehling's solution.

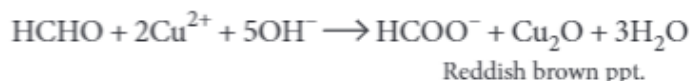
(ii) (c): Aliphatic aldehydes reduce Fehling's solution, but aromatic aldehydes do not.

OR

(a): Fehling's solution is a mild oxidising agent. It cannot oxidise aromatic aldehydes to corresponding carboxylate ion.

(iii) (b): CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ both are aliphatic aldehydes, hence cannot be distinguished by Fehling's solution. CH_3CHO contains CH_3CO -group whereas $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ does not contain any CH_3CO -group. Thus, CH_3CHO will give yellow ppt. with I_2 and NaOH but $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ will not.

(iv) (d): Formaldehyde when heated with Fehling's reagent, undergo oxidation to give formate ion and produce reddish brown ppt. of Cu_2O .

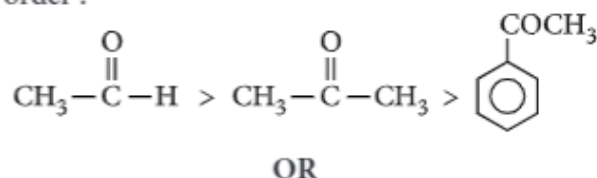


12. (i) (a)

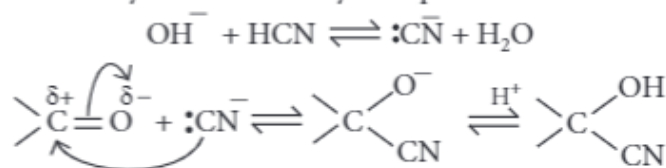
(ii) (b): HSO_3^- is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

(iii) (d): Aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues towards nucleophilic addition reactions due to the +R effect of benzene ring. Further, aldehydes are more reactive than ketones due to +I effect and steric effect of alkyl group.

Therefore, the ease of nucleophilic addition will follow the order :



(a): Formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN because it is feebly ionised. This reaction is catalysed by a base. Base generates CN^- ion which is a stronger nucleophile and readily adds to carbonyl compound.



(iv) (b): Electron withdrawing group ($-\text{NO}_2$) increases the reactivity towards nucleophilic addition reactions, whereas electron donating group ($-\text{CH}_3$) decreases the reactivity towards nucleophilic addition reactions.