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Hydrocarbons

Multiple Choice Questions (MCQs)

Q. 1 Arrange the following in decreasing order of their boiling points.

A. *n* –butane

B. 2-methylbutane

C. *n* –pentane

D. 2, 2-dimethylpropane

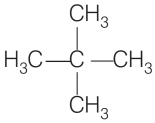
(a) $A > B > C > D$ (b) $B > C > D > A$

(c) $D > C > B > A$ (d) $C > B > D > A$

Ans. *(d)* As the number of carbon atom increases, boiling point increases.

Boiling point decreases with branching

2, 2 -dimethyl propane, ***n* – pentane,** **2-methyl butane**

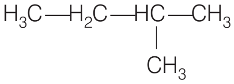


$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

b.pt = 282.5K

$H_3C-CH_2-CH_2-CH_2-CH_3$

b.pt = 309.1 K



$$H_3C-H_2C-\underset{\underset{CH_3}{|}}{HC}-CH_3$$

b.pt = 301K

***n*-butane**

$H_3C-H_2C-CH_2-CH_3$

b.pt = 273 K

(4 carbon atoms with no branching)

Q. 2 Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.

(a) $I_2 < Br_2 < Cl_2 < F_2$ (b) $Br_2 < Cl_2 < F_2 < I_2$

(c) $F_2 < Cl_2 < Br_2 < I_2$ (d) $Br_2 < I_2 < Cl_2 < F_2$

Ans. *(a)* Rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$

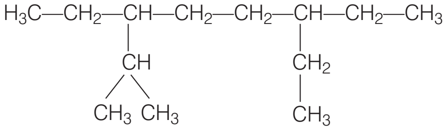
Alkane react with F_2 is vigorously and with I_2 the reaction is too slow that it requires a catalyst. It is because of high electronegativity of fluorine. Reactivity decreases with decrease in electronegativity and electronegativity decreases down the group

Q. 3 The increasing order of reduction of alkyl halides with zinc and dilute HCl is

(a) $R-Cl < R-I < R-Br$
(b) $R-Cl < R-Br < R-I$
(c) $R-I < R-Br < R-Cl$
(d) $R-Br < R-I < R-Cl$

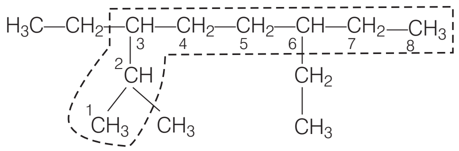
Ans. ***(b)*** The reactivity of halogens with alkane is $F_2 > Cl_2 > Br_2 > I_2$ Hence, reduction of alkyl halide with Zn and dilute HCl follows reverse order *i.e.,* $R-I > R-Br > R-Cl$. Further, the reactivity of this reduction increases as the strength of $C-X$ bond decreases

Q. 4 The correct IUPAC name of the following alkane is



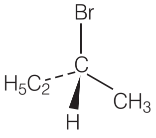
(a) 3,6-diethyl-2-methyloctane
(b) 5-isopropyl -3-ethyloctane
(c) 3-ethyl-5-isopropyloctane
(d) 3-isopropyl-6-ethyloctane

Ans. ***(a)*** The correct IUPAC name is

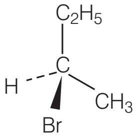


Longest chain - 8C atom alkane = octane
Branch on 2, 3, 6 follows lowest sum rule.
Branch of 2 – C – methyl; 3, 6, C atom-ethyl.
Ethyl comes alphabetically before methyl.
Hence, 3,6-diethyl 2-methyl octane.

Q. 5 The addition of HBr to 1-butene gives a mixture of products *A*, *B* and *C*.



(*A*)



(*B*)

$CH_3-CH_2-CH_2-CH_2-Br$

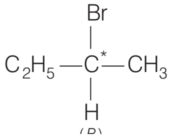
(*C*)

The mixture consists of

(a) *A* and *B* as major and *C* as minor products
(b) *B* as major, *A* and *C* as minor products
(c) *B* as minor, *A* and *C* as major products
(d) *A* and *B* as minor and *C* as major products

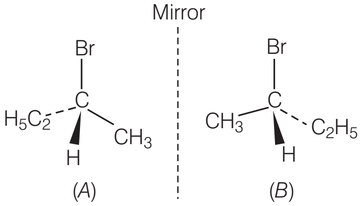
Ans. ***(a)*** The alkene is unsymmetrical, hence will follow Markownikoff's rule to give major product.

$$\underset{\text{Butene -1}}{CH_3-CH_2-CH=CH_2} + H-Br \longrightarrow \underset{(A)}{CH_3-CH_2-CHBr-CH_3} +$$

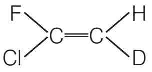


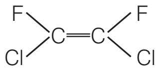
$$C_2H_5-\overset{*}{C}(Br)(H)-CH_3 \quad + \underset{(C)\ (\text{minor product})}{CH_3-CH_2-CH_2-CH_2Br}$$

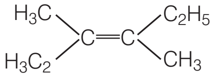
Since, I contains, a chiral carbon, it exists in two enantiomers (*A* and *B*) which are mirror images of each other.

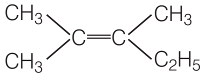


Q. 6 **Which of the following will not show geometrical isomerism?**

(a)


(b)


(c)


(d)


Thinking Process

This question is based upon geometrical isomerism. For geomterical isomerism, it is essential that each carbon atom of the double bond must have different substituents.

Ans. ***(d)*** In option (d), a carbon with double bond has two same functional groups (CH_3) attached. The rotation around carbon will not produce a new compound. Hence, geometrical isomerism is not possible.

Q. 7 **Arrange the following hydrogen halides in order of their decreasing reactivity with propene.**

(a) HCl > HBr > HI
(b) HBr > HI > HCl
(c) HI > HBr > HCl
(d) HCl > HI > HBr

Ans. ***(c)*** Bond energy of HI is 296.8 kJ/mol, HBr is 36.7 kJ/mol and HCl is 430.5 kJ/mol. Hence, HI > HBr > HCl is the order of reactivity with propene.

Q. 8 **Arrange the following carbanions in order of their decreasing stability.**

A. $H_3C—C \equiv C^-$

B. $H-C \equiv C^-$

C. $H_3C—\overline{C}H_2$

(a) A > B > C
(b) B > A > C
(c) C > B > A
(d) C > A > B

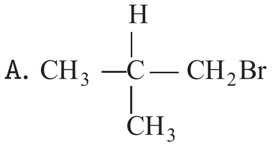
Ans. ***(b)*** + *I*-effect decreases the stability of carbon anion. Since, (CH_3) group has + *I*-effect, therefore, it intensifies the negative charge and hence destabilises (A) relative to (B).

sp hybridised carbanion is more stabilised than sp^3

$$CH \equiv \underset{(B)^{sp}}{C^-} > CH_3 — C \equiv \underset{(A)^{sp}}{C^-} > \underset{(C)}{CH_3} — \underset{sp^3}{CH_2}$$

Hence, B> A> C

Q. 9 Arrange the following alkyl halides in decreasing order of the rate of β – elimination reaction with alcoholic KOH.

A. 

$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2Br$$

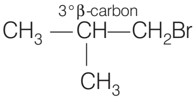
B. CH_3-CH_2-Br

C. $CH_3-CH_2-CH_2-Br$

(a) A > B > C (b) C > B > A (c) B > C > A (d) A > C > B

Ans. *(d)* Alkyl halides on heating with alcoholic potash eliminates one molecule of halogen acid to form alkene. Hydrogen is eliminated from β-carbon atom. Nature of alkyl group determines rate of reaction

i.e., $3° > 2° > 1°$ or $A > \underset{2°\ \beta\text{–Carbon}}{C > B}$



$$CH_3-\overset{3°\beta\text{-carbon}}{\underset{\displaystyle CH_3}{\underset{|}{CH}}}-CH_2Br$$

(*A*)

$$CH_3-\overset{1°\beta\text{-carbon}}{CH_2}-Br$$

(*B*)

$$CH_3-CH_2-CH_2-Br$$

(*C*)

Q. 10 Which of the following reactions of methane is incomplete combustion?

(a) $2CH_4 + O_2 \xrightarrow{Cu/\,523\,K/100\,atm} 2CH_3OH$

(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

(c) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O\ (l)$

(d) $CH_2 + 2O_2 \longrightarrow CO_2\ (g) + 2H_2O(l)$

Ans. *(c)* During incomplete combustion of alkanes with insufficient amount of air or dioxygen carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters. Thus,

$$CH_4(g) + O_2(g) \xrightarrow[\text{combustion}]{\text{Incomplete}} C(s) + 2H_2O\ (l)$$

Multiple Choice Questions (More Than One Options)

Q. 11 Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions?

(a) $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O(l)$

(b) $CH_4\ (g) + O_2\ (g) \longrightarrow C(s) + 2H_2O\ (l)$

(c) $CH_4\ (g) + O_2\ (g) \xrightarrow{Mo_2O_3} HCHO + H_2O$

(d) $2CH_4\ (g) + O_2\ (g) \xrightarrow{Cu/523/100\ atm} 2CH_3OH$

Ans. *(c, d)*

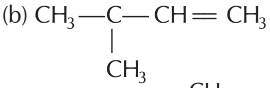
Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

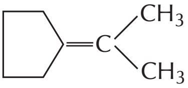
$$2CH_4 + O_2 \xrightarrow{Cu/\,523K/100\,atm} 2CH_3OH$$

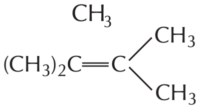
$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O.$$

Q. 12 Which of the following alkenes on ozonolysis give a mixture of ketones only?

(a) $CH_3-CH=CH-CH_3$

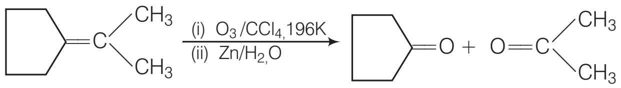
(b)

$CH_3-\underset{\substack{|\\CH_3}}{C}-CH=CH_3$

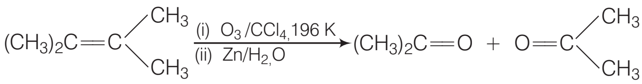
(c)


(d)


Ans. ***(c, d)***

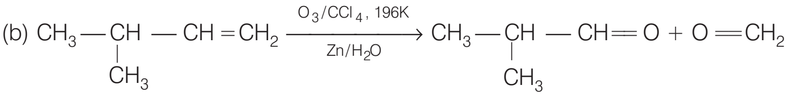
Alkenes which have two substituents on each carbon atom of the double bond, give mixture of ketones on ozonolysis. Thus, option (c) and (d) give mixture of ketones.

(c)


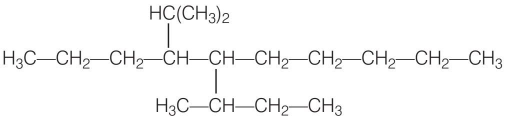
(d)


On the other hand, alkenes (a) and (b) give a mixture of two aldehydes.

(a) $CH_3CH=CH-CH_3 \xrightarrow[Zn/H_2O]{O_3/CCl_4,\ 196K} CH_3CH=O+O=CHCH_3$

(b)

$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH=CH_2 \xrightarrow[Zn/H_2O]{O_3/CCl_4,\ 196K} CH_3-\underset{\substack{|\\CH_3}}{CH}-CH=O+O=CH_2$

Q. 13 Which are the correct IUPAC names of the following compound?


$H_3C-CH_2-CH_2-\overset{\substack{HC(CH_3)_2\\|}}{CH}-\underset{\substack{|\\H_3C-CH-CH_2-CH_3}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_3$

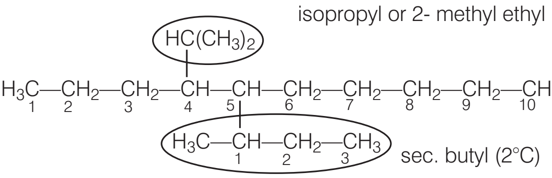
(a) 5-Butyl-4-isopropyldecane

(b) 5-Ethyl-4-propyldecane

(c) 5-*sec*-Butyl -4- *iso*-propyldecane

(d) 4-(1-methylethyl) - 5 - (1-methylpropyl)-decane

Ans. ***(c, d)***

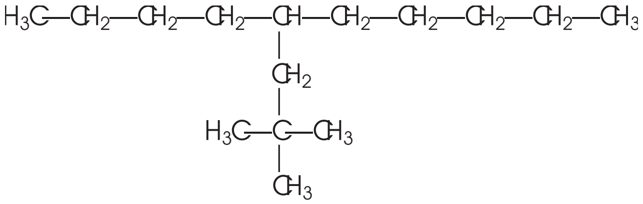


5- sec-Butyl -4 iso -propyldecane

4-(1-methylethyl)-5-(1-methylpropyl)- decane

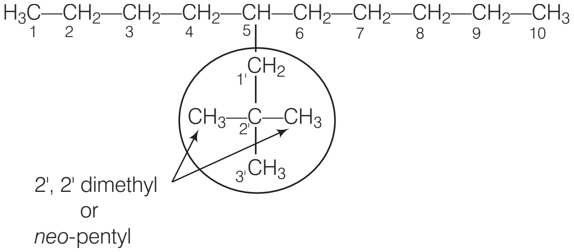
Although IUPAC name for sec- butyl and isopropyl groups are 1methyl propyl and 1-methylethyl respectively yet both these names, are also recommended for IUPAC nomenclature

Q. 14 Which are the correct IUPAC names of the following compound?



(a) 5-(2', 2' - Dimethylpropyl)-decane
(b) 4-Butyl-2,2-dimethylnonane
(c) 2,2- Dimethyl -4- pentyloctane
(d) 5-neo-Pentyldecane

Ans. *(a, d)*



5- (2′,2′- Dimethylpropyl)- decane 5-*neo*- pentyldecane
The IUPAC name for neopentyl groups is 2, 2 dimethyl propyl.

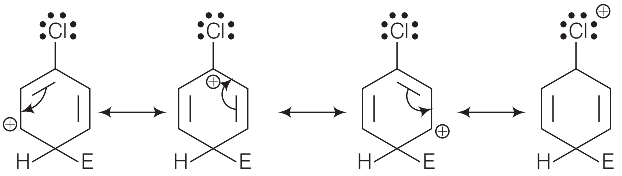
Q. 15 For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring ....

(a) deactivates the ring by inductive effect
(b) deactivates the ring by reasonance
(c) increases the charge density at *ortho* and *para* position relative to *meta* position by resonance.
(d) directs the incoming electrophile to *meta* position by increasing the charge density relative to *ortho* and *para* position.

Ans. *(a, c)*

For an electrophilic substitution reaction, the presence of halogen atom in the benzene ring deactivates the ring by inductive effect and increases the charge density at *ortho* and *para* position relative to *meta* position by resonance.

When chlorine is attached to benzene ring, chlorine being more electronegative pulls the electron *i.e.,–I*-effect. The electron cloud of benzene is less dense. Chlorine makes aryl halide, moderately deactivating group. But due to resonance the electron density on *ortho* and *para* position is greater than in *meta* position.



The last structure contributes more to the orientation and hence halogen are *o*-and *p*-directors.

Q. 16 In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group..........

(a) deactivates the ring by inductive effect

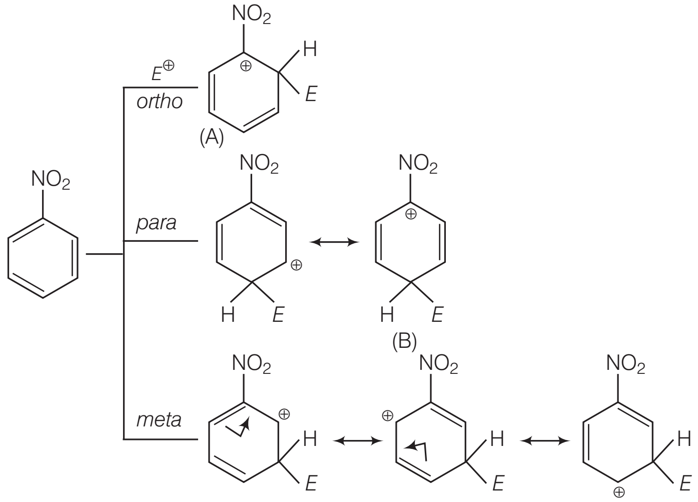
(b) activates the ring by inductive effect

(c) decreases the charge density at *ortho* and *para* position of the ring relative to *meta* position by resonance

(d) increases the charge density at *meta* position relative to the *ortho* and *para* positions of the ring by resonance

Ans. *(a, c)*

Nitro group by virtue of $-I$-effect withdraw electrons from the ring and increase the charge and destabilises carbocation.



In *ortho*, *para*-attack of electrophile on nitrobenzene, we are getting two structures (*A*) and (*B*) in which positive charge is appearing on the carbon atom directly attached to the nitro group.

As nitro group is electron withdrawing by nature, it decreases the stability of such product and hence meta attack is more feasible when electron withdrawing substituents are attached.

Q. 17 Which of the following are correct?

(a) $CH_3—O—CH_2^{\oplus}$ is more stable than $CH_3—CH_2^{\oplus}$

(b) $(CH_3)_2CH^{\oplus}$ is less stable than $CH_3—CH_2—CH_2^{\oplus}$

(c) $CH_2=CH—CH_2^{\oplus}$ is more stable than $CH_3—CH_2—CH_2^{\oplus}$

(d) $CH_2=CH^{\oplus}$ is more stable than $CH_3—CH_2^{\oplus}$

Ans. *(a, c)*

(i) $+I$-effect increases the stability of carbocation $+I$-effect of *i.e.,* $CH_3—O>—CH_3$. Thus, $CH_3—O—\overset{+}{C}H_2$ is more stable than $CH_3-\overset{+}{C}H_2$.

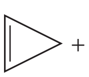
(ii) $(CH_3)_2CH^+$ is more stable than $CH_3—CH_2—\overset{+}{C}H_2$ because former has stabilised by $+I$-effect of two $—CH_3$ groups.

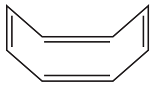
(iii) $CH_2 = CH—\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2 - CH = CH_2$ is stabilised by strong resonance effect while $CH_3 - CH_2 — CH_2$ is stabilised by weak $+I$-effect of the CH_3CH_2 group.

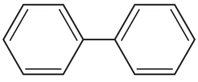
(iv) In $CH_2 = \overset{+}{C}H$, +ve charge is present, on the more electronegatiue, *sp*–hybridised carbon while in $CH_3 - CH_2$, +ve charge is present on the less electronegative sp^2-hybridised carbon therefore, $CH_2 = \overset{+}{C}H$ is less stable than $CH_3 - \overset{+}{C}H_2$.

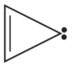
$$CH_2 = \underset{sp^2}{CH} — CH^+ \qquad CH_3 — \underset{sp^3}{CH_2} — \overset{+}{C}H_2$$

Q. 18 **Four structures are given in options (a) to (d). Examine them and select the aromatic structures.**

(a)


(b)


(c)


(d)


Ans. ***(a, c)*** Aromaticity requires following condition

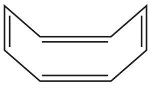
(i) planarity

(ii) complete delocalisation of π electrons in the ring .

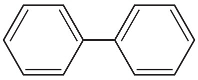
(iii) presence of $(4n + 2)\pi$ electrons in the ring.

(a)

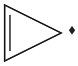

planar
π electrons = 2
$n = 0$

(b)


π electrons = 8
n= not integer
n= not planar

(c)


planar
π electrons
$(4n + 2) = 6$
in each ring
$n = 1$

(d)


π planar
n= not integer

Q. 19 **The molecules having dipole moment are ....**

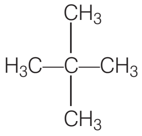
(a) 2,2-Dimethylpropane

(b) *trans*-Pent-2-ene

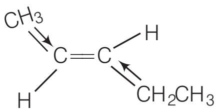
(c) *cis*-Hex-3-ene

(d) 2, 2, 3, 3 - Tetramethylbutane

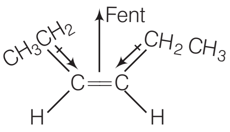
Ans. ***(b, c)***

(a)


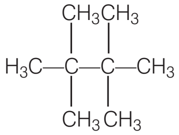
$\mu = 0$

(b)


Different group attached
on oposite side $\mu \neq 0$

(c)


$\mu \neq 0$

(d)


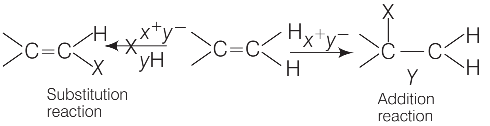
Same group attached
$\mu = 0$

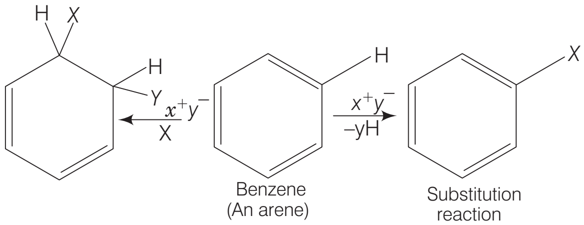
Thus, *trans-pent-2-ene* show net diple moment because different group attached and cis- *Hex* -3- ene show dipole moment because both groups (C_2H_5) are inclined to each other at angle of 60° therefore have a finite resultant.

Short Answer Type Questions

Q. 20 Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

Ans. Alkenes are rich source of loosely held pi (π) electrons, due to which they show electrophilic addition reaction. Electrophilic addition reaction of alkenes are accompanied by large energy changes so these are energetically favourable than that of electrophilic substitution reactions. In special conditions alkenes also undergo free radical substitution reactions.





In arenes during electrophilic addition reactions, aromatic character of benzene ring is destroyed while during electrophilic substitution reaction it remains intact. Electrophilic substitution reactions of arenes are energetically more favourable than that of electrophilic addition reaction.

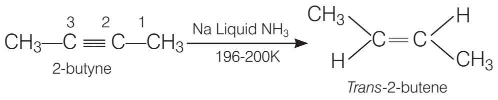
That's why alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reaction.

Q. 21 Alkynes on reduction with sodium in liquid ammonia form *trans* alkenes. Will the butene thus formed on reduction of 2 – butyne show the geometrical isomerism ?

Thinking Process

In geometrical isomerism, when same groups are on the same side it is cis and if same groups are on the opposite side it is trans isomer.

Ans. *Trans*-2-butene formed by the reduction of 2-butyne is capable of showing geometrical isomerism.



$$CH_3-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_3 \xrightarrow[196\text{-}200K]{\text{Na Liquid } NH_3}$$

Q. 22 Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

Thinking Process

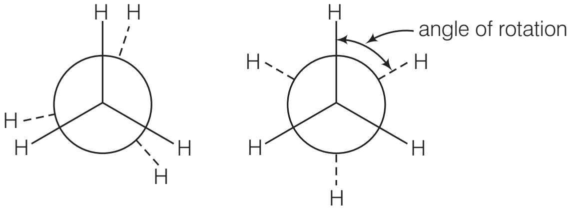
The infinite number of momentary arrangements of the atoms in space which result through rotation about a single bond are called conformations.

In ethane, if one carbon atom is kept stationary and other rotated around C — C *axis, we have eclipsed, skew and staggered conformation.*

Ans. Alkanes can have infinite number of conformations by rotation around C—C single bonds. This rotation around a C—C single bond is hindered by a small energy barrier of 1-20 kJ mol^{-} due to weak repulsive interaction between the adjacent bonds. such a type of repulsive interaction is called torsional strain. In staggered form of ethane, the electron cloud of carbon hydrogen bonds are far apart.

Hence, minimum repulsive force. In eclipsed electron cloud of carbon-hydrogen become close resulting in increase in electron cloud repulsion. This repulsion affects stablity of a conformer.

In all the conformations of ethane the staggered form has least torsional strain and the eclipsed form has the maximum torsional strain. Hence, rotation around C—C bond in ethtane is not completely free.

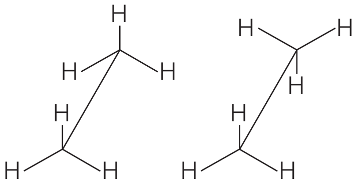


Eclipsed Staggered

Newman's projection of ethane

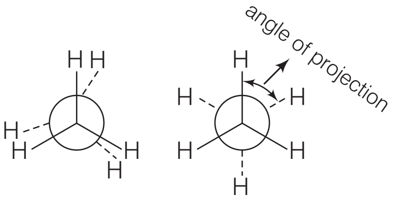
Q. 23 Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why ?

Ans.



Eclipsed Staggered

Sawhorse projections of ethane



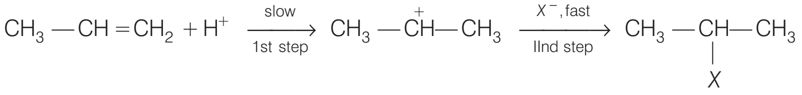
Eclipsed Staggered

Newman projections of ethane

Staggered form of ethane is more stable than the eclipsed conformation, by about 12.55 kJ/mol. This is because any two hydrogen atoms on adjacent carbon atoms of staggered conformation are maximum apart while in eclipsed conformation, they cover or eclipse each other in space. Thus, in staggered form, there is minimum repulsive forces, minimum energy and maximum stability of the molecule.

Q. 24 The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids ?

Ans. Addition of halogen acids to an alkene is an electrophilic addition reaction.



$$CH_3-CH=CH_2+H^+ \xrightarrow[\text{1st step}]{\text{slow}} CH_3-\overset{+}{C}H-CH_3 \xrightarrow[\text{IInd step}]{X^-,\text{ fast}} CH_3-\underset{X}{\underset{|}{C}H}-CH_3$$

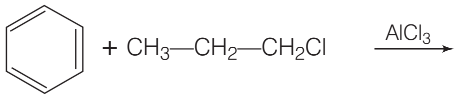
First step is slow so, it is rate determining step. The rate of this step depends on the availability of proton. This in turn depends upon the bond dissociation enthalpy of the $H-X$ molecule.

Lower the bond dissociation enthalpy of $H-X$ molecule, greater the reactivity of halogen halide. Since the bond dissociation energy decreases in the order;

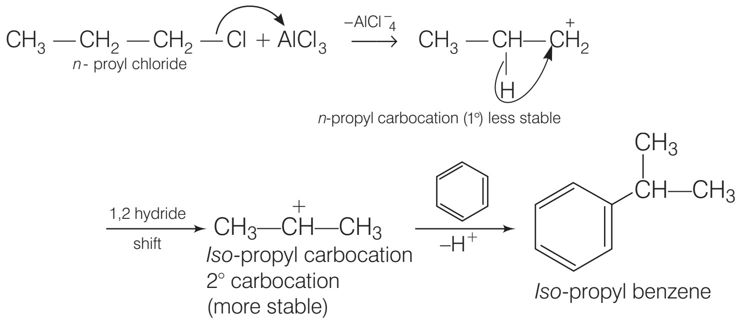
$$\text{HI }(296.8\text{ kJ mol}^{-1}) < \text{HBr }(363.7\text{ kJ mol}^{-1}) < \text{HCl }(430.5\text{ kJ mol}^{-1})$$

Therefore, the reactivity of the halogen acids decreases from HI to HCl. *i.e.,* HI > HBr > HCl

Q. 25 What will be the product obtained as a result of the following reaction and why?



Ans.

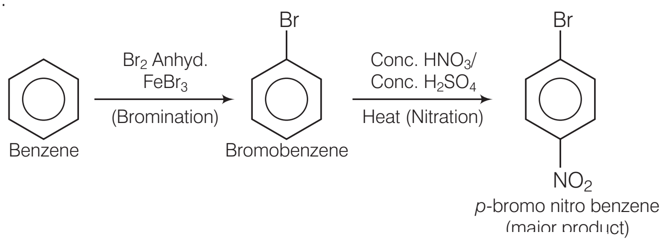


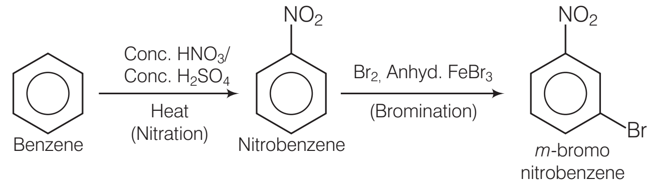
When Friedel-Craft alkylation is carried out with higher alkyl halide, *e.g., n*–propyl chloride, then the electrophile *n*-propyl carbocation (1° carbocation) formed which rearranges to form more stable *iso*-propyl carbocation (2° carbocation). Afterward the main product *iso*-propyl benzene will be formed.

Q. 26 How will you convert benzene into (a) *p*-nitrobromobenzene (b) *m*-nitrobromobenzene

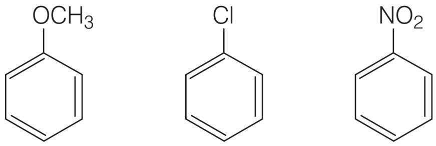
Ans. Halogens attached to benzene ring is *ortho and para* directing where as nitro group is *meta* directing.

(a)

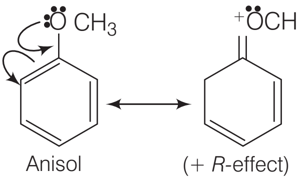


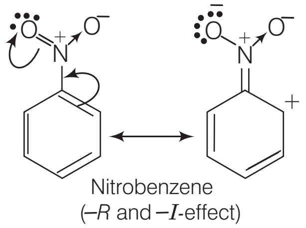
(b) 

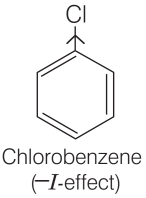
Q. 27 Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason.



Ans. The methoxy group (–OCH_3) is electron releasing group. It increases the electron density in benzene nucleus due to resonance effect (+ *R*-effect). Hence, it makes anisole more reactive than benzene towards electrophile.

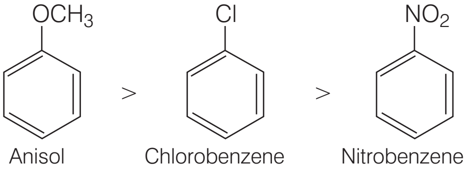






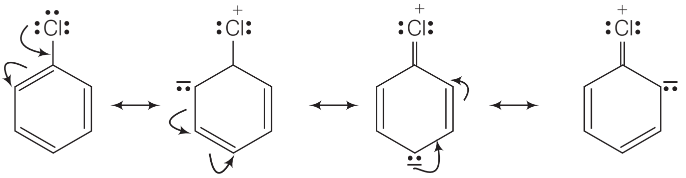
In case of alkyl halides, halogens are moderately deactivating because of their strong – *I* effect. Thus, overall electron density on benzene ring decreases. It makes further substitution difficult.

– NO_2 group is electron withdrawing group. It decreases the electron density in benzene nucleus due to its strong - *R* - effect and strong – *I*-effect. Hence, it makes nitrobenzene less reactive. Therefore, overall reactivity of these three compounds towards electrophiles decreases in the following order



Q. 28 Despite their – *I* effect, halogens are *o*- and *p*- directing in haloarenes. Explain.

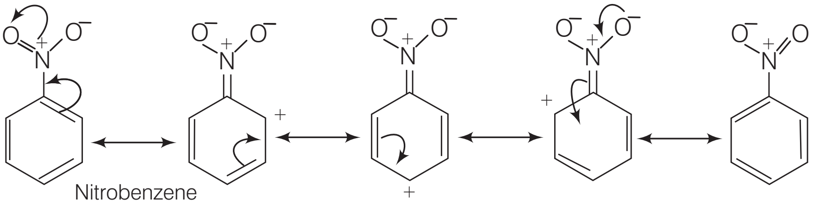
Ans. Halogens have (– *I*) and (+ *R*) effect, these groups are deactivating due to their (– *I*) effect and they are *ortho, para* directing due to (+ *R*) effect.



***ortho, para*-directing influence**

Q. 29 Why does presence of a nitro group make the benzene ring less reactive in comparison to the unsubstituted benzene ring. Explain.

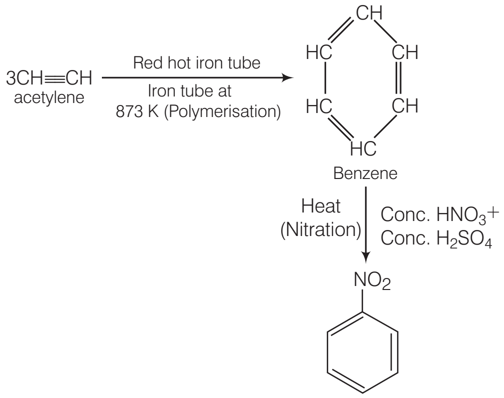
Ans. The *meta* - directing substituents (like - NO_2 group) withdraw electrons from the benzene ring and thus, deactivate the benzene ring for further substitution and make the benzene ring less reactive in comparison to the unsubstituted benzene ring.



Nitrobenzene
(–*R* and –*I* effect)

Q. 30 Suggest a route for the preparation of nitrobenzene starting from acetylene?

Ans. Acetylene when passed through red hot iron tube at 873 K, undergoes cyclic polymerisation benzene which upon subsequent nitration gives nitrobenzene.



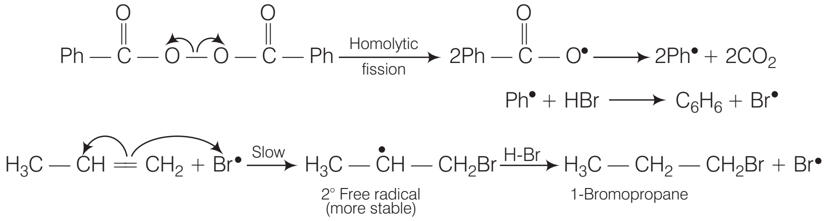
Nitrobenzene

Note *In nitration of benzene ring conc* H_2SO_4 *acts as an catalyst to produce an electrophile* $+ NO_2$. *(from* HNO_3*)*

Q. 31 Predict the major product(s) of the following reactions and explain their formation.

$$H_3C-CH=CH_2 \xrightarrow[HBr]{(Ph-CO-O)_2} \qquad H_3C-CH=CH_2 \xrightarrow{HBr}$$

Ans. In presence of organic peroxides, the addition of HBr to propene follows anti Markowinkov's rule (or peroxide effect) to form 1-bromopropane (*n*-propyl bromide)

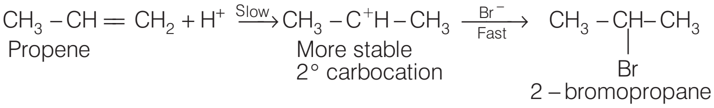


$$Ph-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-Ph \xrightarrow[\text{fission}]{\text{Homolytic}} 2Ph-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow 2Ph^{\bullet}+2CO_2$$

$$Ph^{\bullet}+HBr \longrightarrow C_6H_6+Br^{\bullet}$$

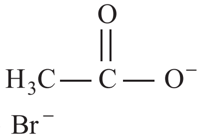
$$H_3C-CH=CH_2+Br^{\bullet} \xrightarrow{\text{Slow}} \underset{\substack{2^\circ\text{ Free radical}\\ \text{(more stable)}}}{H_3C-\dot{C}H-CH_2Br} \xrightarrow{\text{H-Br}} \underset{\text{1-Bromopropane}}{H_3C-CH_2-CH_2Br}+Br^{\bullet}$$

However, in absence of peroxides, addition of HBr to propene follows Markownikoff's rule and gives 2- bromopropane as major product.



$$\underset{\text{Propene}}{CH_3-CH=CH_2}+H^+ \xrightarrow{\text{Slow}} \underset{\substack{\text{More stable}\\ 2^\circ\text{ carbocation}}}{CH_3-C^+H-CH_3} \xrightarrow[\text{Fast}]{Br^-} \underset{2-\text{bromopropane}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3}$$

Q. 32 Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.



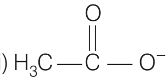
(i) H_3CO^- (ii) $H_3C-\overset{\overset{O}{\|}}{C}-O^-$ (iii) $\dot{C}l$ (iv) $Cl_2C:$

(v) $(H_3C)_3C^+$ (vi) Br^- (vii) H_3COH

(viii) *R*-NH-*R*

Ans. Electrophiles are electron deficient species. They may be natural or positively charged *e.g.,* (iii) $\dot{C}l$, (iv) $Cl_2C:$, (v) $(H_3C)_3C^+$

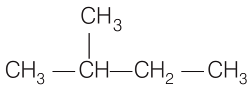
Nucleophiles are electron rich species. They may be neutral or negatively charged *e.g.,*



(i) H_3CO^-, (ii) $H_3C-\overset{\overset{O}{\|}}{C}-O^-$,(vi) Br^- ,(vii) $H_3C-\ddot{\underset{..}{O}}-H$, (viii) $R\ddot{N}HR$

Q. 33 The relative reactivity of 1°, 2° and 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.

Ans. The given organic compound is



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

2-methyl butane

This compound has 9 primary hydrogen, 2 secondary and one tertiary hydrogen atoms. The relative reactivity of 1°, 2° and 3° hydrogen atoms towards chlorination is 1 : 3.8 : 5. Relative amount of product after chlorination = Number of hydrogen × relative reactivity

	1° halide	2° halide	3° halide
Relative amount	$9 \times 1 = 9$	$2 \times 3.8 = 7.6$	$1 \times 5 = 5$

Total amount of mono chloro product = 9 + 7.6 + 5 = 21.6

$$\text{Percentage of 1° mono chloro product} = \frac{9}{21.6} \times 100 = 41.7\%$$

$$\text{Percentage of 2° mono chloro product} = \frac{7.6}{21.6} \times 100 = 35.2\%$$

$$\text{Percentage of 3° mono chloro product} = \frac{5}{21.6} \times 100 = 23.1\%.$$

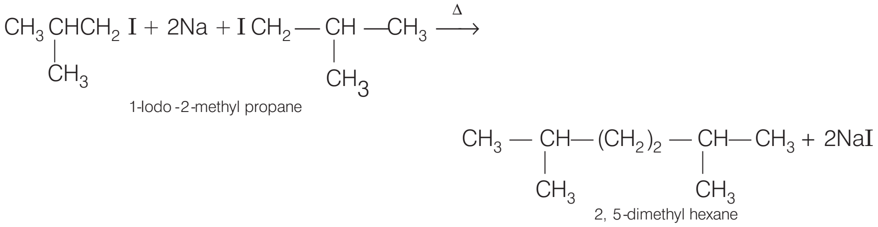
Q. 34 **Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.**

Thinking Process

This question is based upon Wurtz reaction. Wurtz reaction represent that two alkyl groups can be coupled by reacting alkyl halide with

$$2RX + 2Na \xrightarrow[\text{dry ether}]{\Delta} R-R + 2NaX$$

Ans. (i)

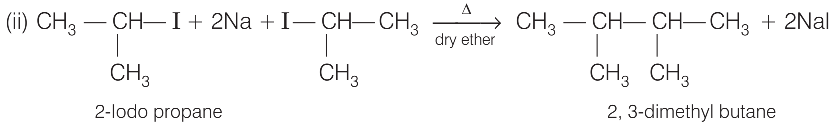


$$\text{(i) } \mathrm{CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2I + 2Na + ICH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 + 2NaI}$$

1-Iodo -2-methyl propane

2, 5-dimethyl hexane

(ii)

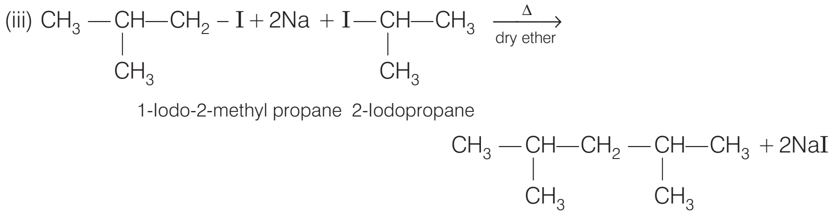


$$\text{(ii) } \mathrm{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-I + 2Na + I-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{dry ether}]{\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 + 2NaI}$$

2-Iodo propane

2, 3-dimethyl butane

(iii)



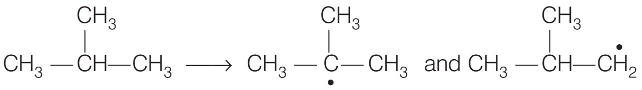
$$\text{(iii) } \mathrm{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-I + 2Na + I-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{dry ether}]{\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 + 2NaI}$$

1-Iodo-2-methyl propane 2-Iodopropane

2, 4-dimethyl pentane

Q. 35 **Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane? Which of them is more stable? Give reasons.**

Ans. 2-methylpropane gives two types of radicals.



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\bullet}{C}}}-CH_3 \text{ and } CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\dot{C}H_2}$$

(2-methyl propane) (I) (II)

Radical (I) is more stable because it is 3° free radical and stabilised by nine hyperconjugative structures (as it has 9 α-hydrogens)

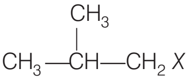
Radical (II) is less stable because it is 1° free radical and stabilised by only one hyperconjugative structure (as it has only 1 α- hydrogen)

Q. 36 **An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.**

Ans. From Wurtz reaction of an alkyl halide gives an alkane with double the number of carbon atoms present in the alkyl halide. Here, Wurtz reaction of a primary alkyl halide gives an alkane (C_8H_{18}), therefore, the alkyl halide must contain four carbon atoms.Now the two possible primary alkyl halides having four corbon atoms each are I and II.

$CH_3CH_2CH_2CH_2-X$

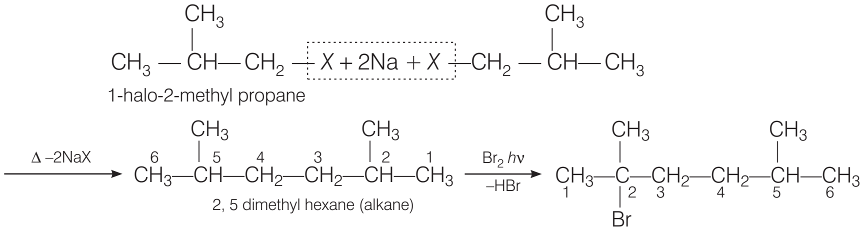
I



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2X$

II

Since, alkane C_8H_{18} on monobromination yields a single isomer of tertiary alkyl halide, therefore, the alkane must contain tertiary hydrogen. This is possible, only if primary alkyl halide (which undergoes Wurtz reaction) has a tertiary hydrogen.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-\boxed{X+2Na+X}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

1-halo-2-methyl propane

$$\xrightarrow[]{\Delta\ -2NaX} \overset{6}{C}H_3-\overset{\overset{\displaystyle CH_3}{|}}{\overset{5}{C}H}-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3 \xrightarrow[-HBr]{Br_2\ h\nu} \underset{1}{C}H_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{3}{C}H_2-\underset{4}{C}H_2-\underset{5}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}-\underset{6}{C}H_3$$

2, 5 dimethyl hexane (alkane)

2-bromo-2, 5 dimethyl hexane
(3° bromide)

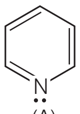
Q. 37 **The ring systems having following characteristics are aromatic.**

(i) Planar ring containing conjugated π bonds.

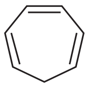
(ii) Complete delocalisation of the π-electrons in ring system *i.e.,* each atom in the ring has unhybridised *p*-orbital, and

(iii) Presence of $(4n+2)$ π- electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots\ldots\ldots$) [Huckel rule].

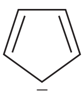
Using this information classify the following compounds as aromatic/non-aromatic.



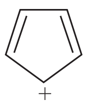
(A)



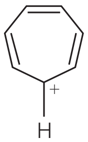
(B)



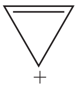
(C)



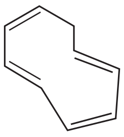
(D)



(E)

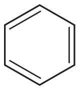
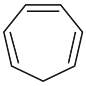
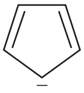
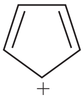
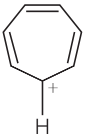
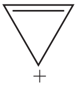
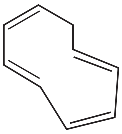


(F)

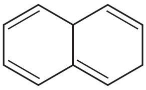


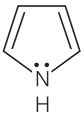
(G)

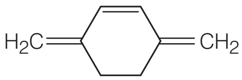
Ans.

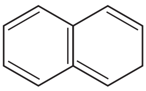
	Compound	Planar ring	Complete delocalisation of π-electron	Huckel rule $(4n+2)$ π electron	Aromatic or non-aromatic
A.		P	P	$6\pi e^-$ Huckel rule obeyed	Aromatic
B.		Í	Í Incomplete (sp^3 hybrid carbon)	$6\pi e^-$	Non-aromatic
C.		P	P	$6\pi e^-$ $(4n+2$+lone pair $e^-)$ Huckel rule verified	Aromatic
D.		P	Í	$4\pi e^-$	Anti-aromatic
E.		P	P	Huckel rule obeyed	Aromatic
F.		P	P	$2\pi e^-$ Huckel rule verified $n=0$	Aromatic
G.		P	Í	$8\pi e^-$ Huckel rule not verified	Non-aromatic

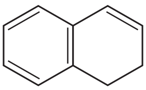
Q. 38 Which of the following compounds are aromatic according to Huckel's rule?

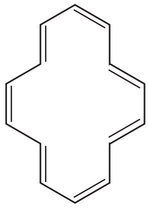
(A)


(B)


(C)


(D)


(E)


(F)


Ans. A. The compound has 8π electrons. It will be non-aromatic. Both rings are non-benzenoid.

B. The compound is aromatic. It has $6\pi e^-$ delocalised electron ($4\pi e^- + 2$ lone pair electrons), all the four carbon atoms and the N atom are sp^2 hybridised.

C. The compound contains 6π electrons but not in the ring hence it is non-aromatic.

D. $10\pi e^-$ obeying Huckel rule and the ring is planar. It is aromatic.

E. In this compound one six membered planar ring has $6\pi e^-$ although it has 8π electrons in two rings. It is therefore aromatic.

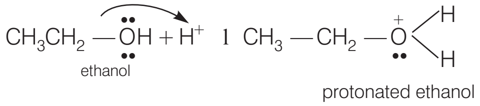
F. It has 14π electrons in conjugation and in the planar ring, Huckel rule is verified. It will be aromatic.

Q. 39 Suggest a route to prepare ethyl hydrogensulphate ($CH_3—CH_2—OSO_2—OH$) starting from ethanol (C_2H_5OH).

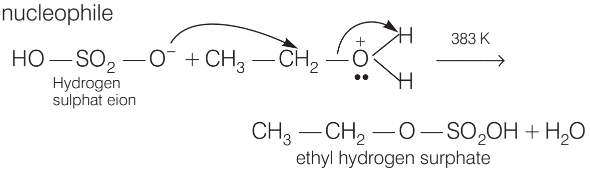
Ans. For preparation of ethyl hydrogensulphate ($CH_3-CH_2-OSO_2-OH$) starting from ethanol (C_2H_5OH), it is the two steps mechanism.

Step I Protonation of alcohol

$$H_2SO_4 \longrightarrow H^+ + {}^-OSO_2OH$$



Step II Attack of nucleophile



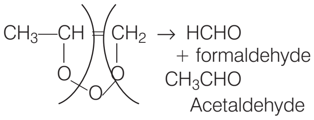
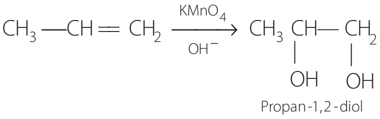
Temperature should not be allowed to rise above 383 K, otherwise diethyl ether will be produced at 413 K or ethene at 433 K.

Matching The Columns

Q. 40 Match the reagent from Column I which on reaction with $CH_3—CH=CH_2$ gives some product given in Column II as per the codes given below

	Column I		Column II
A.	O_3 / Zn + H_2O	1.	Acetic acid and CO_2
B.	$KMnO_4$ / H^+	2.	Propan-1-ol
C.	$KMnO_4$ / OH^-	3.	Propan-2-ol
D.	H_2O / H^+	4.	Acetaldehyde and formaldehyde
E.	B_2H_6 / $NaOH^+$ and H_2O_2	5.	Propane-1, 2-diol

Ans. **A.** → (4) **B.** → (1) **C.** → (5) **D.** → (3) **E.** → (2)

	Reagent	Recation with propene
A.	O_3 / Zn + H_2O	 $CH_3—CH=CH_2$ → HCHO + formaldehyde CH_3CHO Acetaldehyde
B.	$KMnO_4$ / H^+	$CH_3CH=CH_2 \xrightarrow[H^+]{KMnO_4} CH_3COOH + CO_2$ Acetic acid
C.	$KMnO_4$ / OH^-	 $CH_3—CH=CH_2 \xrightarrow[OH^-]{KMnO_4} \underset{OH}{CH_3\ CH}—\underset{OH}{CH_2}$ Propan-1,2-diol
D.	H_2O / H^+	$CH_3\ CH=CH_2 \xrightarrow[\text{(Markn addition)}]{H_2O/H^+} CH_3 - CH(OH) - CH_3$ Propan–2–ol
E.	B_2H_6 / $NaOH^+$ and H_2O_2	$CH_3CH=CH_2 \xrightarrow[\text{(ii) NaOH}/H_2O_2]{\text{(i)}B_2H_6} CH_3CH_2CH_2OH$ (Hydroboration o idationx) propan–1–of

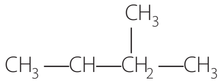
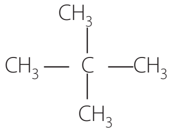
Q. 41 Match the hydrocarbons in Column I with the boiling points given in Column II.

	Column I		Column II
A.	*n*-pentane	1.	282.5 K
B.	*iso*-pentane	2.	309 K
C.	*neo*-pentane	3.	301 K

Thinking Process

To solve this question, it keep in mind that branching of hydrocarbons decreases boiling — point of the compound

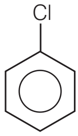
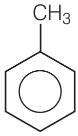
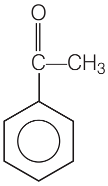
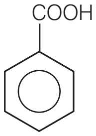
Ans. **A.** → (2) **B.** → (3) **C.** → (1)

	Hydrocarbons	Boiling point	
A.	*n*-pentane	309 K due to	no branch
B.	*iso*-pentane	301 K due to one branch	 $CH_3—\overset{CH_3}{CH}—CH_2—CH_3$
C.	*neo*-pentane	282.5 K due to two branches	 $CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH_3$

Q. 42 Match the following reactants in Column I with the corresponding reaction products in Column II.

Column I	Column II
A. Benzene + $Cl_2 \xrightarrow{AlCl_3}$	1. Benzoic acid
B. Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	2. Methyl phenyl ketone
C. Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	3. Toluene
D. Toluene $\xrightarrow{KMnO_4 / NaOH}$	4. Chlorobenzene
	5. Benzene hexachloride

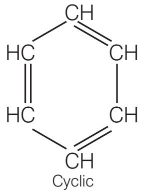
Ans. **A.** → (4) **B.** → (3) **C.** → (2) **D.** → (1)

Reactants	Products
A. Benzene + $Cl_2 \xrightarrow{AlCl_3}$	Friedel Craft's reaction 
B. Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	Friedel Craft's alkylation reaction  Toluene
C. Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	 Methyl phenyl ketone (Friedal Craft's acetylation reaction)
D. Toluene $\xrightarrow{KMnO_4 / NaOH}$	Oxidation reaction  Benzoic acid

Q. 43 Match the reactions given in Column I with the reaction types in Column II.

	Column I		Column II
A.	$CH_2 = CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$	1.	Hydrogenation
B.	$CH_2 = CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$	2.	Halogenation
C.	$CH_2 = CH_2 + Cl_2 \longrightarrow Cl—CH_2—CH_2—Cl$	3.	Polymerisation
D.	$3CH \equiv CH \xrightarrow[\text{Heat}]{\text{Cu tube}} C_6H_6$	4.	Hydration
		5.	Condensation

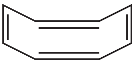
Ans. A. → (4) B. → (1) C. → (2) D. → (3)

	Reactions	Types of reaction	
A.	$CH_2 = CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$	Hydration	Addition of water
B.	$CH_2 = CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$	Hydrogenation	Addition of hydrogen
C.	$CH_2 = CH_2 + Cl_2 \longrightarrow Cl—CH_2—CH_2—Cl$	Halogenation	Addition of halogen
D.	$3CH \equiv CH \xrightarrow[\text{Heat}]{\text{Cu tube}} C_6H_6$	Polymerisation	 Cyclic polymer

Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below in each question.

Q. 44 **Assertion (A)** The compound tetraene has the following structural formula.



It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.

Reason (R) $(4n + 2)\ \pi$ electrons rule does not hold good and ring is not planar.

(a) Both A and R are correct and R is the correct explanation of A
(b) Both A and R are correct but R is not the correct explanation of A
(c) Both A and R are not correct
(d) A is not correct but R is correct

Ans. *(a)* Both assertion and reason are correct and reason is the correct explanation of assertion.

According to Huckel rule Aromaticity is shown by compounds possessing following characteristics

(i) Compound must be planar and cyclic

(ii) Complete delocalisation of π electrons in the ring

(iii) Presence of conjugated $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots$) cyclo octatetraene (given) has a tub like structure. It loses planarity. No. of πe^- delocalised = 8. and n is not integer. Hence, cycloctatetraene is a non-aromatic compound.

Q. 45 Assertion (A) Toluene on Friedal Crafts methylation gives *o* - and *p*-xylene.

Reason (R) CH_3-group bonded to benzene ring increases electron density at *o*- and *p*- position.

(a) Both A and R are correct and R is the correct explanation of A

(b) Both A and R are correct but R is not the correct explanation of A

(c) Both A and R are not correct

(d) A is not correct but R is correct

Ans. *(a)* Both assertion and reason are correct and reason is the correct explanation of assertion.

Toluene has $-CH_3$ group attached to benzene. $-CH_3$ group activates the benzene ring for the attack of an electrophile.

In resonating structure of toluene, electronic density is more on *ortho* and *para* position. Hence, substitution takes place mainly at these positions.

Q. 46 Assertion (A) Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason (R) The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

(a) Both A and R are correct and R is the correct explanation of A

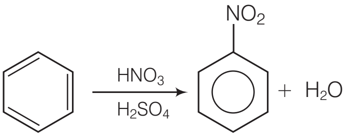
(b) Both A and R are correct but R is not the correct explanation of A

(c) Both A and R are not correct

(d) A is not correct but R is correct

Ans. *(a)* Both assertion and reason are correct and reason is the correct explanation of assertion. In nitration of benzene with nitric acid sulphuric acid acts as a calatyst. It helps in the formation of electrophile *i.e.,* nitronium ion NO_2^+.

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$



Q. 47 Assertion (A) Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.

Reason (R) Branching does not affect the boiling point.

(a) Both A and R are correct and R is the correct explanation of A
(b) Both A and R are correct but R is not the correct explanation of A
(c) Both A and R are not correct
(d) A is not correct but R is correct

Ans. *(c)* Both assertion and reason are correct

Correct assertion Among isomeric pentanes, 2, 2 - dimethylpentane has the lowest boiling point.

Correct reason Branching decrease the boiling point.

Long Answer Type Questions

Q. 48 An alkyl halide C_5H_{11} *(A)* reacts with ethanolic KOH to give an alkene *'B'*, which reacts with Br_2 to give a compound *'C'*, which on dehydrobromination gives an alkyne *'D'*. On treatment with sodium metal in liquid ammonia, one mole of *'D'* gives one mole of the sodium salt of *'D'* and half a mole of hydrogen gas. Complete hydrogenation of *'D'* yields a straight chain alkane. Identify *A*, *B*, *C* and *D*. Give the reactions involved.

Ans. The reaction scheme involved in the problem is

$$\underset{\substack{(A)\\ \text{Alkyl halide}}}{C_5H_{11}Br} \xrightarrow{\text{Alc.KOH}} \underset{\substack{(B)\\ \text{Alkene}}}{C_5H_{10}} \xrightarrow{Br_2/CS_2} \underset{\substack{(C)\\ \text{Dibromo alkane}}}{C_5H_{10}\,Br_2} \xrightarrow[-2HBr]{\text{Alc.KOH}} \underset{\substack{(D)\\ \text{Alkyne}}}{C_5H_8} \xrightarrow{H_2}$$

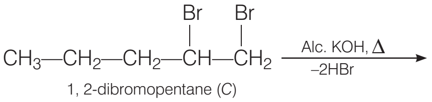
$$C_5H_8 \xrightarrow[\text{Liq } NH_3]{\text{Na,}} C_5H_7^-\ Na^+ + \frac{1}{2}H_2$$

(straight chain alkane)

Hydrogenation of alkyne *(D)* gives straight chain alkane hence all the compounds *(A)*, *(B)*, *(C)* and *(D)* must be straight chain compounds. Alkyne *(D)* form sodium salt which proves that it is terminal alkyne. Involved reactions are as follows

$$\underset{\text{1-bromopentane (A)}}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow[-HBr]{\text{Alc.KOH, }\Delta}$$

$$\underset{\text{1-pentene }(B)}{CH_3CH_2CH_2CH{=}CH_2} \xrightarrow{Br_2 \text{ in } CS_2}$$



$$\underset{\text{1, 2-dibromopentane }(C)}{CH_3{-}CH_2{-}CH_2{-}\underset{}{\overset{\overset{\displaystyle Br}{|}}{C}H}{-}\overset{\overset{\displaystyle Br}{|}}{C}H_2} \xrightarrow[-2HBr]{\text{Alc. KOH, }\Delta}$$

$$\underset{\text{1-pentene }(D)}{CH_3{-}CH_2{-}CH_2{-}C \equiv CH} \xrightarrow{H_2} CH_3CH_2CH_2CH_2CH_3$$

$$CH_3{-}CH_2{-}CH_2{-}C \equiv CH \xrightarrow{\text{Na/Liq } NH_3} CH_3CH_2CH_2C \equiv \overset{-}{C}\overset{+}{N}a + \frac{1}{2}H_2$$

It is important point that alkyl halide (*A*) can not be 2-bromopentane because dehydrobromination of (*A*) would have given 2-pentene as the major product in accordance with Markownikoff's rule.

Q. 49 **896 mL vapour of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.**

Ans. To determine the molecular mass of hydrocarbon (A) 896 mL vapour of C_xH_y (A) weighs 3.28 g at STP

22700 mL vapour of C_xH_y (*A*) weighs $\frac{3.28 \times 22700}{896}$ g/mol at STP

$$= 83.1 \text{ g/mol}$$

Hence, molecular mass of $C_xH_y(A) = 83.1\text{g mol}^{-1}$. To determine the empirical formula of hydrocarbon (*A*).

Element	%	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.8	12	7.31	1	3
H	12.19	1	12.19	1.66	$4.98 \approx 5$

Thus, Empirical formula of *A* is C_3H_5.

$\therefore$ Empirical formula mass = 36 + 5 = 41.

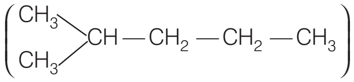
$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{83.1}{41} = 2.02 \approx 2$$

Molecular mass is double of empirical formula mass.

$\therefore$ Molecular formula is C_6H_{10}

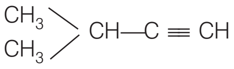
To determine the structure of compounds (*A*) and (*B*)

$$\underset{(A)}{C_6H_{10}} \longrightarrow \text{2-methyl pentane}$$

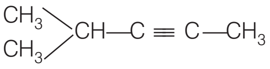


$$\left((CH_3)_2CH-CH_2-CH_2-CH_3\right)$$

Hence, hydrogenation of hydrocarbon (A) requires 2 moles of hydrogen to form 2-methylpentane. Therefore, hydrocarbon(A) is an alkyne having five carbon atoms in a staight chain and a methyl substituent at position 2. Thus, the possible structures for the alkyne (*A*) are I and II.



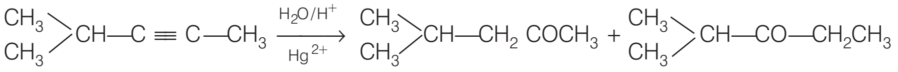
$$(CH_3)_2CH-C\equiv CH$$



$$(CH_3)_2CH-C\equiv C-CH_3$$

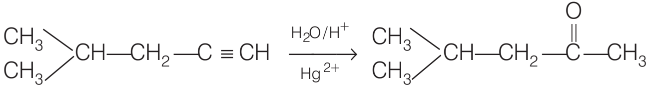
Since, addition of H_2O to alkyne (*A*) in presence of Hg^{2+}, give a ketone which gives positive iodoform test, therefore, ketone (*B*) must be a methyl ketone, *i.e.,* it must contain a $COCH_3$ group.

Now addition of H_2O to alkyne (II) should give a mixture of two ketones in which 2- methyl pentan -3 one (minor) and 4-methylpentan -2-one ketone (B) (which shows +ve iodoform test) predominates.



(B) 4-Methylpentan 2-one 2-Methylpentan -3-one (minor)

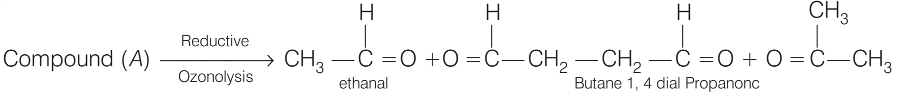
In contrast, addition of H_2O to alkyne (I) will give only one ketone, *i.e.,* 4- methylpentan-2-one which gives iodoform test.



Thus, hydrocabon C_xH_y (*A*) is 4-methylpent –1–yne. 4- methylpentan -2 one (gives + ve iodoform test)

Q. 50 **An unsaturated hydrocarbon *'A'* adds two molecules of H_2 and on reductive ozonolysis gives butane-1, 4-dial, ethanal and propanone. Give the structure of *'A'*, write its IUPAC name and explain the reactions involved.**

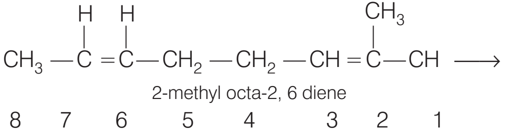
Ans. The scheme of reaction is



$$\text{Compound }(A) \xrightarrow[\text{Ozonolysis}]{\text{Reductive}} \underset{\text{ethanal}}{CH_3-\overset{H}{\overset{|}{C}}=O} + O=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=O + O=\overset{CH_3}{\overset{|}{C}}-CH_3$$

Butane 1, 4 dial Propanonc

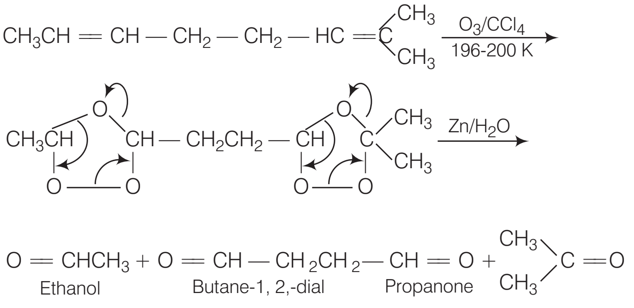
Thus, structure of *A* may be given as



$$\underset{8}{CH_3}-\underset{7}{\overset{H}{\overset{|}{C}}}=\underset{6}{\overset{H}{\overset{|}{C}}}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{\overset{CH_3}{\overset{|}{C}}}-\underset{1}{CH} \longrightarrow$$

2-methyl octa-2, 6 diene

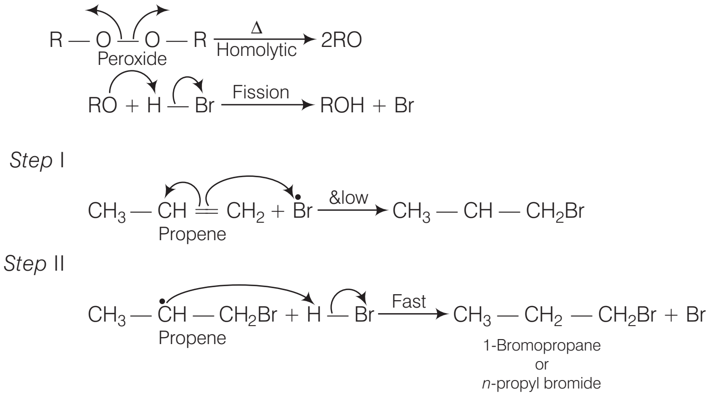
The reactions involved in the question



Q. 51 In the presence of peroxide addition of HBr to propene takes place according to anti Markownikoff's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

Ans. $$\underset{\text{propene}}{CH_3-CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{n\text{-propyl bromide}}{CH_3-CH_2CH_2Br}$$

The mechanism of the reaction is



$$\underset{\text{Peroxide}}{R-O-O-R} \xrightarrow[\text{Homolytic}]{\Delta} 2RO$$

$$RO + H-Br \xrightarrow{\text{Fission}} ROH + Br$$

Step I

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + \dot{B}r \xrightarrow{\&low} CH_3-CH-CH_2Br$$

Step II

$$\underset{\text{Propene}}{CH_3-\dot{C}H-CH_2Br} + H-Br \xrightarrow{\text{Fast}} \underset{\substack{\text{1-Bromopropane}\\ \text{or}\\ n\text{-propyl bromide}}}{CH_3-CH_2-CH_2Br} + Br$$

Peroxide effect is effective only in the case of HBr and not seen in the case of HCl and HI. This is due to the following reasons.

(i) H — Cl bond (103 kcal/mol) is stronger than H — Br bond (87 kcal/mol)

H — Cl bond is not decomposed by the peroxide free radical whereas the H — I bond is weaker (71 kcal/mol) form iodine free radicals.

(ii) Iodine free radical (I°) formed as H — I bond is weaker but iodine free radicals readily combine with each other to form iodine molecules rather attacking the double bond.