Chapter 10

Haloalkanes and Haloarenes

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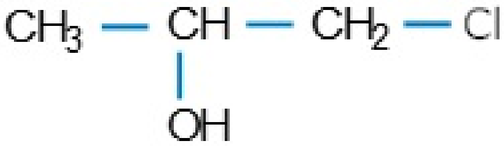
1 Marks Questions

1. Give IUPAC names of following compounds

(i).

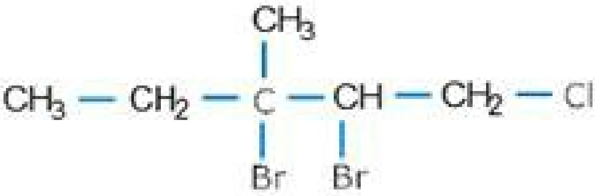
$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-Br$

(ii).



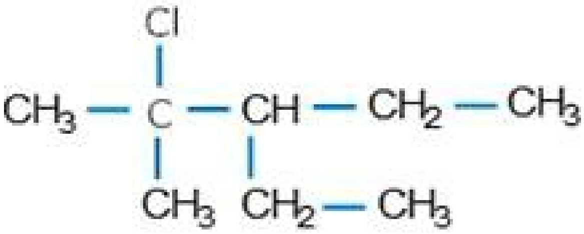
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-Cl$

(iii).



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

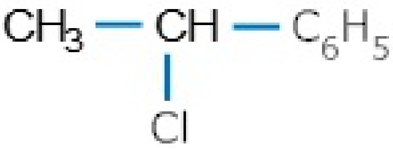
(iv).



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

(v). $C_6H_5CH_2CH_2Cl$

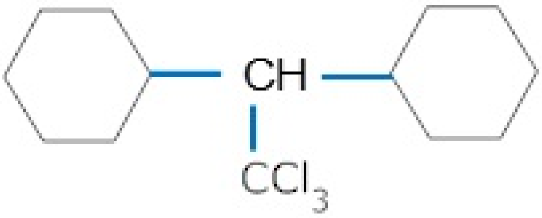
(vi).



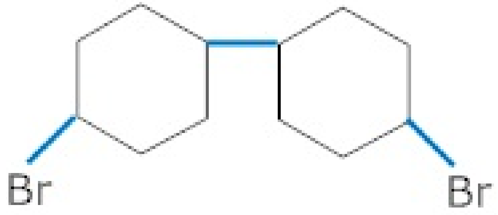
$CH_3-\underset{\underset{Cl}{|}}{CH}-C_6H_5$

(vii). $C_6H_6Cl_6$

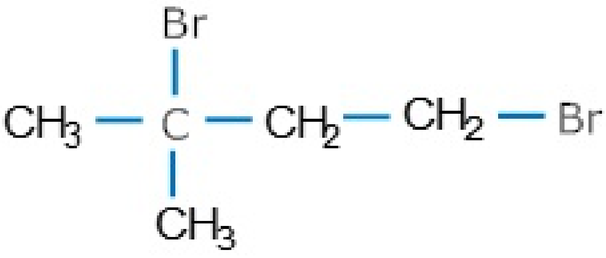
(viii).



(ix).



(x).



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

Ans.(i). 1, 3- Dibromobutane

(ii). 1- Cholopropan-2-ol

(iii). 2, 3 – Dibromo-1-chloro-3-methylpentane

(iv). 2-Choloro-3-ethyl-2-methyl pentane (v). 1-Chloro-2-phenylethane

(vi). 1-Chloro-1-phenyl ethane

(vii). 1, 2, 3, 4, 5, 6- hexachlorocyclohexane

(viii). 2, 2- Dihexyl 1, 1, 1-Trichloro ethane

(ix). 4, 4-dibromobiphenyl

(x). 1, 3-Dibromo -3- methyl butane

(2). Give the structures of following.:

(i). 1,3-Dichloro -2-(bromomethyl) propane

(ii). Isobutylchloride

(iii). Ortho bromotoluene

(iv). 1 – Bromo – 4 – chlorobutane

(v). 3 – Bromo – 5 – chloro – 3,5 – dimethyloctane

(vi). 2,3 – Dibromo – 1 – chloro -3- methylpentane

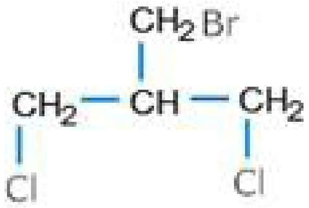
(vii). 2 – Chloro – 3 – ethyl -1, 4- pentadieme

(viii). 2,3 – Dibromo – 1 – chloro -3- methylpentane

(ix). 2 – Chloro – 1 – phemylpropane

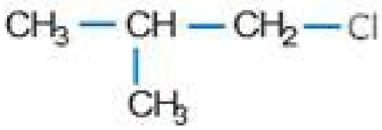
(x). Tert – butylchloride

Ans.(i)



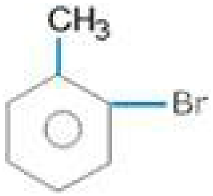
$$\overset{\displaystyle CH_2Br}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}-CH-\underset{\displaystyle Cl}{\underset{|}{CH_2}}}}$$

(ii).



$$\mathrm{CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-Cl}$$

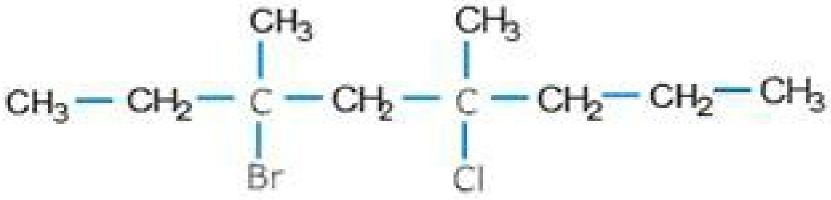
(iii).



(iv).

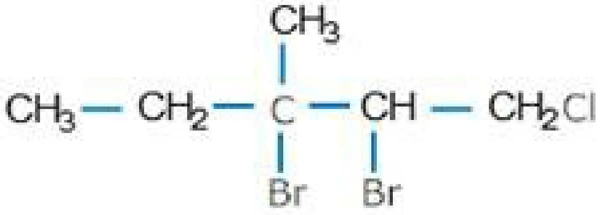
$\mathrm{Br-CH_2-CH_2-CH_2-CH_2-Cl}$

(v).



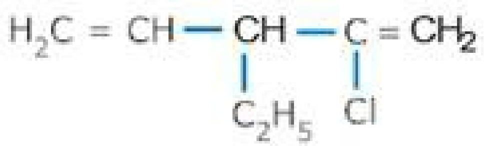
$$\mathrm{CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_2-CH_2-CH_3}$$

(vi).



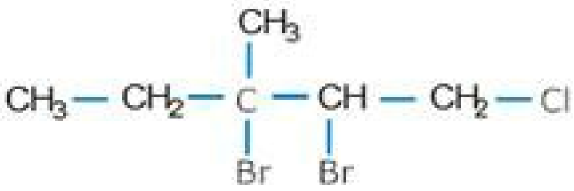
$$\mathrm{CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-\underset{\displaystyle Br}{CH}-CH_2Cl}$$

(vii).



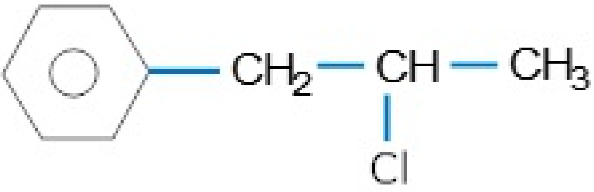
$H_2C=CH-\underset{C_2H_5}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{C}}=CH_2$

(viii).

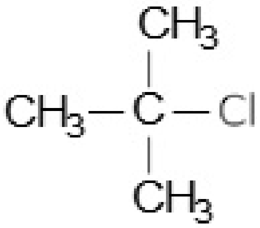


$CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\underset{Br}{\underset{|}{CH}}-CH_2-Cl$

(ix).



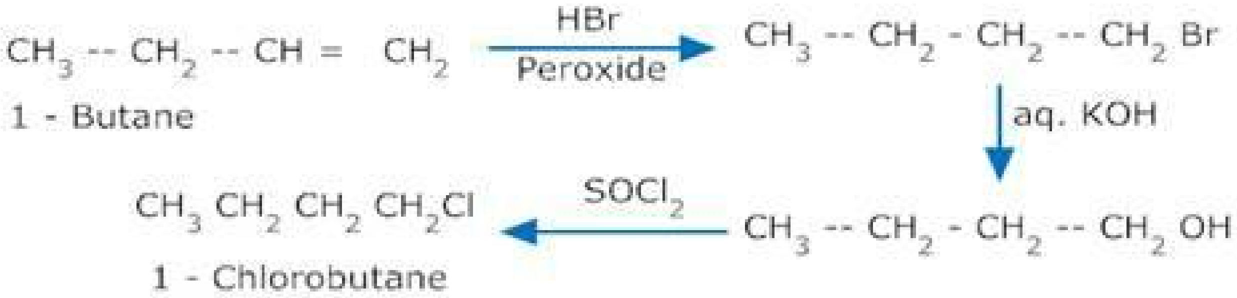
(x).



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

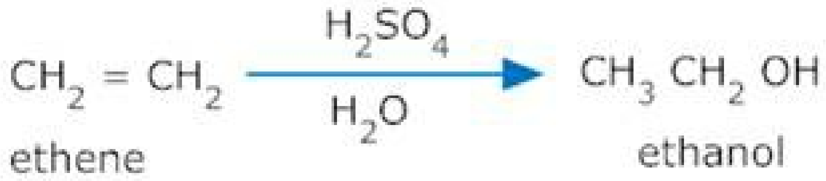
3. Convert

(i). 1 - Butene to 1 — chlorobutane.

Ans. 

$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-CH_2Br \xrightarrow{\text{aq. KOH}} CH_3-CH_2-CH_2-CH_2OH \xrightarrow{SOCl_2} CH_3CH_2CH_2CH_2Cl$$

(ii). Ethene to ethanol.

Ans. 

$$CH_2=CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3CH_2OH$$

(iii). Chlorobenzene to phenol.

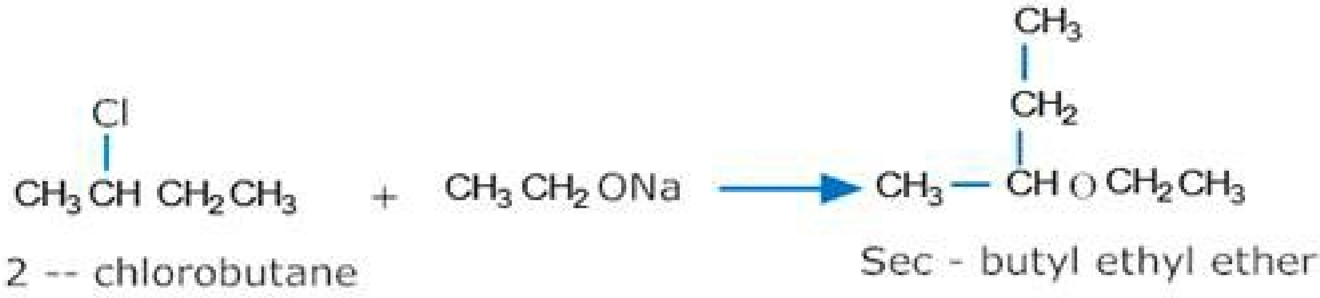
Ans. 

(iv). Methyl bromide to acetic acid.

Ans. 

$$CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{H_2O} CH_3COOH$$

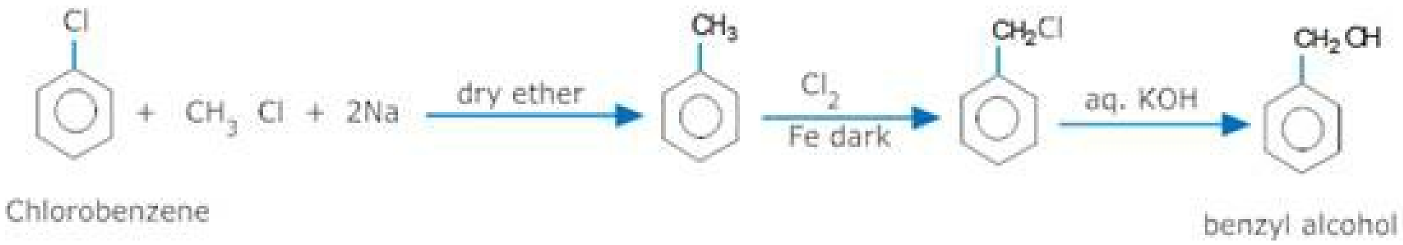
(v). 2- chlorobutane to sec- butyl ethyl ether.

Ans. 

$$CH_3CH(Cl)CH_2CH_3 + CH_3CH_2ONa \longrightarrow CH_3-CH(CH_2CH_3)OCH_2CH_3$$

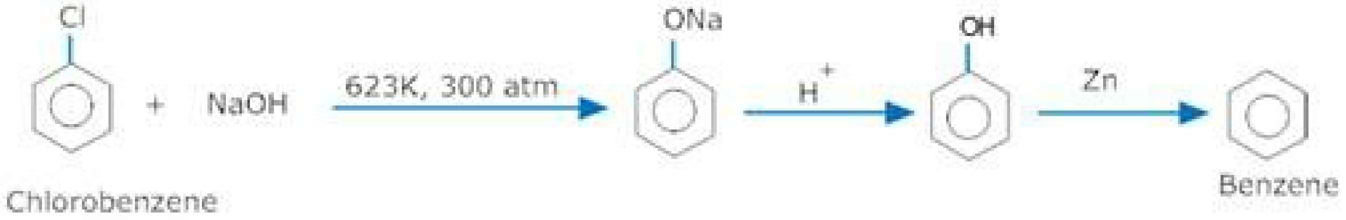
(vi). Chlorobenzene to benzyl chloride.

Ans.



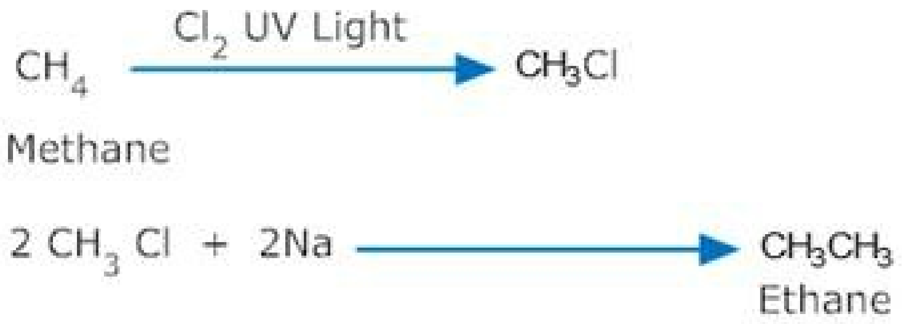
(vii). Chlorobenzene to Benzene.

Ans.



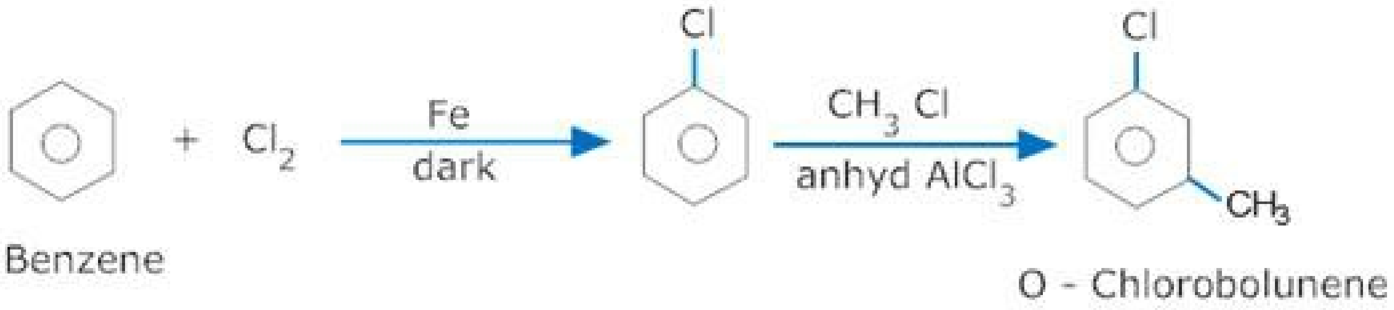
(viii). Methane to Ethane.

Ans.



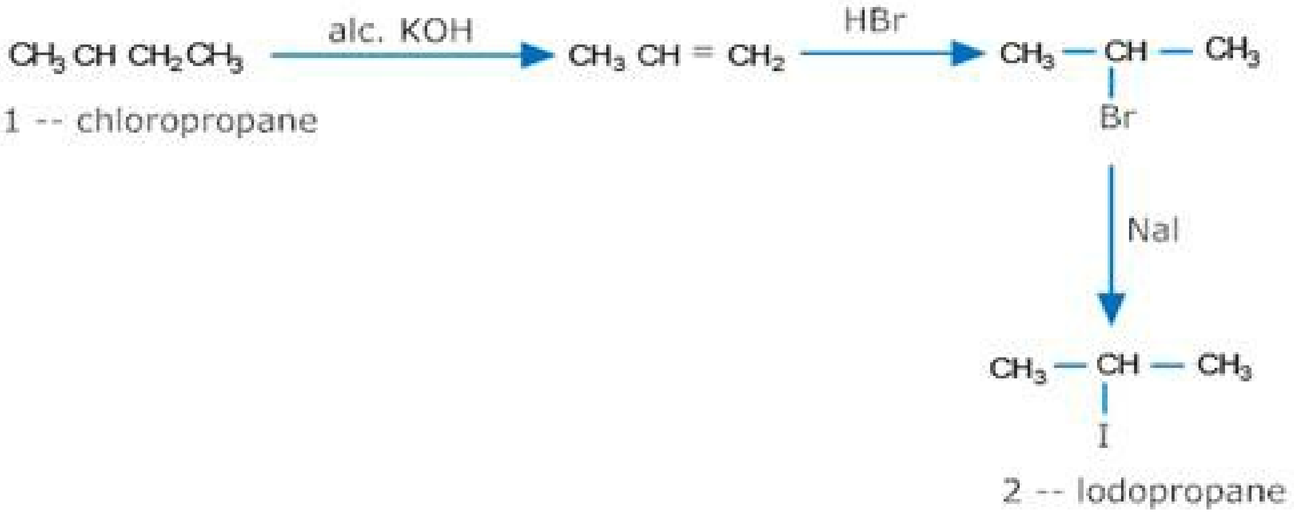
(ix). Benzene to o- chlorotoluene.

Ans.



(x). 1- chloropropane to 2- iodopropane.

Ans.



4. What is lucas reagent?

Ans. A mixture of HCl and anhydrous $ZnCl_2$ is known as Lucas reagent.

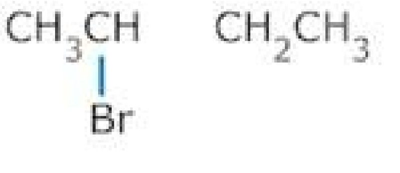
5. Which of the following will show optical is omerism

1 – bromobutane or 2 – bromobutane?

Ans.

$CH_3CH_2CH_2CH_2Br$

1 -- bromobutane



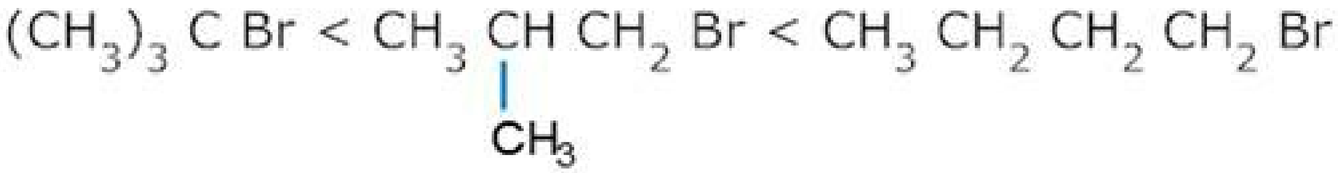
$CH_3CH(Br)CH_2CH_3$

2 -- bromobutane

2- bromobutane will be optically active as it has one chiral carbon (C_2).

6. Arrange $CH_3CH_2CH_2CH_2$Br, $(CH_3)_3C$Br, $CH_3CH\ (CH_3)\ CH_2$Br in order of increasing boiling points.

Ans. The order of increasing boiling points is



$$(CH_3)_3CBr < CH_3\underset{CH_3}{\underset{|}{CH}}CH_2Br < CH_3CH_2CH_2CH_2Br$$

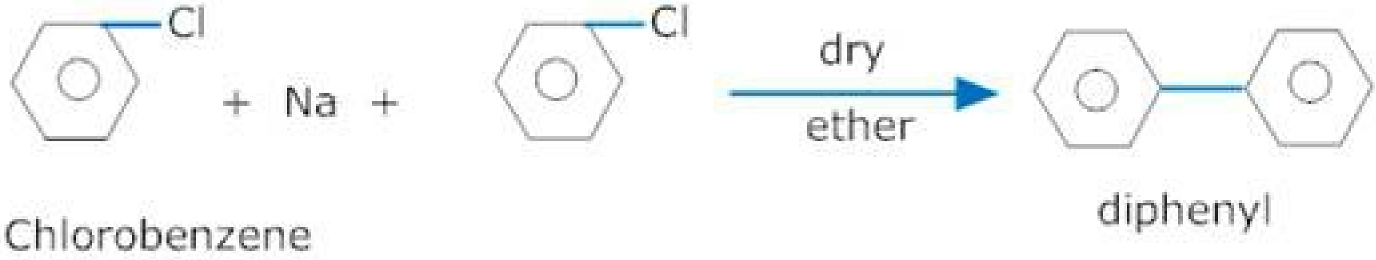
Boiling point decreases with increase in branching as it reduces the surface area.

7. Give an example of

(a) Fittig reaction

(b) Finkelstein reaction.

Ans. (a) Fittig reaction



(b) Finkelstein reaction

$$CH_3CH_2Cl + NaI \longrightarrow CH_3CH_2I + NaCl$$

chloroethane

Iodoethane

2 Marks Questions

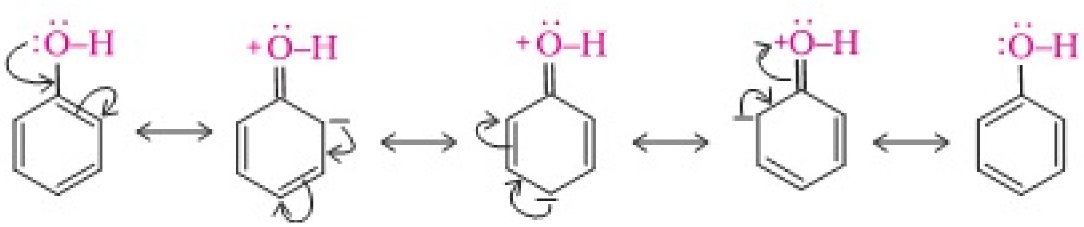
1. Thionyl chloride is preferred for converting alcohol to haloalkane.

Ans. Thionyl chloride is preferred for converting alcohol to haloalkane because the bi-products formed are all gases which escape into the atmosphere.

$$R-OH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

2. Phenol cannot be converted to chlorobenzene by reacting with HCl.

Ans. In phenol, due to resonance, the carbon –oxygen bond has a partial double bond character and is difficult to break being stronger than a single bond. Therefore it can not be converted to chlorobenzene by reacting with HCl.

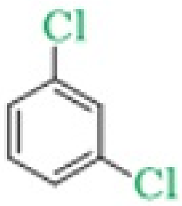


3. HNO_3 is added during iodination of benzene.

Ans. When benzene is reacted with iodine, the reaction is reversible in nature. It leads to the formation of reactants back. Therefore and oxidizing agent like HNO_3 oxidizes the HI formed in the reaction and keeps the reaction in forward direction.

4. p- dichlorobenzene has higher melting point than meta – dichlorobenzene.

Ans.



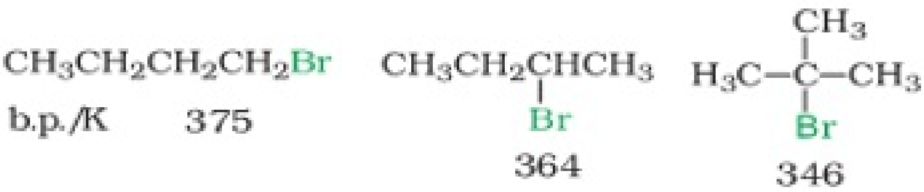
m – dichlorobenzene

p - dichlorobenzene

p- dichlorebenzene is having symmetrical structure therefore it can fit better into the crystal lattice which increases its melting point.

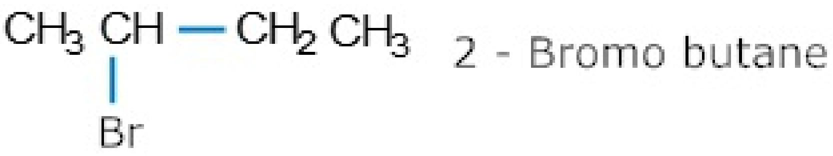
5. The boiling points of isomeric haloalkenes decrease with increase in branching.

Ans. The boiling points of isomeric haloakanes decreases with branching due to decrease in surface areas with branching. As branching increasing the structure becomes more spherical and the surface area decreases. e.g. the boiling points of isomers of C_4H_9 Br follows the order.

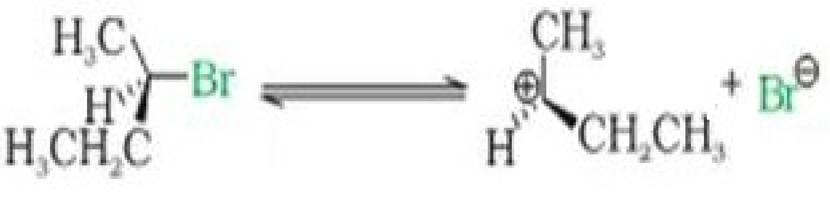


6. Hydrolysis of optically active 2- bromobutane forms optically inactive butan - 2 - ol.

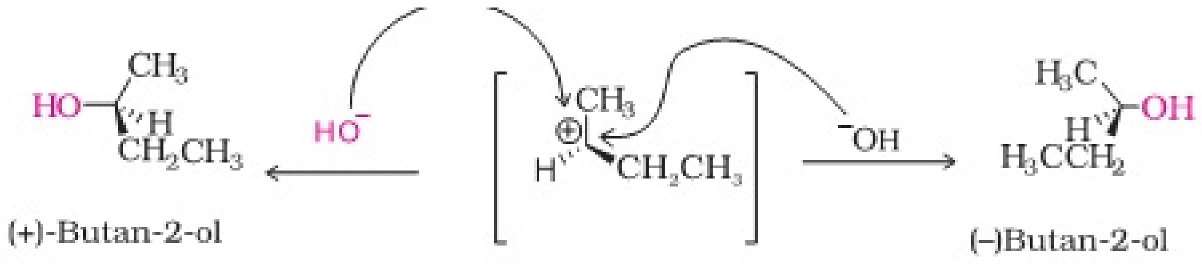
Ans.



The compound undergoes hydrolysis by S_N^1 mechanism via the formation of carbocation which is planar.



The attack of nucleophile can result in product which is a mixture of compounds both with same configuration and inverted configuration.

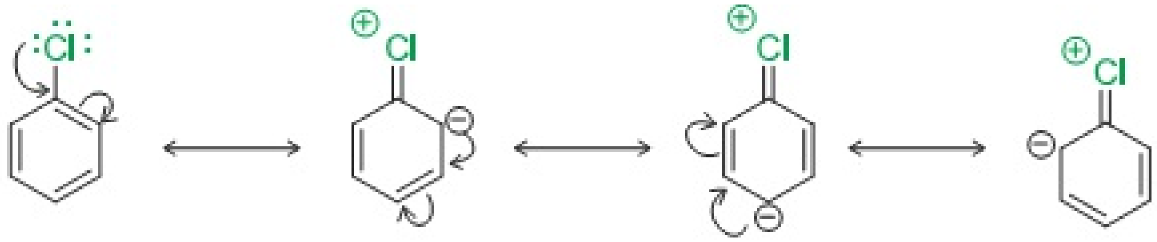


Therefore it results in the formation of racemic mixture which is optically inactive.

7. Chlorobenzene is less reactive towards nucleophilic substitution reaction.

Ans. Chlorobenzene is less reactive towards nucleophillic substitution due to –

i. resonance, C- Cl bond acquires a double bond character and becomes stronger than a single bond.



ii. SP^2 hybridisation in C of C-X bond, the carbon becomes more electronegative and holds the electron pair of C-X bond more tightly decreasing the bond length .
iii. Instability of phenyl cation.
iv. Repulsion for incoming nucleophile from electron rich ring.

8. Chloroform is stored in dark coloured bottles.

Ans. Chloroform gets oxidsed slowly by air in the presence of light to an extremely poisonous gas phosgene. Therefore to avoid any exposure to air and sunlight, it is kept in dark coloured bottles.

$$2CHCl_3 + O_2 \xrightarrow[light]{} 2COCl_2 + 2HCl$$

9. The order of boiling points is RCl < RBr < RI.

Ans. The boiling points of alkyl halides depends on dipole and van-der-waal's interaction.

These attractions get stronger as the molecules get bigger in size and have more electrons. As the size of halogens increases in the order –

$Cl < Br < I$

The boiling points also follow the order
RCl < RBr <RI

10. Vinyl chloride is less reactive than allyl chloride.

Ans. Due to resonance C- Cl bond gets double bond character and becomes stronger than a single bond, making vinyl chloride less reactive than allyl chloride.

11. What happens when

a) Thionyl chloride acts upon I - propanol.

b) Ethanol reacts with PBr_3

Ans. (a) When thionyl chloride acts upon 1- propanol chloropropane is formed .

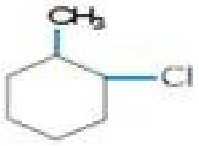
$$CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$

(b) When ethanol reacts with PBr_3, bromoethane is formed.

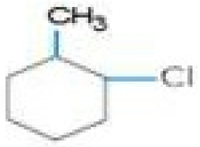
$$3CH_3CH_2OH + PBr_3 \rightarrow 3CH_3CH_2Br + H_3PO_3$$

12. How many aromatic isomers are possible for the formula C_7H_7Cl? Write the structure and names.

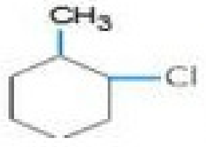
Ans. C_7H_7Cl-Three aromatic isomers are possible.



3 - methylcholorobenzene



2 - methylcholorobenzene



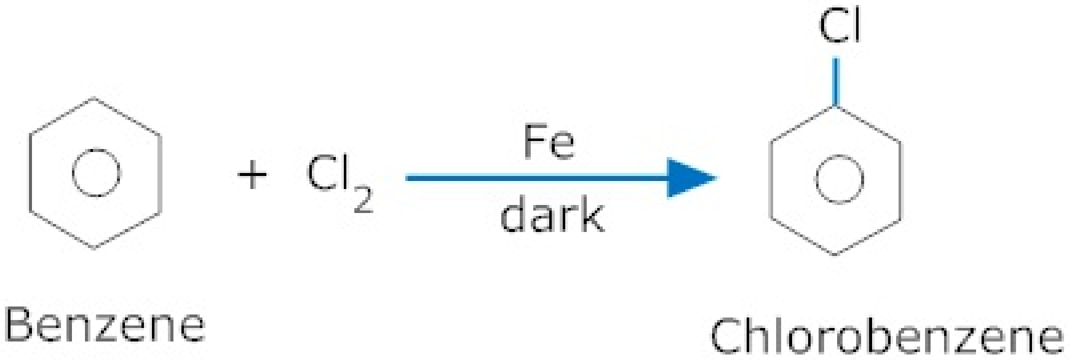
4 - methylcholorobenzene

13. How is chlorobenzene prepared by

(a) direct chlorination

(b) diazotization method?

Ans. (a) by direct chlorination-



(b) by diazotization method.

14. How can we distinguish between an alkyl halide and aryl halide?

Ans. Alkyl halide e.g. C_2H_5X, $C_6H_5CH_2X$ etc. can be distinguished from aryl halide, C_6H_5X, by $AgNO_3$ test.

$$\text{Alkyl halide} + \text{aqKOH} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \underset{\text{ppt.}}{\text{AgX}}$$

$$\text{Alylk halide} + \text{aqKOH} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{NO ppt.}$$

3 Marks Questions

1. $CH_3CH_2CH_2Br \xrightarrow{alc\ KOH} (X) \xrightarrow{H/H_2O} (Y) \xrightarrow{PCl_5} (Z)$

Ans. X = $CH_3CH = CH_2$

Y =

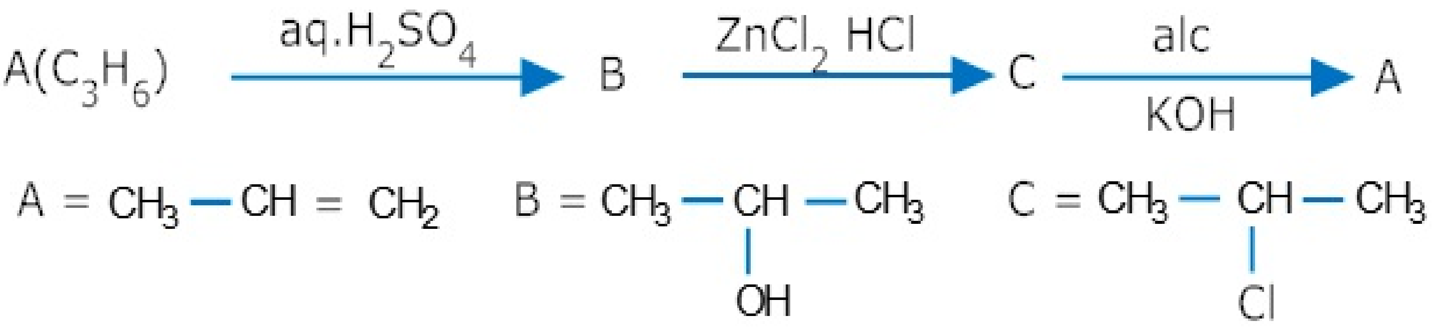
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

Z =

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

2. An organic compound ‘A’ having molecular formula C_3H_6 on treatment with aqueous H_2SO_4 given’ B’ which on treatment with Lucas reagent gives ‘C’. The compound ‘C’ on treatment with ethanolic KOH gives back on compound ‘A’. Identify A, B, & C.

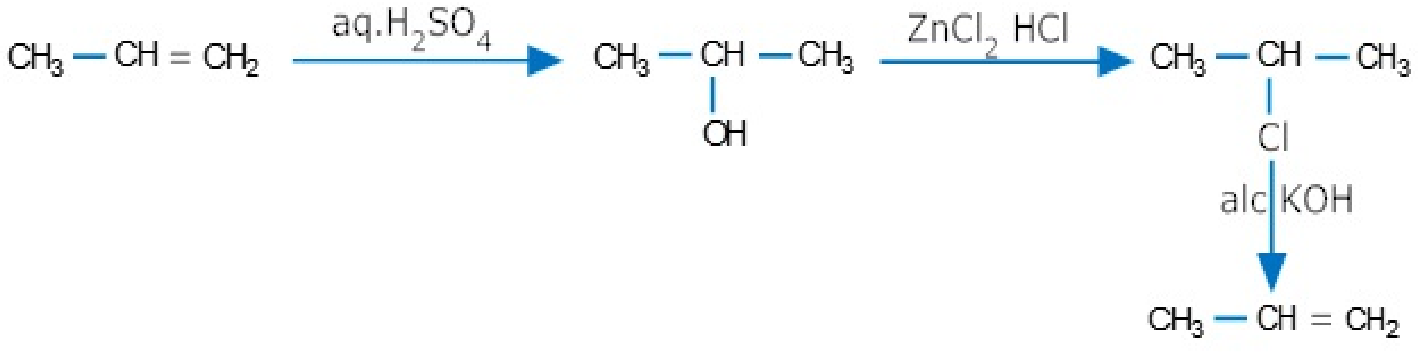
Ans.



$$A(C_3H_6) \xrightarrow{aq.H_2SO_4} B \xrightarrow{ZnCl_2\ HCl} C \xrightarrow[KOH]{alc} A$$

$$A = CH_3-CH = CH_2 \qquad B = CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \qquad C = CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

The question are



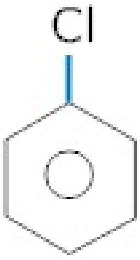
$$CH_3-CH = CH_2 \xrightarrow{aq.H_2SO_4} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{ZnCl_2\ HCl} CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{alc\ KOH} CH_3-CH = CH_2$$

3. An organic compound 'A' on heating with NH_3 and cuprous oxide at high pressure gives compound 'B'. The compound 'B' on treatment with ice cold solution of $NaNO_2$ and HCl gives 'C" , which on heating with copper turning and HCl gives 'A' again. Identify A, B & C. compound

Ans.

$$A \xrightarrow[Cu_2O]{NH_3} B \xrightarrow[HCl]{NaNO_2} C \xrightarrow{Cu/HCl} A$$

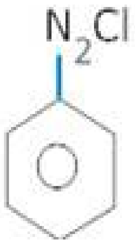
A =



B =

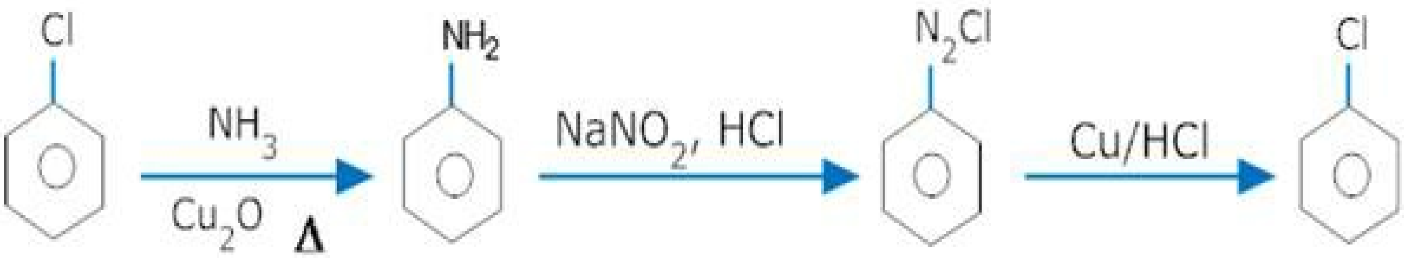
Aniline

C =



Bengene diazonium chloride

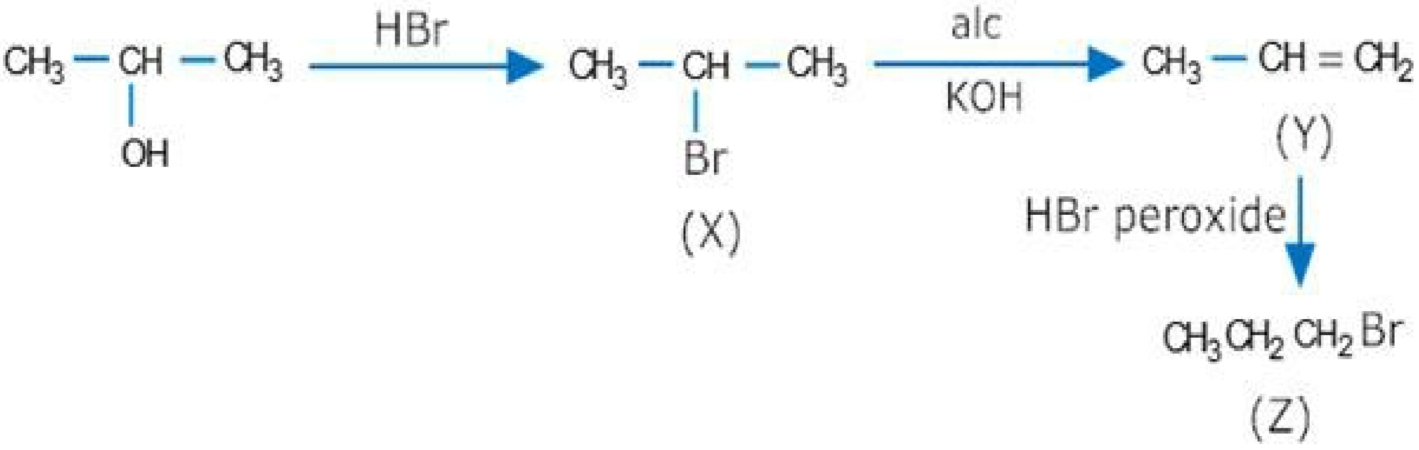
The question are



4.

$$\underset{\displaystyle OH}{CH_3 - \underset{|}{CH} - CH_3} \xrightarrow{HBr} X \xrightarrow[KOH]{alc} Y \xrightarrow{HBr\ peroxide} Z$$

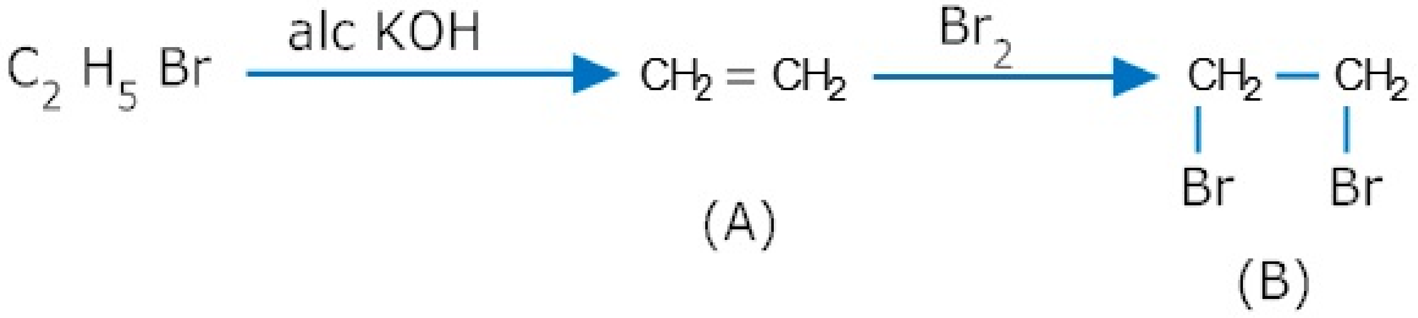
Ans.



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{HBr} \underset{(X)}{CH_3-\underset{Br}{\underset{|}{CH}}-CH_3} \xrightarrow[KOH]{alc} \underset{(Y)}{CH_3-CH=CH_2} \xrightarrow{HBr\ peroxide} \underset{(Z)}{CH_3CH_2CH_2Br}$$

5. $C_2H_5Br \xrightarrow{alc\ KOH} A \xrightarrow{Br_2} B$

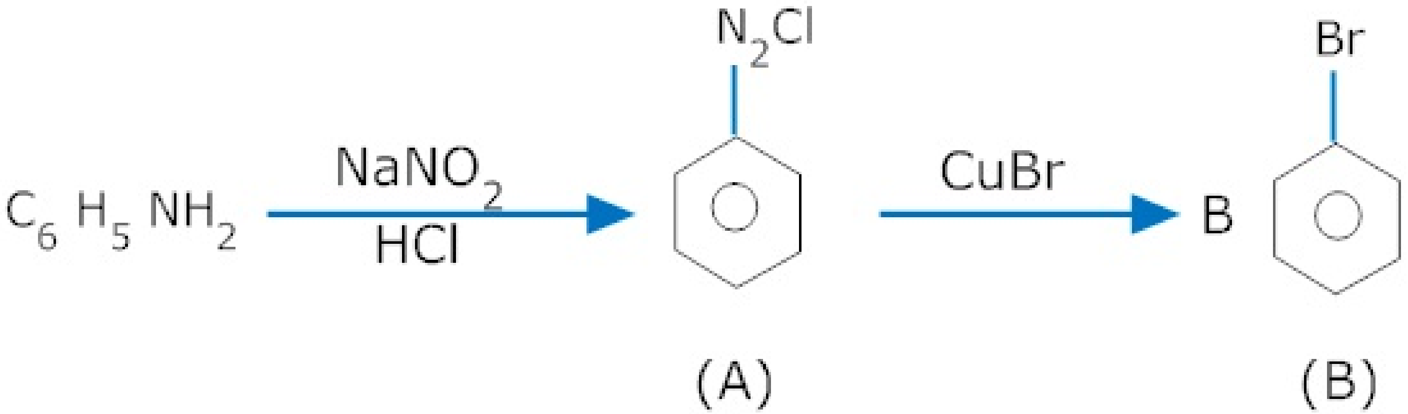
Ans.

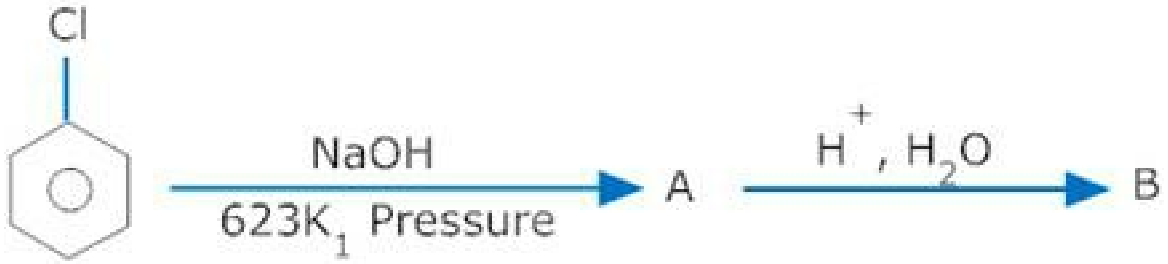


$$C_2H_5Br \xrightarrow{alc\ KOH} \underset{(A)}{CH_2=CH_2} \xrightarrow{Br_2} \underset{(B)}{\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}}$$

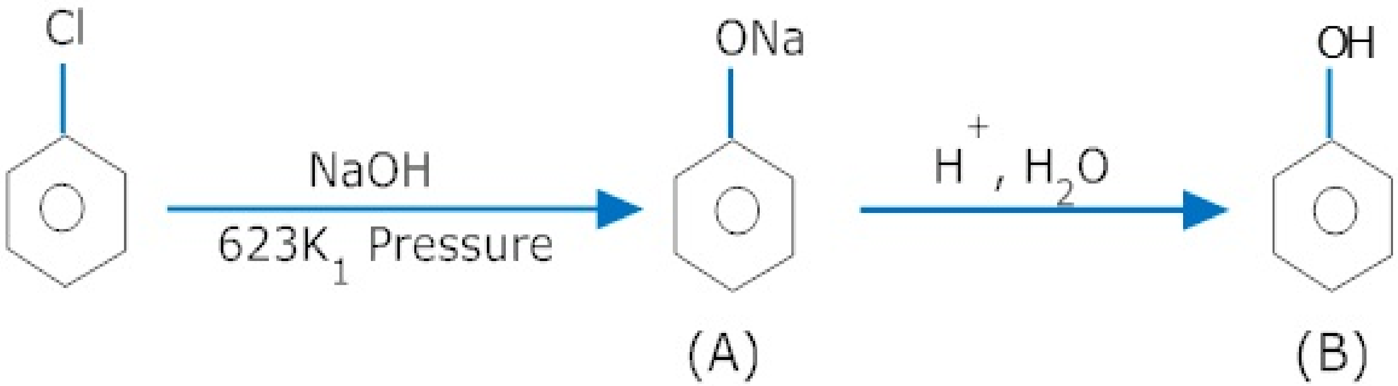
6. $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} A \xrightarrow{CuBr} B$

Ans.


C6 H5 NH2
NaNO2
HCl
N2Cl
(A)
CuBr
B
Br
(B)

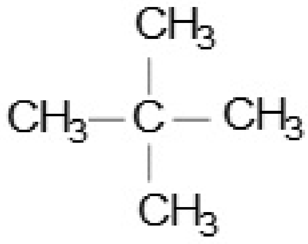
7. 
Cl
NaOH
623K, Pressure
A
H+, H2O
B

Ans.

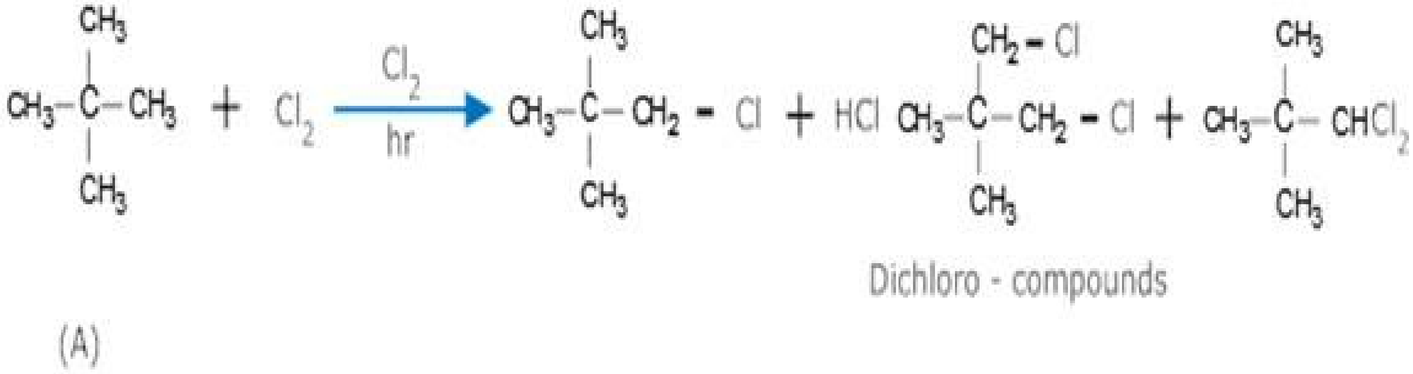

Cl
NaOH
623K, Pressure
ONa
(A)
H+, H2O
OH
(B)

8. A compound 'A' contains carbon and hydrogen only and has molecular mass of 72. Its photo chlorination gives a mixture containing only one monochloro and two dichloro hydrocarbons. Deduce the structure of A and chlorinated products.

Ans. A is C_5H_{12} (mol. Wt. 72) Since its gives one mono chloro and two dichloro derivatives on photochemical chlorination, it is



The reactions are



9. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans. In the presence of sulphuric acid (H_2SO_4), KI produces HI

$$2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

Since H_2SO_4 is an oxidizing agent, it oxidizes HI (produced in the reaction to I_2).

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

As a result, the reaction between alcohol and HI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H_3PO_4 is used.

10. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

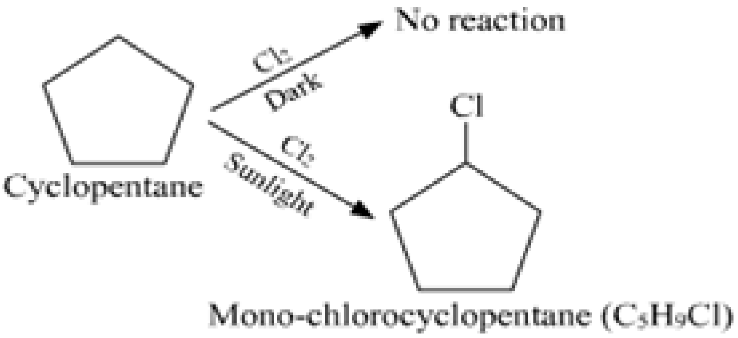
Ans. A hydrocarbon with the molecular formula, C_5H_{10} belongs to the group with a general molecular formula C_nH_{2n}. Therefore, it may either be an alkene or a cycloalkane.

Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound, C_5H_9Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H-atoms that are all equivalent. Also, as all H-atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.

Cyclopentane (C_5H_{10})

The reactions involved in the question are:



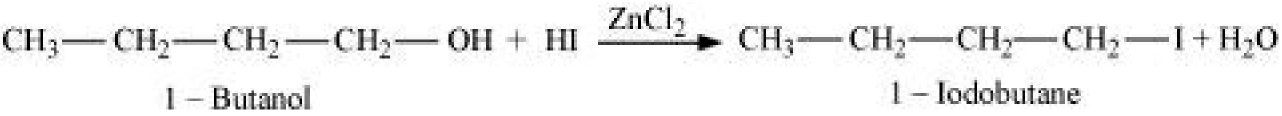
11. Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol

(ii) 1-chlorobutane

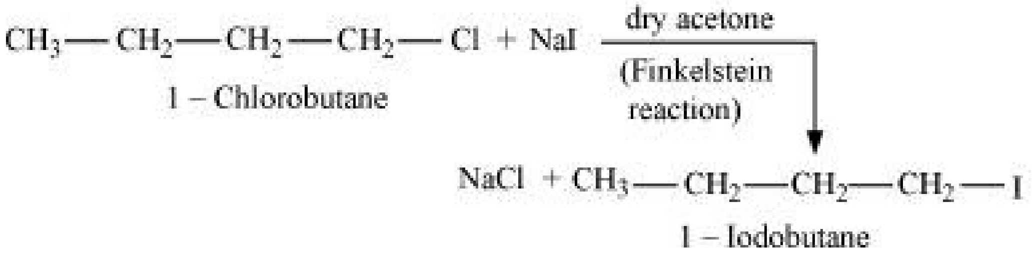
(iii) but-1-ene.

Ans. (i)



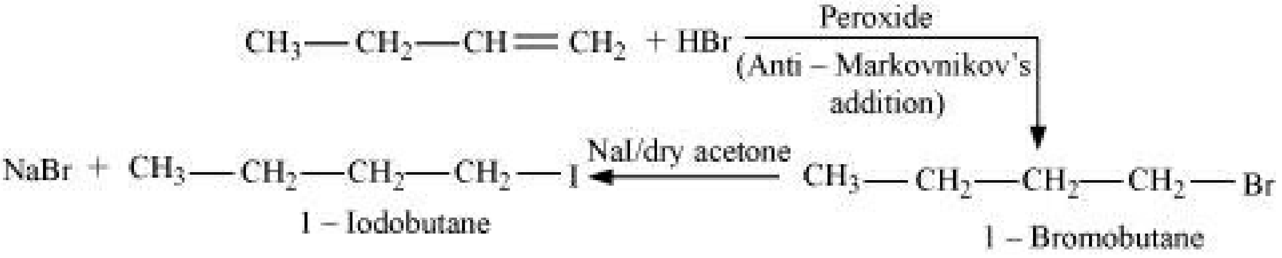
$$\underset{\text{1 – Butanol}}{CH_3-CH_2-CH_2-CH_2-OH} + HI \xrightarrow{ZnCl_2} \underset{\text{1 – Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I} + H_2O$$

(ii)



$$\underset{\text{1 – Chlorobutane}}{CH_3-CH_2-CH_2-CH_2-Cl} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{dry acetone}} NaCl + \underset{\text{1 – Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

(iii)



$$CH_3-CH_2-CH=CH_2 + HBr \xrightarrow[\text{(Anti – Markovnikov's addition)}]{\text{Peroxide}} \underset{\text{1 – Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br}$$

$$\underset{\text{1 – Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br} \xrightarrow{\text{NaI/dry acetone}} NaBr + \underset{\text{1 – Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

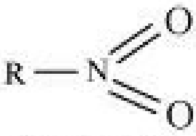
12. What are ambident nucleophiles? Explain with an example.

Ans. Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack.

For example, nitrite ion is an ambident nucleophile.

Nitrite ion can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.

Alkylnitrite



Nitroalkane

13. Which compound in each of the following pairs will react faster in S_N^2 reaction with OH^-?

(i) $CH_3Br\ or\ CH_3I$

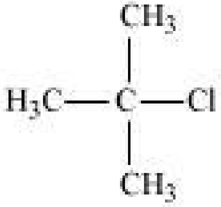
(ii) $(CH_3)_3CCl\ or\ CH_3Cl$

Ans. (i) In the S_N^2 mechanism, the reactivity of halides for the same alkyl group increases in the order. This happens because as the size increases, the halide ion becomes a better leaving group.

R-F << R-Cl < R-Br < R-I

Therefore, CH_3I will react faster than CH_3Br in S_N^2 reactions with OH^-.

(ii)



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

CH_3-Cl

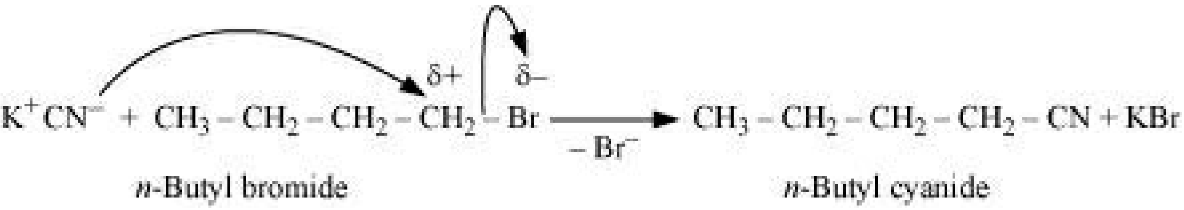
The S_N^2 mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCl$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving group in CH_3Cl . Hence, CH_3Cl reacts faster than $(CH_3)_3CCl$ in S_N^2 reaction with OH^- .

14. Write the mechanism of the following reaction:

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

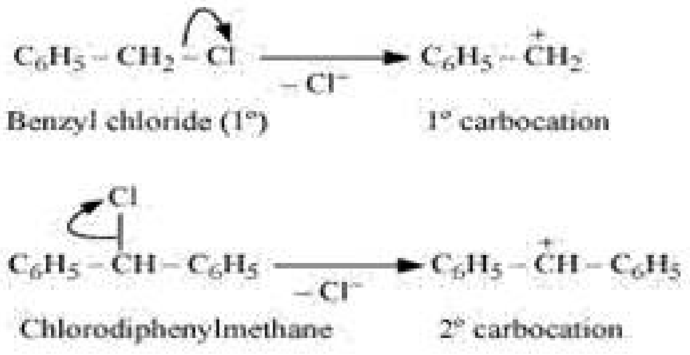
Ans. $nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$

The given reaction is an S_N^2 reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



15. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Ans.

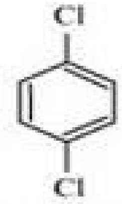


Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now $C_6H_5CH_2Cl$, forms

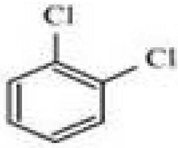
$1^\circ -$ carbocation, while $C_6H_5CHClC_6H_5$ forms $2^\circ -$ carbocation, which is more stable than $1^\circ -$ carbocation. Hence $C_6H_5CHClC_6H_5$, is hydrolyzed more easily than $C_6H_5CH_2Cl$ by aqueous KOH.

16. *p*-Dichlorobenzene has higher m.p. and lower solubility than those of *o*- and *m*-isomers. Discuss.

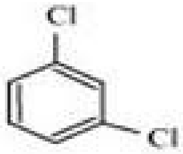
Ans.



p-Dichlorobenzene



o-Dichlorobenzene



m-Dichlorobenzene

p-Dichlorobenzene is more symmetrical than *o*-and *m*-isomers. For this reason, it fits more closely than *o*-and *m*-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of *p*-dichlorobenzene. As a result, *p*-dichlorobenzene has a higher melting point and lower solubility than *o*-and *m*-isomers.

5 Marks Questions

1. Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

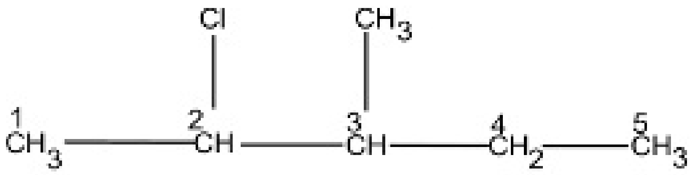
(ii) 1-Chloro-4-ethylcyclohexane

(iii) 4-tert. Butyl-3-iodoheptane

(iv) 1,4-Dibromobut-2-ene

(v) 1-Bromo-4-sec. butyl-2-methylbenzene

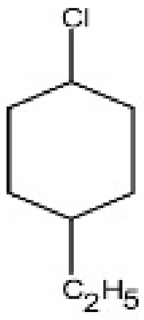
Ans. (i)



$$\overset{1}{C}H_3-\overset{\overset{Cl}{|}}{\overset{2}{C}H}-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_3$$

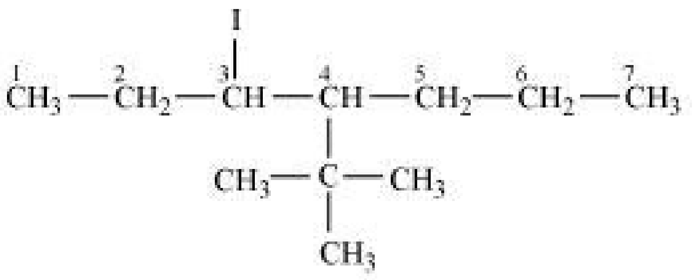
2-Chloro-3-methyl pentane

(ii)



1-Chloro-4-ethylcyclohexane

(iii)



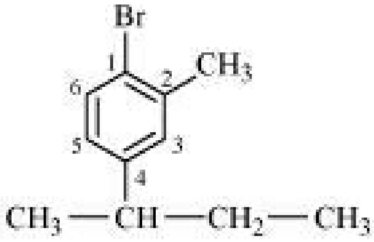
4- tert-Butyl-3-iodoheptane

(iv)

$$\mathrm{Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br}$$

1, 4-Dibromobut-2-ene

(v)

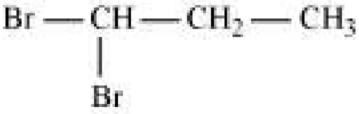


1-Bromo-4-sec-butyl-2-methylbenzene

2. Write structures of different dihalogen derivatives of propane.

Ans. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

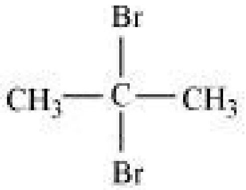
(i)



$$\mathrm{Br-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_2-CH_3}$$

1, 1-Dibromopropane

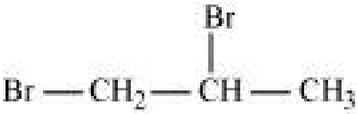
(ii)



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

2, 2-Dibromopropane

(iii)



$$Br-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3$$

1, 2-Dibromopropane

(iv)

$Br-CH_2-CH_2-CH_2-Br$

1, 3-Dibromopropane

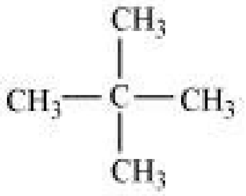
3. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Ans. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.

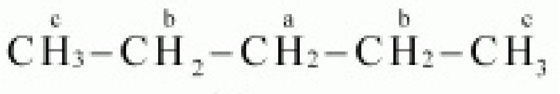


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

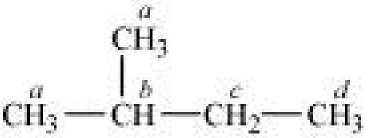
Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.



$\overset{c}{C}H_3-\overset{b}{C}H_2-\overset{a}{C}H_2-\overset{b}{C}H_2-\overset{c}{C}H_3$

n-Pentane

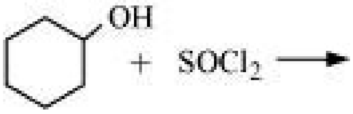
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12}should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c,* and *d* in 2-methylbutane.



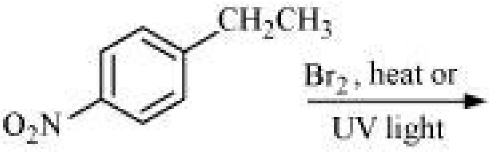
$\overset{a}{C}H_3-\overset{\overset{a}{CH_3}\,|\,b}{C}H-\overset{c}{C}H_2-\overset{d}{C}H_3$

4. **Draw the structures of major monohalo products in each of the following reactions:**

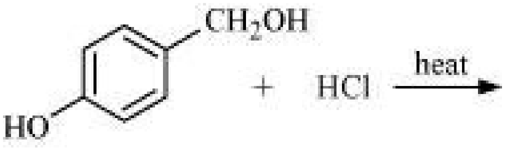
(i)



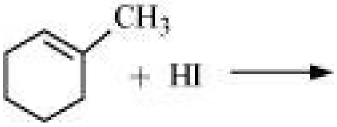
(ii)



(iii)



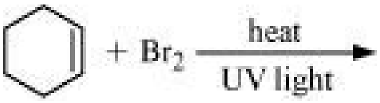
(iv)



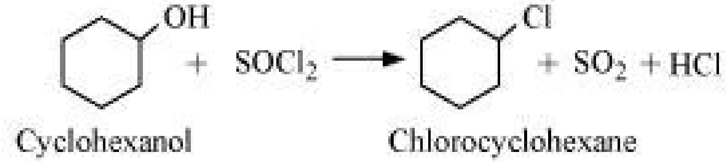
(v)

$CH_3CH_2Br + NaI \longrightarrow$

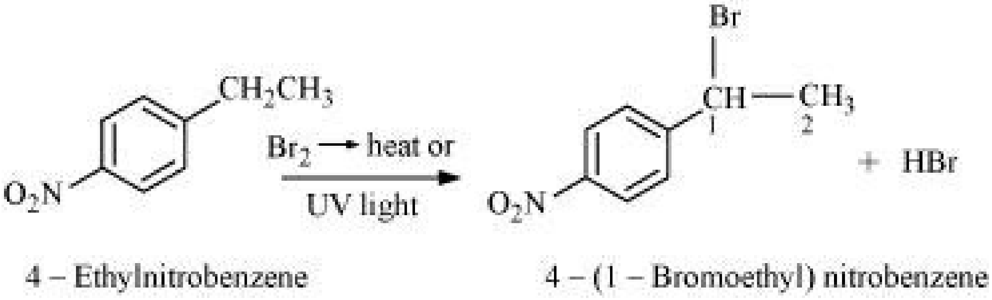
(vi)



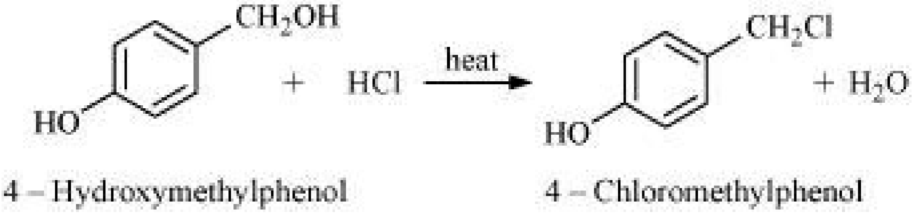
Ans. (i)



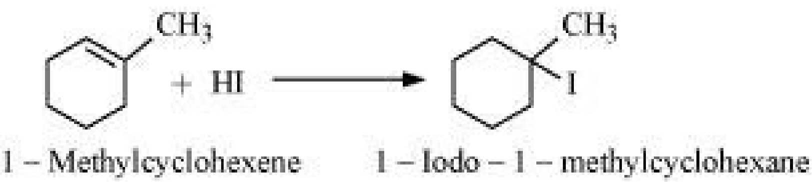
(ii)



(iii)



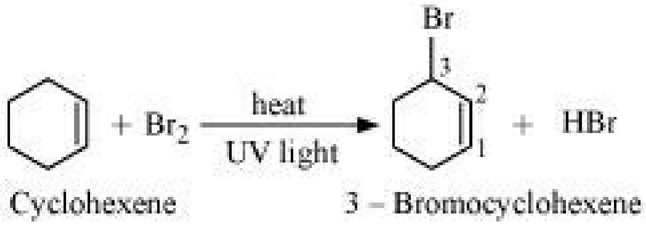
(iv)



(v)

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + NaI \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2I} + NaBr$$

(vi)

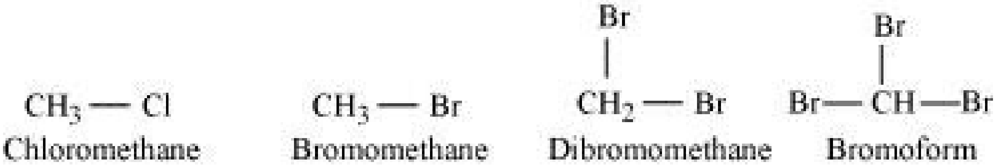


5. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Ans. (i)



$$\underset{\text{Chloromethane}}{CH_3-Cl} \qquad \underset{\text{Bromomethane}}{CH_3-Br} \qquad \underset{\text{Dibromomethane}}{\overset{\overset{\displaystyle Br}{|}}{CH_2}-Br} \qquad \underset{\text{Bromoform}}{Br-\overset{\overset{\displaystyle Br}{|}}{CH}-Br}$$

For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

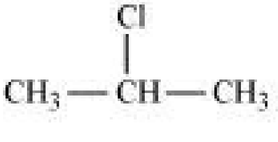
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



$CH_3-\overset{\overset{Cl}{|}}{CH}-CH_3$

Isopropyl chloride

$Cl-CH_2-CH_2-CH_3$

1 – Chloropropane

$Cl-CH_2-CH_2-CH_2-CH_3$

1 – Chlorobutane

For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

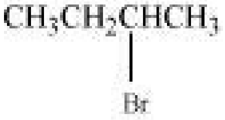
Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

6. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

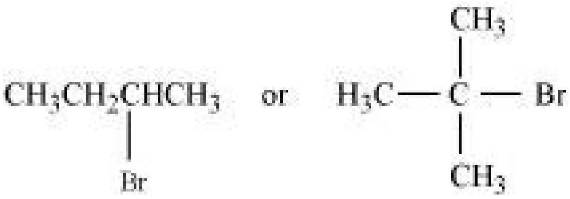
(i)

$CH_3CH_2CH_2CH_2Br$ or



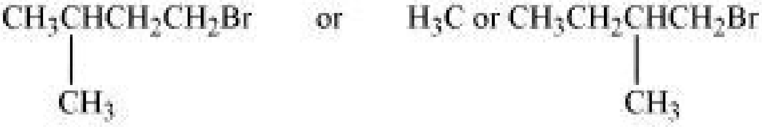
$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$

(ii)



$CH_3CH_2\underset{\mid \atop Br}{CH}CH_3$ or $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br$

(iii)

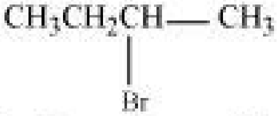


$CH_3\underset{\mid \atop CH_3}{CH}CH_2CH_2Br$ or H_3C or $CH_3CH_2\underset{\mid \atop CH_3}{CH}CH_2Br$

Ans. (i)

$CH_3CH_2CH_2CH_2Br$

1 – Bromobutane (1°)

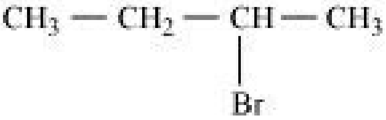


$CH_3CH_2\underset{\mid \atop Br}{CH}-CH_3$

2 – Bromobutane (2°)

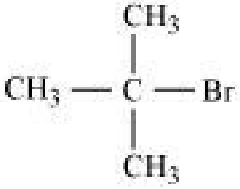
2-bromobutane is a $2°$ alkylhalide whereas 1-bromobutane is a $1°$ alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)



$CH_3-CH_2-\underset{\mid \atop Br}{CH}-CH_3$

2 – Bromobutane (2°)

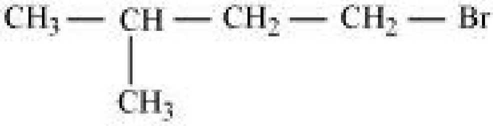


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

2 – Bromo – 2 – methylpropane (3°)

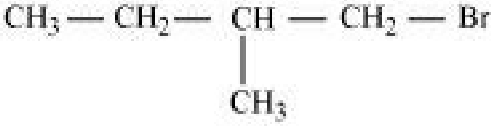
2-Bromobutane is $2°$ alkylhalide whereas 2-bromo-2-methylpropane is $3°$ alkyl halide. Therefore, greater numbers of substituents are present in $3°$ alkyl halide than in $2°$ alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)



$CH_3-\underset{\mid \atop CH_3}{CH}-CH_2-CH_2-Br$

1 – Bromo – 3 – methylbutane (1°)



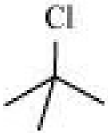
$CH_3-CH_2-\underset{\mid \atop CH_3}{CH}-CH_2-Br$

1 – Bromo – 2 – methylbutane (1°)

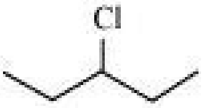
Both the alkyl halides are primary. However, the substituent $-CH_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

7. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)



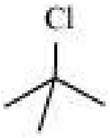
and



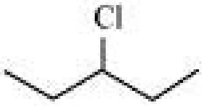
(ii)

and

Ans. (i)



2 – Chloro – 2 – methylpropane (3°)
(I)



3 – chloropentane (2°)
(II)

S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2°. Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

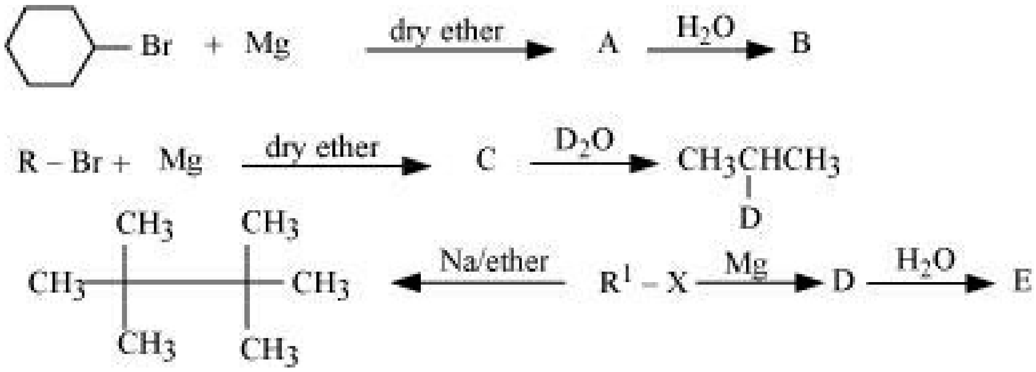
(ii)

2 – chloroheptane (2°)
(I)

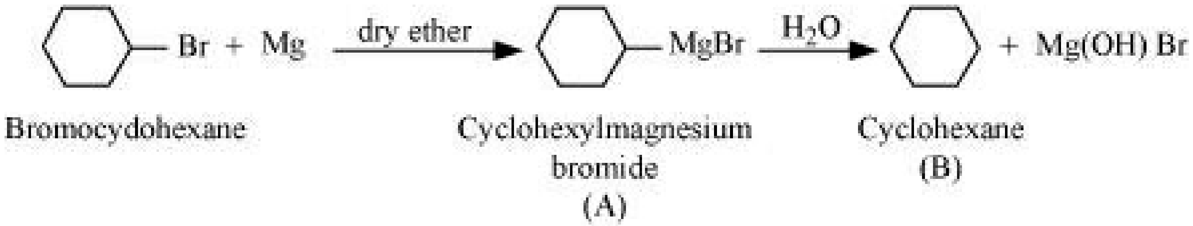
1 – chlorohexane (1°)
(II)

The alkyl halide (I) is $2°$ while (II) is $1°$. $2°$ carbocation is more stable than $1°$ carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

8. Identify A, B, C, D, E, R and R^1 in the following:



Ans.

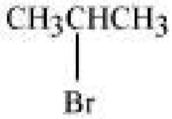


Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is

$$\underset{\displaystyle MgBr}{CH_3\overset{}{C}HCH_3}$$

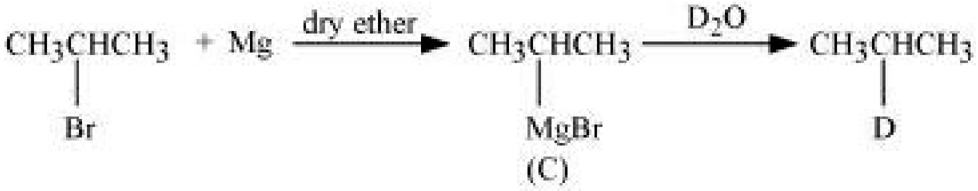
Isopropylmagnesium bromide

Therefore, the compound R - Br is

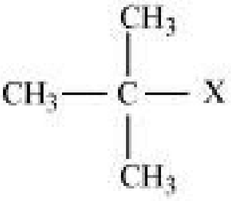


$$\underset{\displaystyle Br}{CH_3CHCH_3}$$

2 – Bromopropane



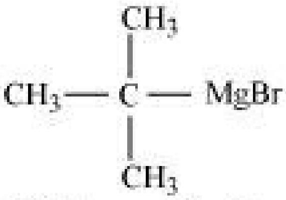
When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1-X, is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-X$

tert – Butylhalide

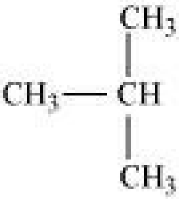
Therefore, compound D is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-MgBr$

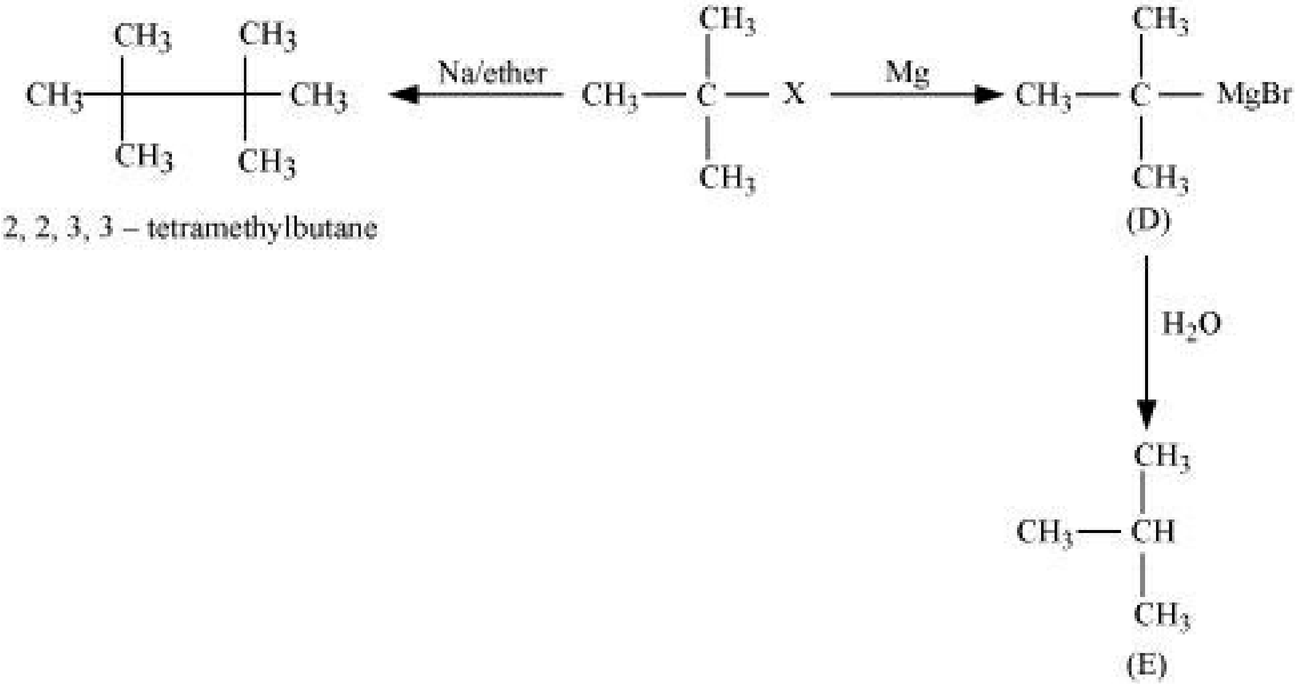
tert – Bulytmagnesiumbromide

And, compound E is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}}$

2 – Methylpropane



9. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$

(vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$

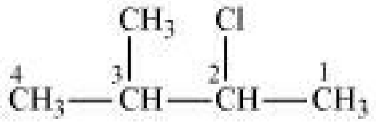
(ix) $CH_3CH=CHC(Br)(CH_3)_2$

(x) $p-ClC_6H_4CH_2CH(CH_3)_2$

(xi) $m-ClCH_2C_6H_4CH_2C(CH_3)_3$

(xii) $o-Br-C_6H_4CH(CH_3)CH_2CH_3$

Ans. (i)

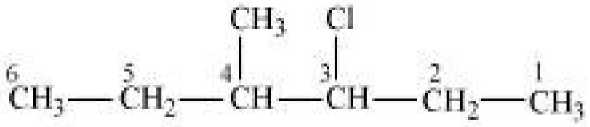


$\overset{4}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{\overset{Cl}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$

2-Chloro-3-methylbutane

(Secondary alkyl halide)

(ii)

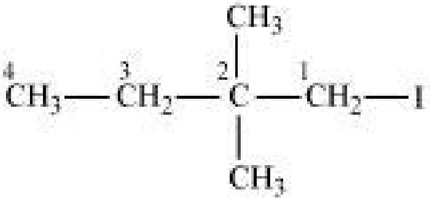


$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H(CH_3)-\overset{3}{C}H(Cl)-\overset{2}{C}H_2-\overset{1}{C}H_3$

3-Chloro-4-methyhexane

(Secondary alkyl halide)

(iii)

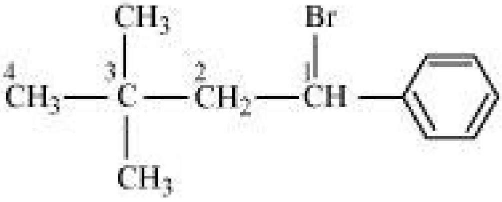


$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_2-I$

1-Iodo-2, 2 -dimethylbutane

(Primary alkyl halide)

(iv)

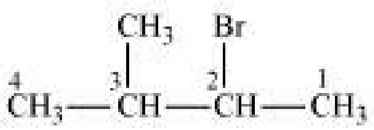


$\overset{4}{C}H_3-\overset{3}{C}(CH_3)_2-\overset{2}{C}H_2-\overset{1}{C}H(Br)-C_6H_5$

1-Bromo-3, 3-dimethyl-1-phenylbutane

(Secondary benzyl halide)

(v)

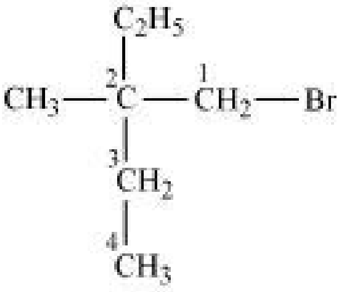


$$\overset{4}{\mathrm{CH_3}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{\overset{\mathrm{Br}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CH_3}}$$

2-Bromo-3-methylbutane

(Secondary alkyl halide)

(vi)

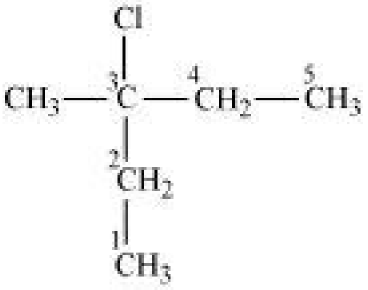


$$\mathrm{CH_3}-\underset{\underset{\underset{\underset{\overset{4}{\mathrm{CH_3}}}{|}}{\overset{3}{\mathrm{CH_2}}}}{|}}{\overset{\overset{\mathrm{C_2H_5}}{|}}{\overset{2}{\mathrm{C}}}}-\overset{1}{\mathrm{CH_2}}-\mathrm{Br}$$

1-Bromo-2-ethyl-2-methylbutane

(Primary alkyl halide)

(vii)

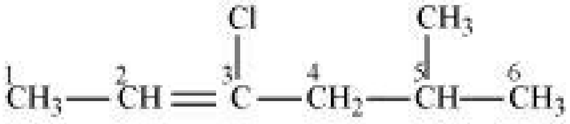


$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_2-CH_3}{|}}{C}}-CH_2-CH_3$

3-Chloro-3-methylpentane

(Tertiary alkyl halide)

(viii)

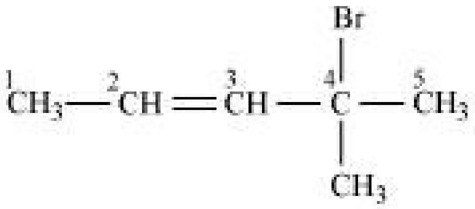


$CH_3-CH=\overset{\overset{Cl}{|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

3-Chloro-5-methylhex-2-ene

(Vinyl halide)

(ix)

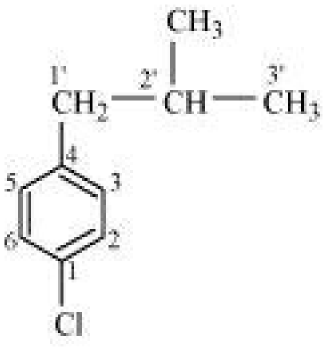


$CH_3-CH=CH-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

4-Bromo-4-methylpent-2-ene

(Allyl halide)

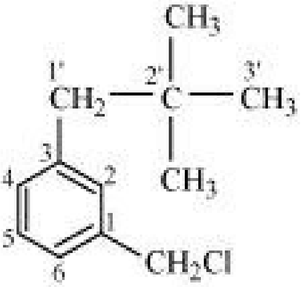
(x)



1-Chloro-4-(2-methylpropyl) benzene

(Aryl halide)

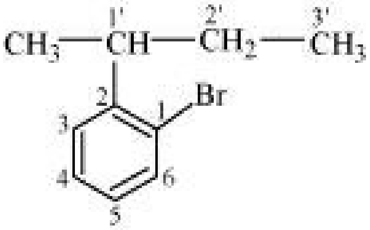
(xi)



1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene

(Primary benzyl halide)

(xii)



1-Bromo-2-(1-methylpropyl) benzene

(Aryl halide)

10. Give the IUPAC names of the following compounds:

(i) $CH_3CH\left(Cl\right)CH\left(Br\right)CH_3$

(ii) $CHF_2CBrClF$

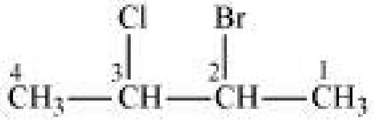
(iii) $ClCH_2C=CCH_2Br$

(iv) $\left(CCl_3\right)_3CCl$

(v) $CH_3C(p-ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH=CClC_6H_4I-p$

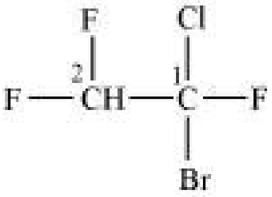
Ans. **(i)**



$\overset{4}{C}H_3-\overset{3}{C}H(Cl)-\overset{2}{C}H(Br)-\overset{1}{C}H_3$

2-Bromo-3-chlorobutane

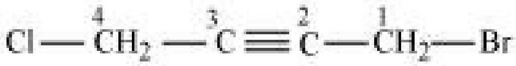
(ii)



$F-\overset{2}{C}HF-\overset{1}{C}(Cl)(Br)-F$

1-Bromo-1-chloro-1, 2, 2-trifluoroethane

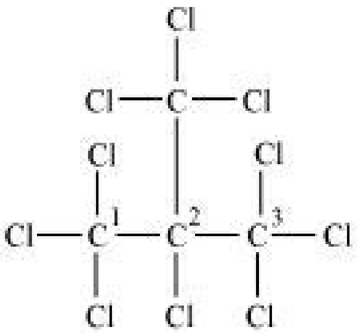
(iii)



$Cl-\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$

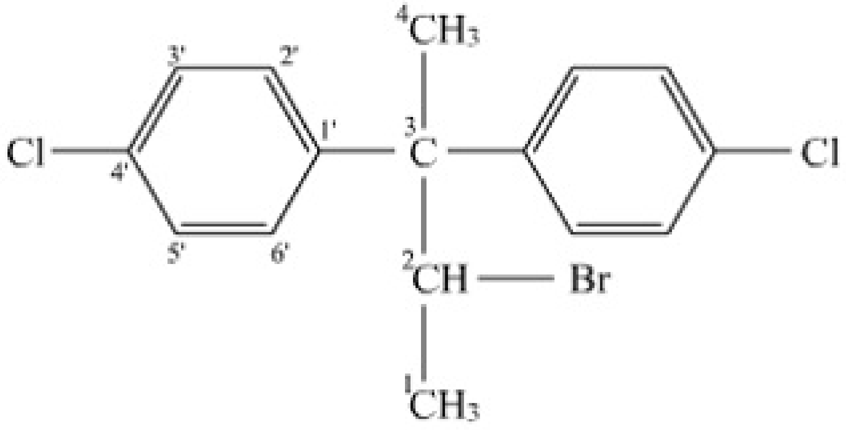
1-Bromo-4-chlorobut-2-yne

(iv)



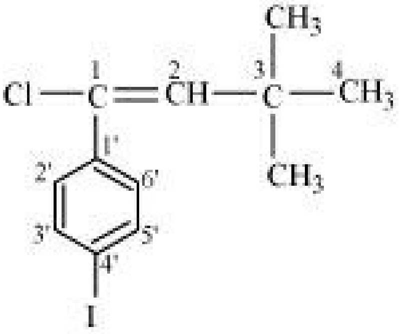
2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(v)



2-Bromo-3, 3-bis(4-chlorophenyl) butane

(vi)



1-chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene

11. Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane

(ii) *p*-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane

(iv) 2-(2-Chlorophenyl)-1-iodooctane

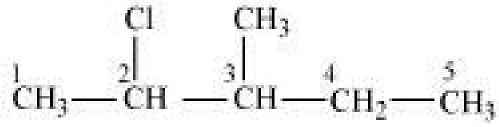
(v) Perfluorobenzene

(vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene

(viii) 1,4-Dibromobut-2-ene

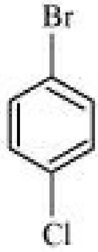
Ans. (i)



$$\overset{1}{\mathrm{CH_3}}-\overset{\overset{\mathrm{Cl}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{\overset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$$

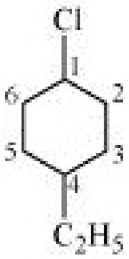
2-Chloro-3-methylpentane

(ii)



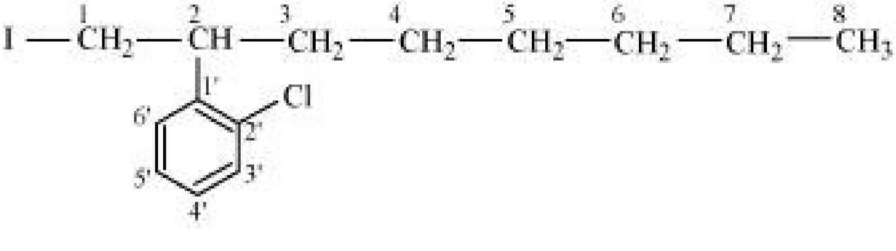
p-Bromochlorobenzene

(iii)



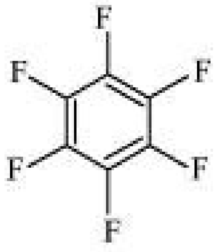
1-Chloro-4-ethylcyclohexane

(iv)



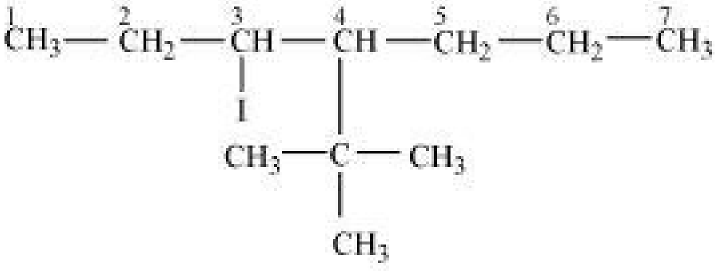
2-(2-Chlorophenyl)-1-iodooctane

(v)



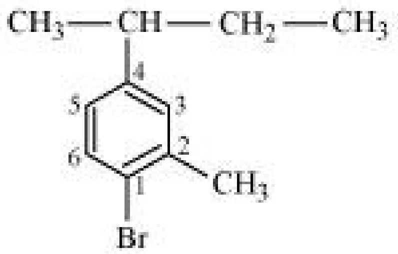
Perfluorobenzene

(vi)



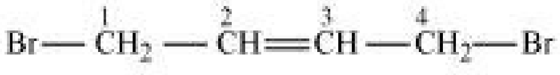
4-Tert-Butyl-3-iodoheptane

(vii)



1-Bromo-4-sec-butyl-2-methylbenzene

(viii)



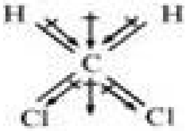
$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$

1,4-Dibromobut-2-ene

12. Which one of the following has the highest dipole moment?

(i) CH_2Cl_2 **(ii)** $CHCl_3$ **(iii)** CCl_4

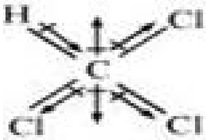
Ans. (i)



Dichlormethane (CH_2Cl_2)

μ = 1.60D

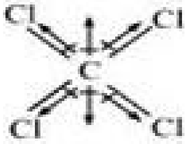
(ii)



Chloroform ($CHCl_3$)

μ = 1.08D

(iii)



Carbon tetrachloride (CCl_4)

μ = 0D

CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C-Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in $CHCl_3$, the resultant of dipole moments of two C-Cl bonds is opposed by the resultant of dipole moments of one C-H bond and one C-Cl bond. Since the resultant of one C-H bond and one C-Cl bond dipole moments is smaller than two C-Cl bonds, the opposition is to a small extent. As a result, $CHCl_3$ has a small dipole moment of 1.08 D.

On the other hand, in case of CH_2Cl_2 , the resultant of the dipole moments of two C-Cl bonds is strengthened by the resultant of the dipole moments of two C-H bonds. As a result,

CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$ l_3 i.e., CH_2Cl_2 has the highest dipole moment.

Hence, the given compounds can be arranged in the increasing order of their dipole moments as:

$CCl_4 < CHCl_3 < CH_2Cl_2$

13. Write the isomers of the compound having formula C_4H_9Br .

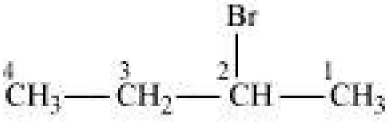
Ans. There are four isomers of the compound having the formula C_4H_9Br . These isomers are given below.

(a)

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-Br$$

1-Bromobutane

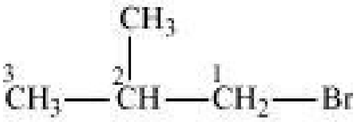
(b)



$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{\overset{Br}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2-Bromobutane

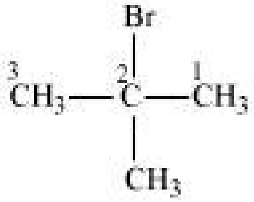
(c)



$$\overset{3}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_2}-Br$$

1-Bromo-2-methylpropane

(d)



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

2-Bromo-2-methylpropane

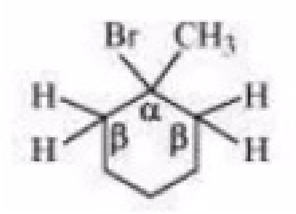
14. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

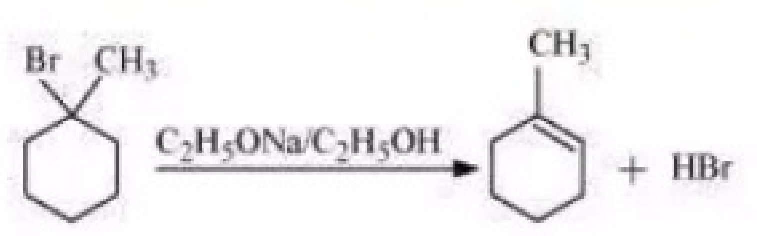
(ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

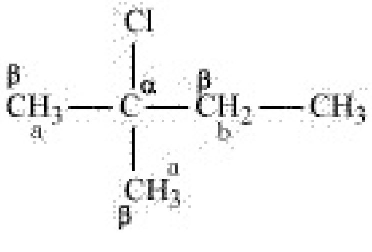
Ans. (i)



In the given compound, there are two types of -hydrogen atoms are present. Thus, dehydrohalogenation of this compound gives only one alkenes.

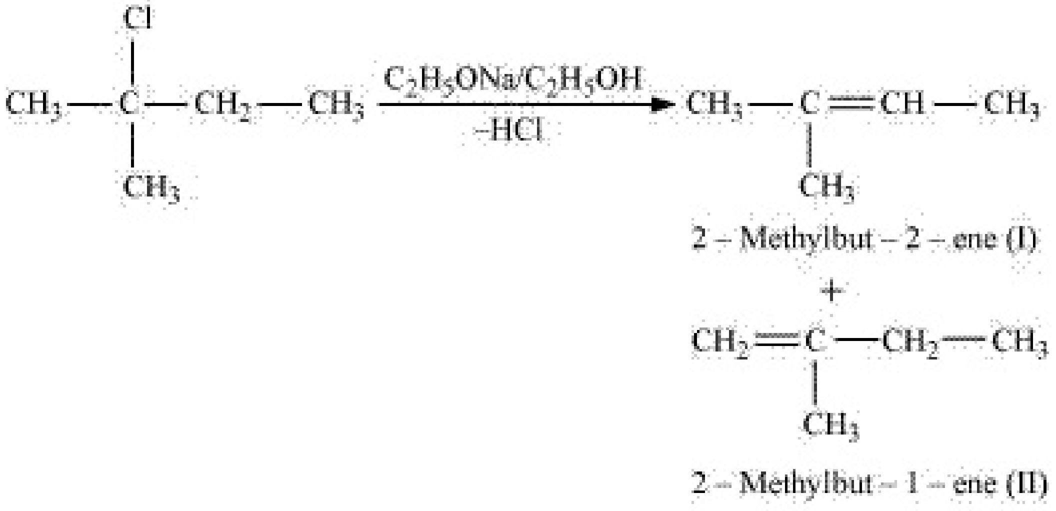


(ii)



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

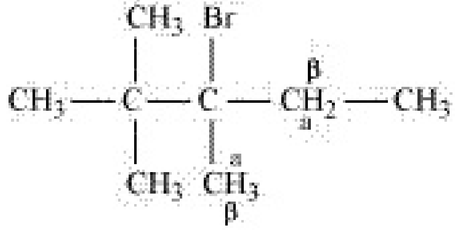
In the given compound, there are two different sets of equivalent -hydrogen atoms labelled as*a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced.

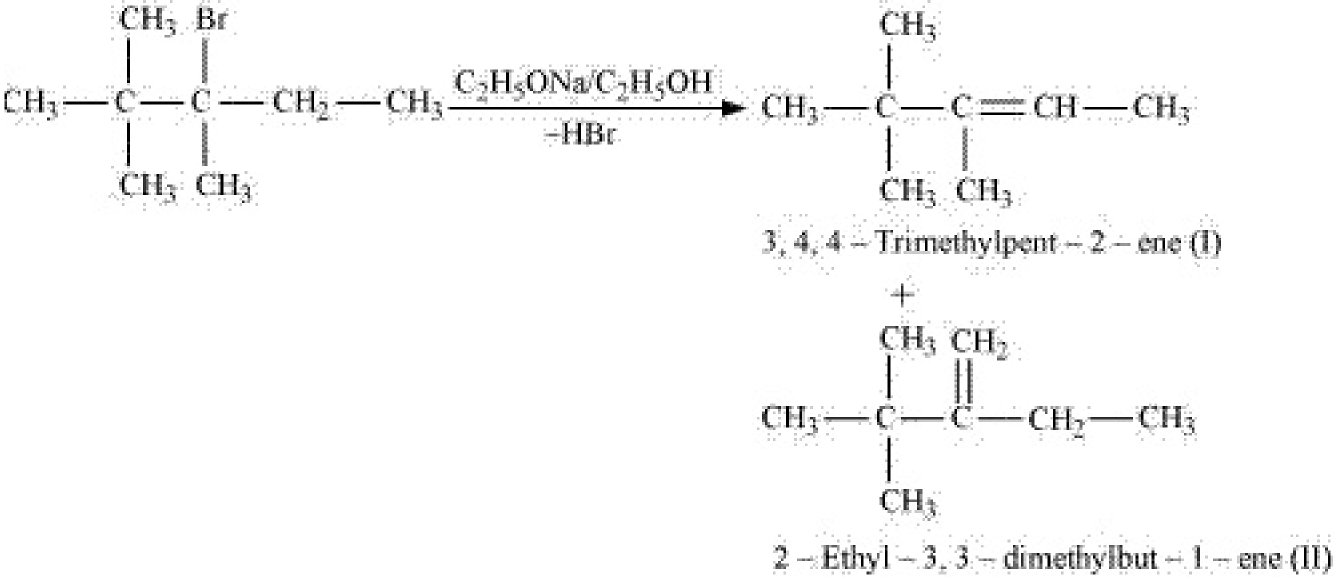
Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

(iii)



2,2,3-Trimethyl-3-bromopentane

In the given compound, there are two different sets of equivalent -hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed.

Hence, alkene (I) i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

15. How will you bring about the following conversions?

(i) Ethanol to but-1-yne

(ii) Ethane to bromoethene

(iii) Propene to 1-nitropropane

(iv) Toluene to benzyl alcohol

(v) Propene to propyne

(vi) Ethanol to ethyl fluoride

(vii) Bromomethane to propanone

(viii) But-1-ene to but-2-ene

(ix) 1-Chlorobutane to n-octane

(x) Benzene to biphenyl.

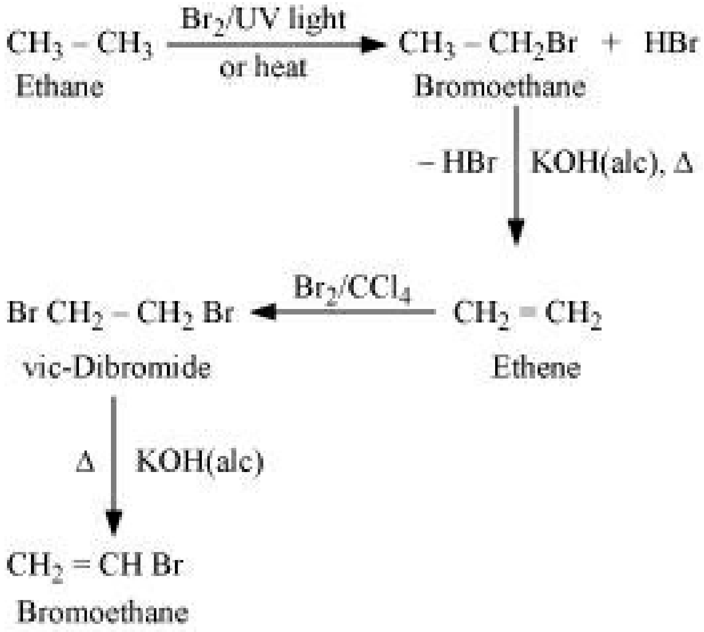
Ans. (i)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{SOCl_2\text{, Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2 + HCl$$

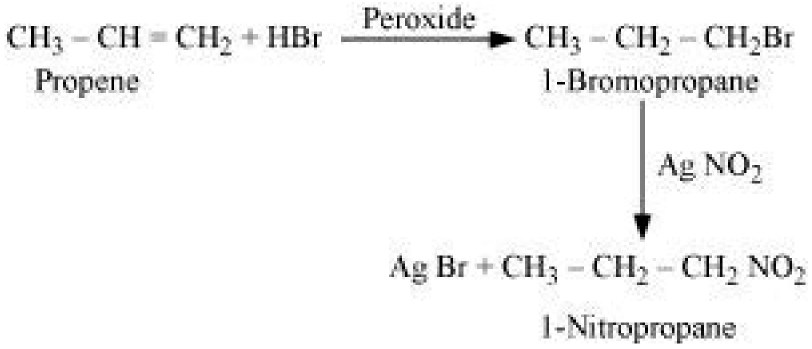
$$\underset{\text{Ethyne}}{HC \equiv CH + NaNH_2} \xrightarrow{\text{Liq } NH_3} \underset{\text{Sodium acetylide}}{HC \equiv \overset{-}{C}\overset{+}{N}a}$$

$$\underset{\text{Chloroethane}}{CH_3CH_2 - Cl + HC \equiv \overset{-}{C}\overset{+}{N}a} \longrightarrow \underset{\text{But}-1-\text{yne}}{CH_3CH_2C \equiv CH + NaCl}$$

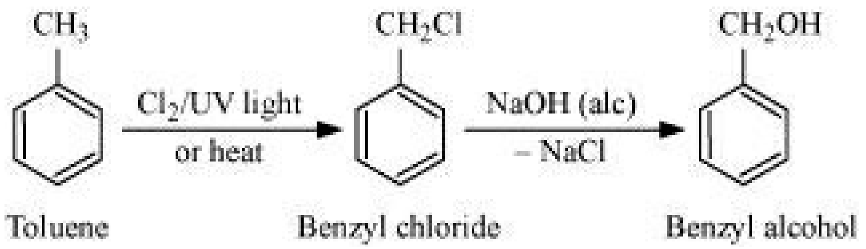
(ii)



(iii)

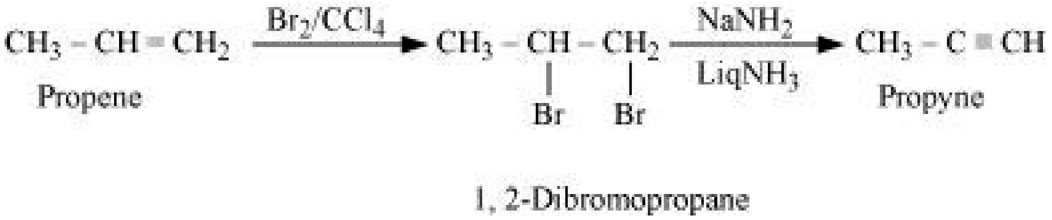


(iv)



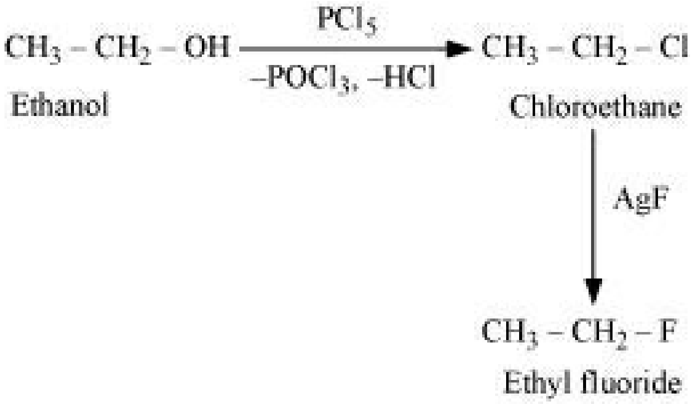
Toluene Benzyl chloride Benzyl alcohol

(v)



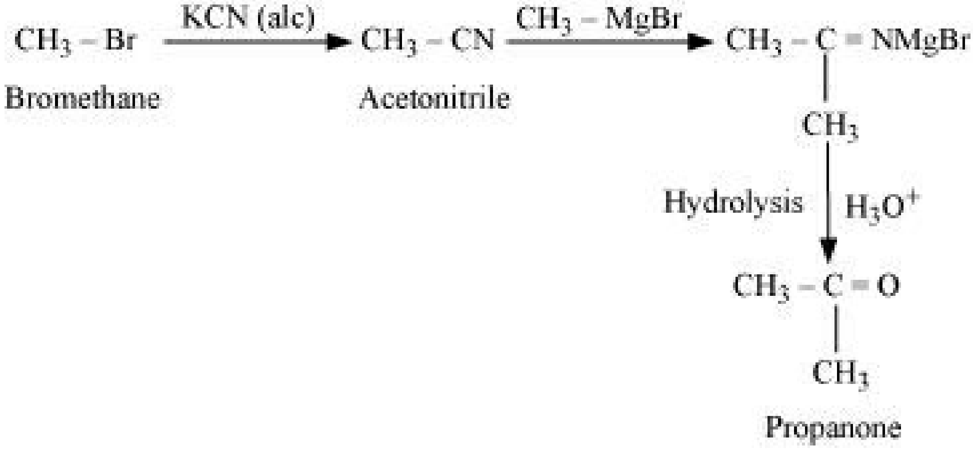
$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{1, 2-Dibromopropane}}{CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}} \xrightarrow[\text{Liq}NH_3]{NaNH_2} \underset{\text{Propyne}}{CH_3-C\equiv CH}$$

(vi)



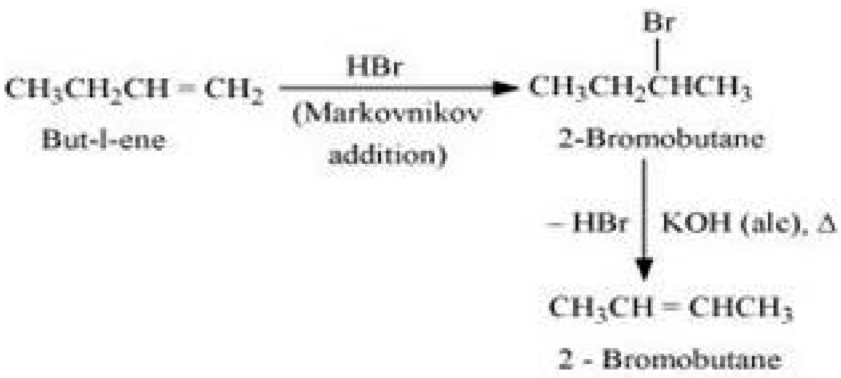
$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[-POCl_3,\ -HCl]{PCl_5} \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow{AgF} \underset{\text{Ethyl fluoride}}{CH_3-CH_2-F}$$

(vii)



$$\underset{\text{Bromethane}}{CH_3-Br} \xrightarrow{KCN\ (alc)} \underset{\text{Acetonitrile}}{CH_3-CN} \xrightarrow{CH_3-MgBr} CH_3-\underset{CH_3}{\underset{|}{C}}=NMgBr \xrightarrow[\text{Hydrolysis}]{H_3O^+} \underset{\text{Propanone}}{CH_3-\underset{CH_3}{\underset{|}{C}}=O}$$

(viii)

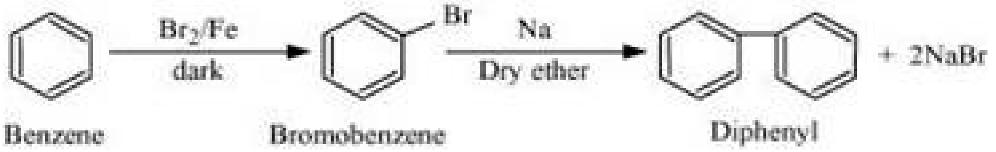


(ix)

$$2CH_3CH_2CH_2CH_2-Cl+2Na \xrightarrow[-2NaCl]{dry\ ether} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

1 − Chlordrutane n − Octane

(x)



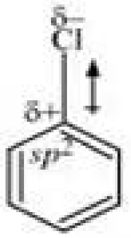
16. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

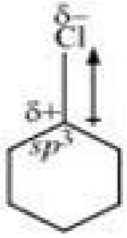
(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

Ans. (i)



Chlorobenzene



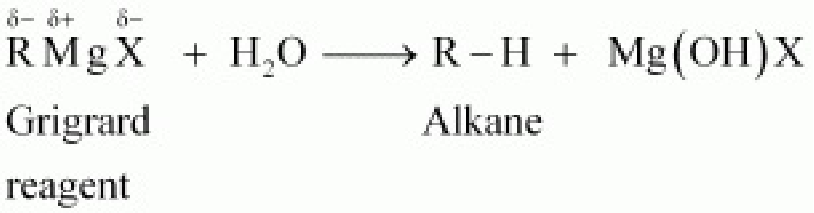
Cyclohexyl chloride

In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a sp^3 hybridized carbon atom. Now, sp^2 hybridized carbon has more s-character than sp^3 hybridized carbon atom. Therefore, the former is more electronegative than the latter. Therefore, the density of electrons of C - Cl bond near the Cl-atom is less in chlorobenzene than in cydohexyl chloride.

Moreover, the - R effect of the benzene ring of chlorobenzene decreases the electron density of the C - Cl bond near the Cl-atom. As a result, the polarity of the C - Cl bond in chlorobenzene decreases. Hence, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes.



$$\underset{\text{Grigrard reagent}}{\overset{\delta-}{R}\overset{\delta+}{Mg}\overset{\delta-}{X}} + H_2O \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

Therefore, Grignard reagents should be prepared under anhydrous conditions.

17. Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

Ans. Uses of Freon - 12

Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is commonly known as CFC. It is used as a refrigerant in refrigerators and air conditioners. It is also used in aerosol spray propellants such as body sprays, hair sprays, etc. However, it damages the ozone layer. Hence, its manufacture was banned in the United States and many other countries in 1994.

Uses of DDT

DDT (*p, p*-dichlorodiphenyltrichloroethane) is one of the best known insecticides. It is very effective against mosquitoes and lice. But due its harmful effects, it was banned in the United States in 1973.

Uses of carbontetrachloride $(\mathrm{CCl_4})$

(i) It is used for manufacturing refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

(iii) It is used as a solvent in the manufacture of pharmaceutical products.

(iv) Until the mid 1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

Uses of iodoform $(\mathrm{CHI_3})$

Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

18. Write the structure of the major organic product in each of the following reactions:

(i) $\mathrm{CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}}$

(ii) $\mathrm{(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}}$

(iii) $\mathrm{CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}}$

(iv) $\mathrm{CH_3CH_2Br + KCN \xrightarrow{\text{aq.ethanol}}}$

(v) $\mathrm{C_6H_5ONa + C_2H_5Cl \longrightarrow}$

(vi) $\mathrm{CH_3CH_2CH_2OH + SOCl_2 \longrightarrow}$

(vii) $\mathrm{CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}}$

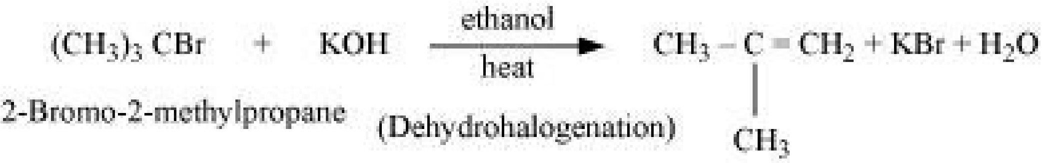
(viii) $CH_3CH=C(CH_3)_2+HBr\longrightarrow$

Ans.

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}} CH_3CH_2CH_2I + NaCl$

1 – Chloropropane (Finkelstein reaction) 1 – Iodopropane

(ii)



$$(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + KBr + H_2O$$

2-Bromo-2-methylpropane (Dehydrohalogenation)

2-Methylpropene

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}} CH_3CH(OH)CH_2CH_3 + NaBr$

2 – Bromobutane Butan – 2 – ol

(iv) $CH_3CH_2Br + KCN \xrightarrow[\left(\substack{\text{Nucleophilic}\\ \text{substitution}}\right)]{\text{aq. ethanol}} CH_3CH_2CN + KBr$

Bromobutane Cyanoethane

(v) $C_6H_5ONa + C_2H_5Cl \xrightarrow[\left(\substack{\text{Williamson}\\ \text{synthesis}}\right)]{} C_6H_5-O-C_2H_5 + NaCl$

Sodium phenoxide Chloroethane Phenetole

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

1 – Propanol 1 – Chloropropane

(vii) $CH_3CH_2CH=CH_2 + HBr \xrightarrow[\left(\substack{\text{Anti-Markovnikov's}\\ \text{addition}}\right)]{\text{Peroxide}} CH_3CH_2CH_2CH_2-Br$

But – 1 – ene 1 – Bromobutane

(viii)

$$CH_3CH=C(CH_3)_2 + HBr \xrightarrow[\text{addition)}]{\text{(Markovnikov}} CH_3-CH_2-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

19. Arrange the compounds of each set in order of reactivity towards S_N^2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2- methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

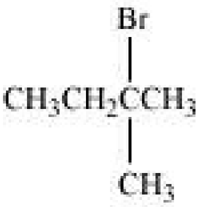
Ans. (i)

$CH_3CH_2CH_2CH_2CH_2-Br$

1-Bromopentane (1°)

$$CH_3CH_2CH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

2-Bromopentane (2°)



$$CH_3CH_2\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$

2-Bromo-2-methylbutane (3°)

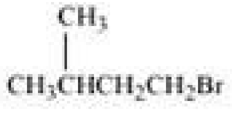
An S_N^2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards S_N^2 displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

1-Bromopentane < 2-bromopentane < 2-Bromo-2-methylbutane

Hence, the increasing order of reactivity towards S_N^2 displacement is:

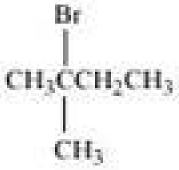
2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)



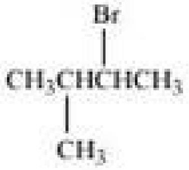
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2Br$

1-Bromo-3-methylbutane
(1°)



$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}CH_2CH_3$

2-Bromo-2-methylbutane
(3°)



$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{Br}{|}}{C}HCH_3$

2-Bromo-3-methylbutane
(2°)

Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards S_N^2 displacement is

$3^\circ < 2^\circ < 1^\circ$.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards S_N^2 displacement as:

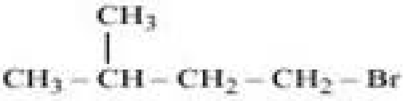
2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

[2-Bromo-3-methylbutane is incorrectly given in NCERT]

(iii)

$CH_3-CH_2-CH_2-CH_2-Br$

1-Bromobutane

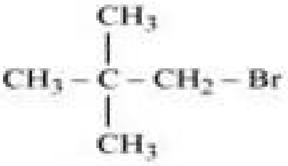


$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-Br$

1-Bromo-3-methylbutane

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

1-Bromo-2-methylbutane



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

1-Bromo-2, 2-dimethylpropane

The steric hindrance to the nucleophile in the S_N^2 mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents. Therefore, the increasing order of steric hindrances in the given compounds is as below:

1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane

< 1-Bromo-2, 2-dimethylpropane

Hence, the increasing order of reactivity of the given compounds towards S_N2 displacement is:

1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3- methylbutane < 1-Bromobutane

20. How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-Bromopropane to 2-bromopropane

(iv) Toluene to benzyl alcohol

(v) Benzene to 4-bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid

(vii) Ethanol to propanenitrile

(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(xi) Ethyl chloride to propanoic acid

(xii) But-1-ene to n-butyliodide

(xiii) 2-Chloropropane to 1-propanol

(xiv) Isopropyl alcohol to iodoform

(xv) Chlorobenzene to *p*-nitrophenol

(xvi) 2-Bromopropane to 1-bromopropane

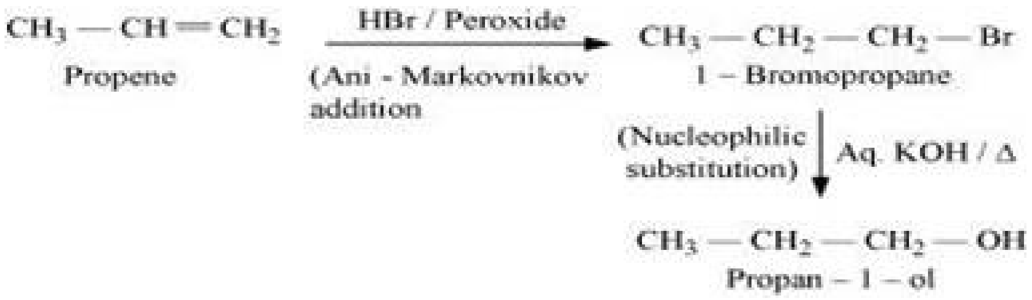
(xvii) Chloroethane to butane

(xviii) Benzene to diphenyl

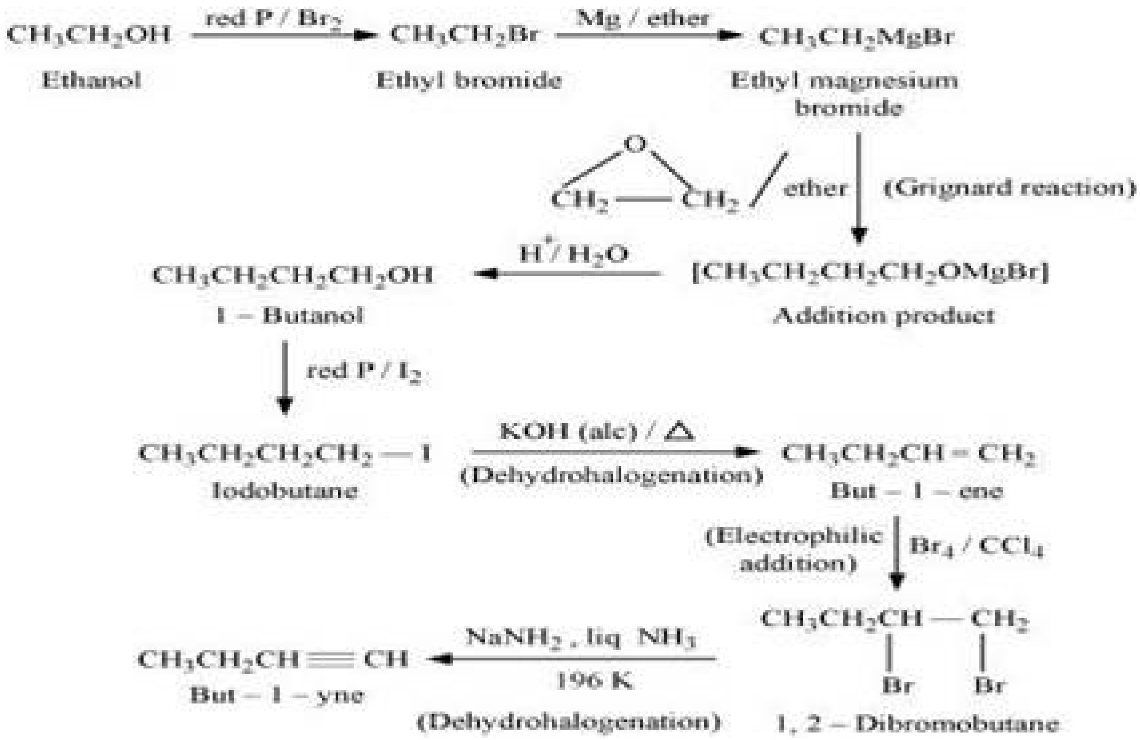
(xix) *tert*-Butyl bromide to isobutyl bromide

(xx) Aniline to phenylisocyanide

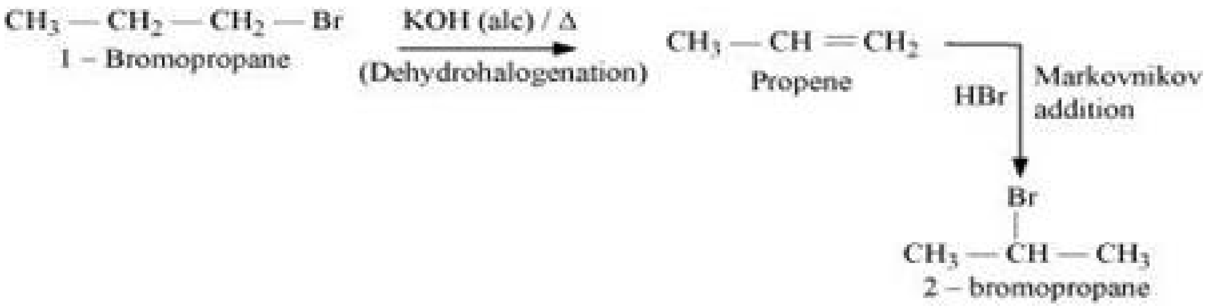
Ans. (i)



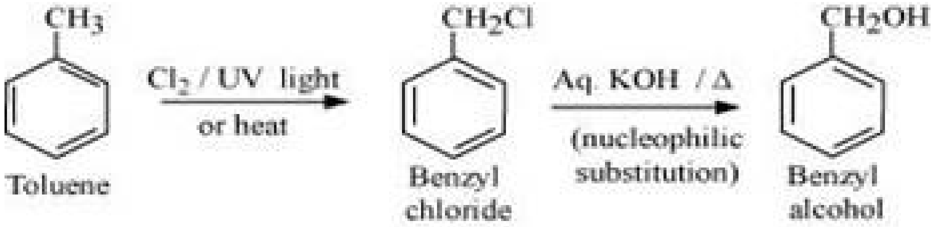
(ii)



(iii)


$CH_3 — CH_2 — CH_2 — Br$
1 – Bromopropane
KOH (alc) / Δ
(Dehydrohalogenation)
$CH_3 — CH = CH_2$
Propene
HBr
Markovnikov addition
Br
$CH_3 — CH — CH_3$
2 – bromopropane

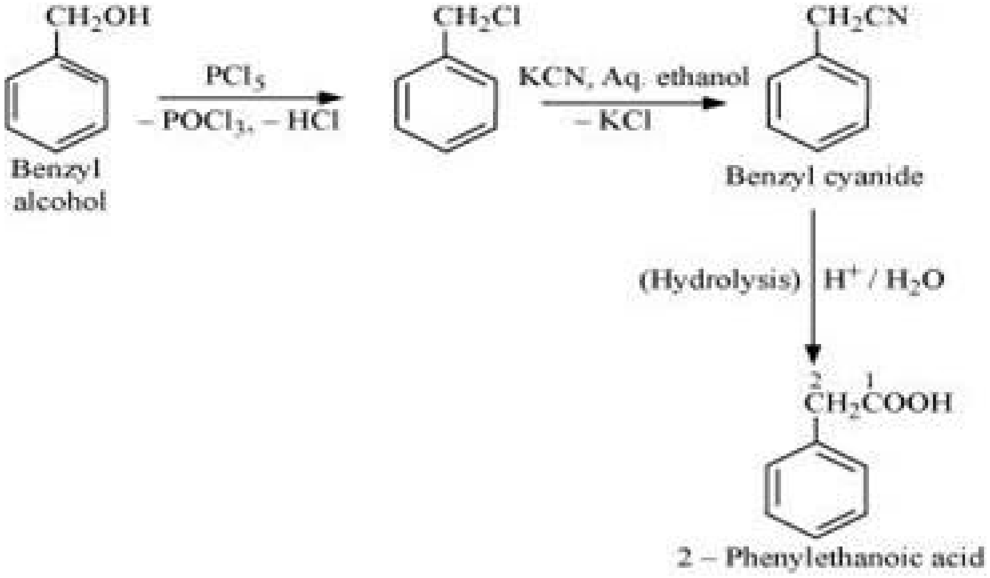
(iv)


CH_3
Toluene
Cl_2 / UV light
or heat
CH_2Cl
Benzyl chloride
Aq. KOH / Δ
(nucleophilic substitution)
CH_2OH
Benzyl alcohol

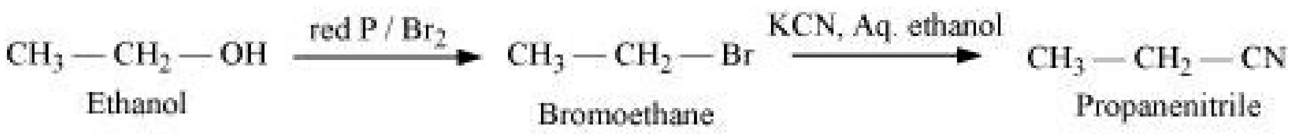
(v)


Benzene
Br_2 / $FeBr_3$
Dark
Br
Bromobenzene
HNO_3 / H_2SO_4
(Nitration)
Br
NO_2
4 – Bromonitrobenzene

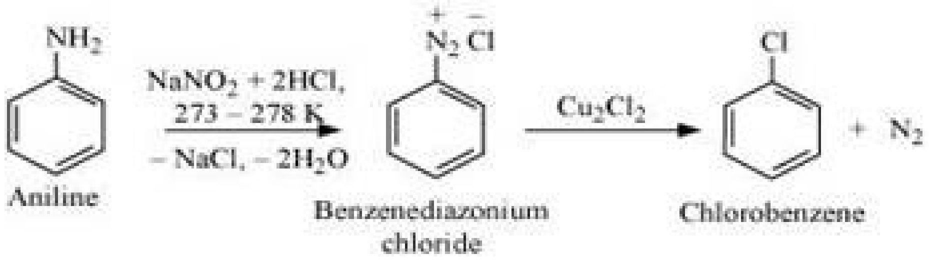
(vi)


CH_2OH
Benzyl alcohol
PCl_5
– $POCl_3$, – HCl
CH_2Cl
KCN, Aq. ethanol
– KCl
CH_2CN
Benzyl cyanide
(Hydrolysis)
H^+ / H_2O
$\overset{2}{C}H_2\overset{1}{C}OOH$
2 – Phenylethanoic acid

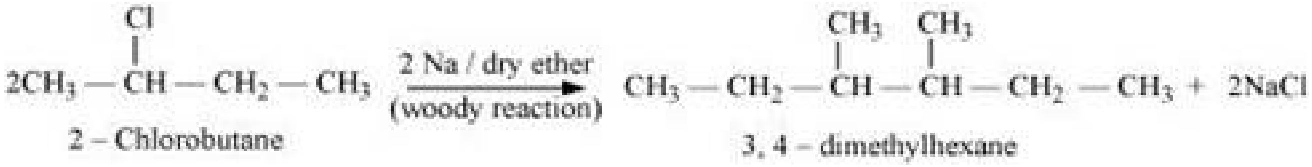
(vii)



(viii)

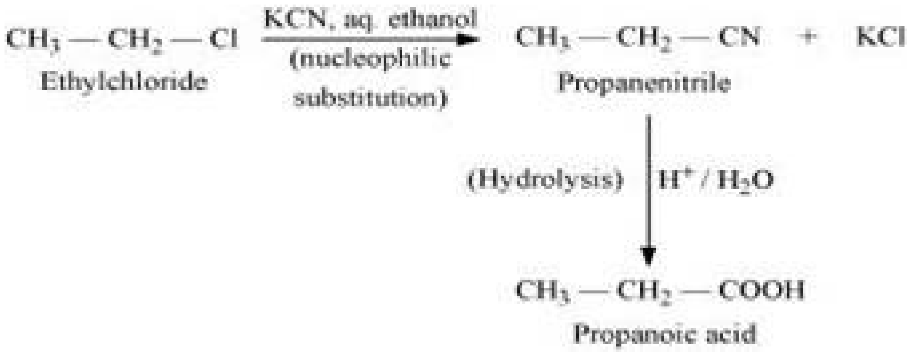


(ix)

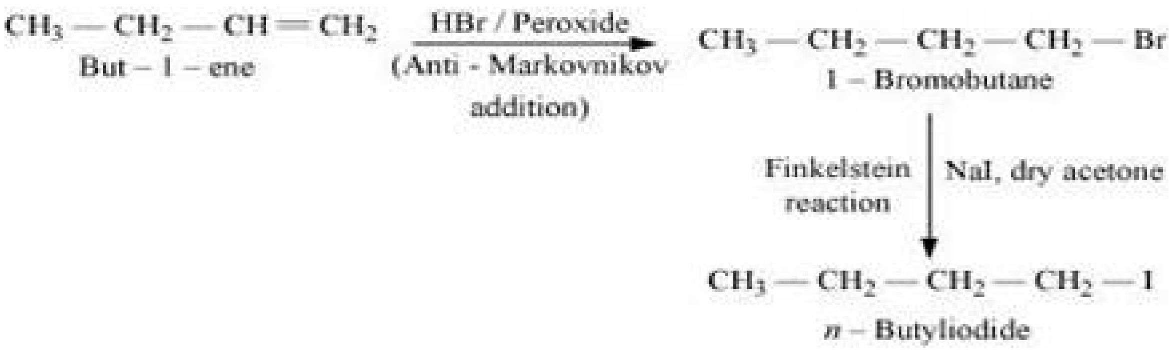


(x)

(xi)

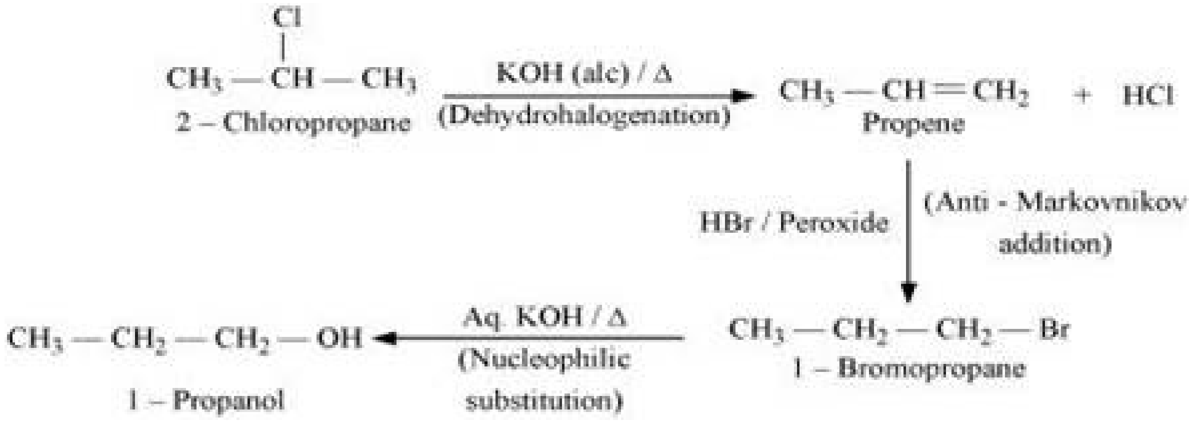


(xii)



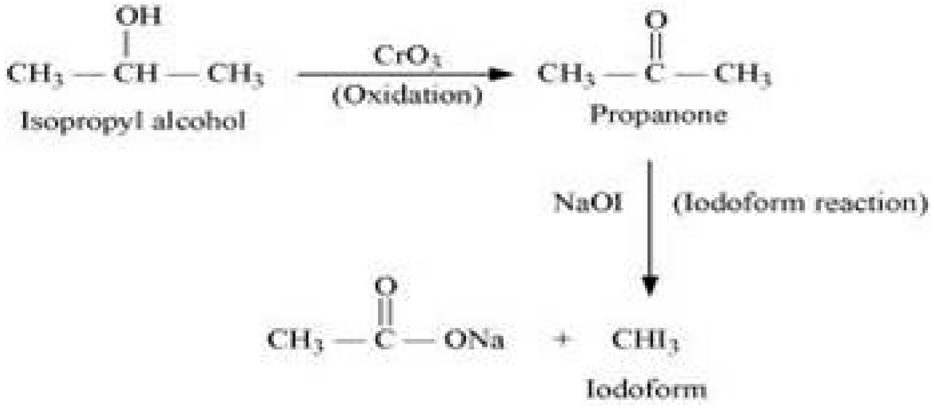
CH₃ — CH₂ — CH = CH₂
But – 1 – ene
HBr / Peroxide
(Anti - Markovnikov addition)
CH₃ — CH₂ — CH₂ — CH₂ — Br
1 – Bromobutane
Finkelstein reaction
NaI, dry acetone
CH₃ — CH₂ — CH₂ — CH₂ — I
n – Butyliodide

(xiii)



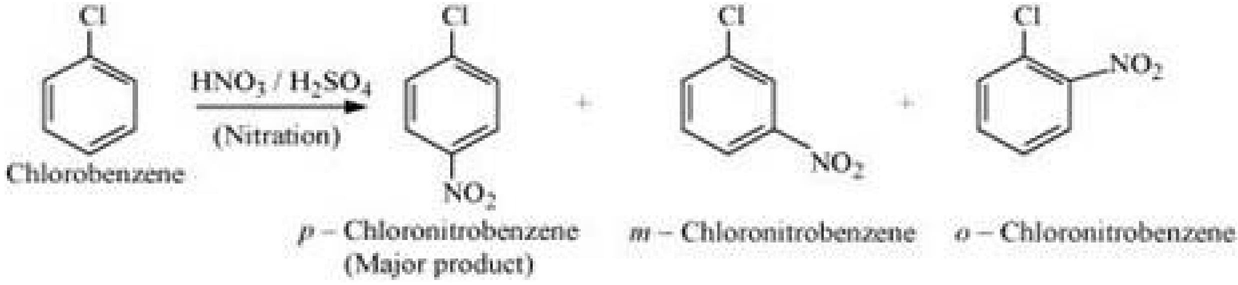
Cl
CH₃ — CH — CH₃
2 – Chloropropane
KOH (alc) / Δ
(Dehydrohalogenation)
CH₃ — CH = CH₂
Propene
+
HCl
HBr / Peroxide
(Anti - Markovnikov addition)
CH₃ — CH₂ — CH₂ — Br
1 – Bromopropane
Aq. KOH / Δ
(Nucleophilic substitution)
CH₃ — CH₂ — CH₂ — OH
1 – Propanol

(xiv)

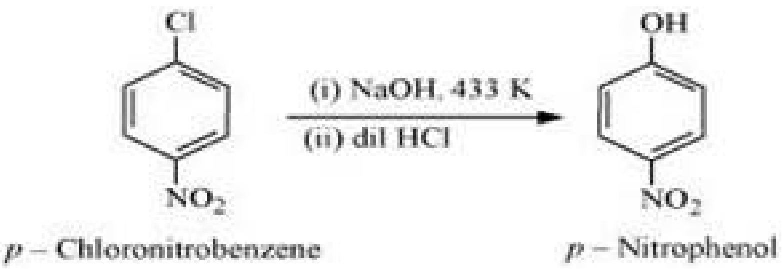


OH
CH₃ — CH — CH₃
Isopropyl alcohol
CrO₃
(Oxidation)
O
CH₃ — C — CH₃
Propanone
NaOI
(Iodoform reaction)
O
CH₃ — C — ONa
+
CHI₃
Iodoform

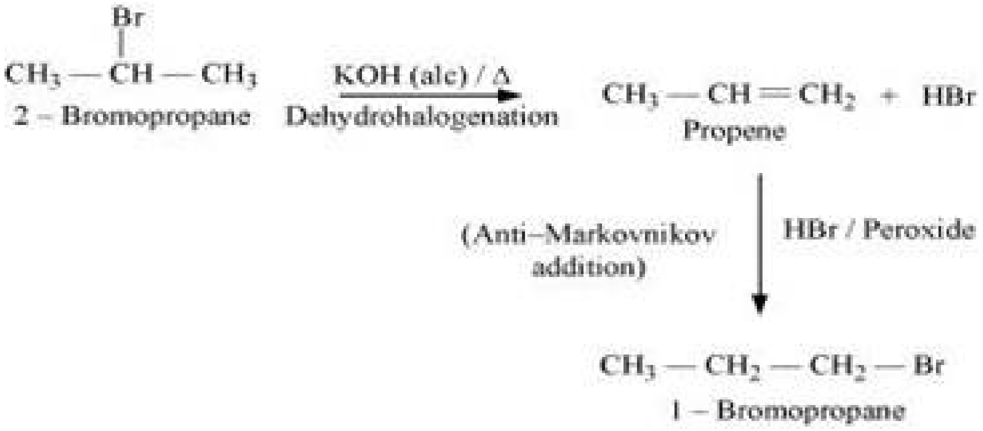
(xv)



Cl
Chlorobenzene
HNO₃ / H₂SO₄
(Nitration)
Cl
NO₂
p – Chloronitrobenzene
(Major product)
+
Cl
NO₂
m – Chloronitrobenzene
+
Cl
NO₂
o – Chloronitrobenzene



(xvi)



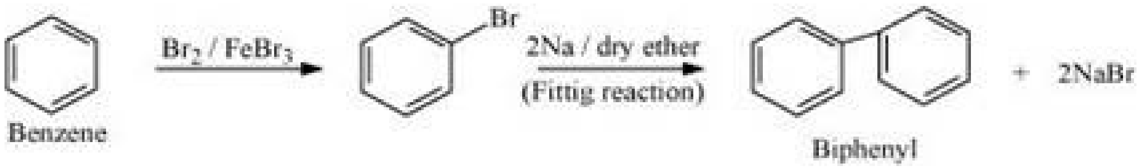
$$\underset{\text{2 – Bromopropane}}{CH_3-\overset{\overset{Br}{|}}{C}H-CH_3} \xrightarrow[\text{Dehydrohalogenation}]{KOH\ (alc)\ /\ \Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} + HBr$$

$$\xrightarrow[\text{(Anti–Markovnikov addition)}]{HBr\ /\ Peroxide} \underset{\text{1 – Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

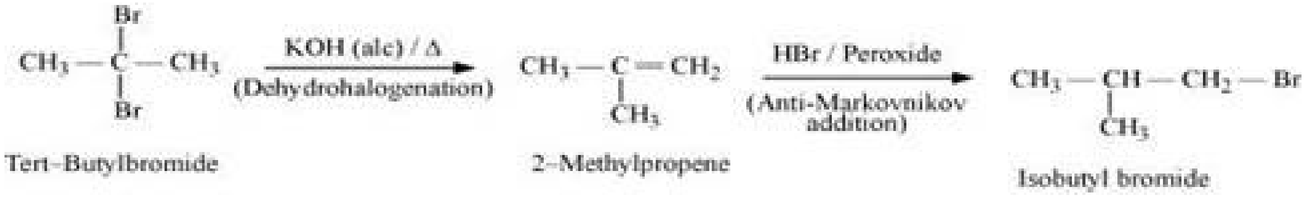
(xvii)

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Wurtz reaction)}]{2\ Na\ /\ dry\ ether} \underset{\text{Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

(xviii)

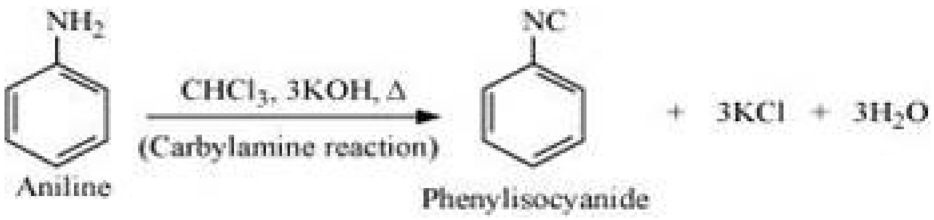


(xix)



$$\underset{\text{Tert–Butylbromide}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3} \xrightarrow[\text{(Dehydrohalogenation)}]{KOH\ (alc)\ /\ \Delta} \underset{\text{2–Methylpropene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow[\text{(Anti-Markovnikov addition)}]{HBr\ /\ Peroxide} \underset{\text{Isobutyl bromide}}{CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-Br}$$

(xx)



21. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Ans. In an aqueous solution, KOH almost completely ionizes to give OH^- ions. OH^- ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

$$\underset{\text{Alkyl chloride}}{R-Cl} + KOH_{(aq)} \longrightarrow \underset{\text{Alcohol}}{R-OH} + KCl$$

On the other hand, an alcoholic solution of KOH contains alkoxide $\left(RO^-\right)$ ion, which is a strong base. Thus, it can abstract a hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

$$\underset{\text{Alkyl chloride}}{R-\underset{\beta}{C}H_2-\underset{\alpha}{C}H_2-Cl} + KOH(alc) \longrightarrow \underset{\text{Alkene}}{R-CH=CH_2} + KCl + H_2O$$

OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon.

Concept Insight: OH^- is a strong nucleophile but weaker base than RO^-

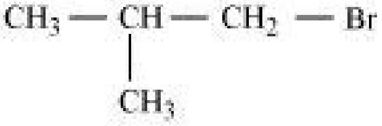
22. Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the

compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Ans. There are two primary alkyl halides having the formula, C_4H_9Br . They are *n* - bulyl bromide and isobutyl bromide.

$CH_3 - CH_2 - CH_2 - CH_2 - Br$

n – Butyl bromide



$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - Br$$

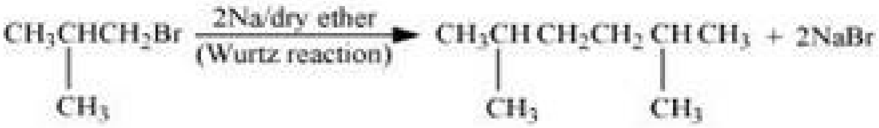
Isobutyl bromide

Therefore, compound (a) is either *n*-butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18} , which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

n – Butyl bromide *n* – Octane



$$\underset{\underset{CH_3}{|}}{CH_3CH}CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2\underset{\underset{CH_3}{|}}{CH}CH_3 + 2NaBr$$

Isobutyl bromide
(a)

2, 5 – Dimethylhexane
(d)

Thus, compound (d) is 2, 5-dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2-methylpropene.

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - Br \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)/}\Delta} CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + HBr$$

Isobutyl chloride
(a)

2 – Methylpropene
(b)

Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2-bromo-2-methylpropane.

$$CH_3-\underset{\underset{CH_3}{|}}{C}H=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{HBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}H}-CH_3$$

2 – Methylpropene
(b)

2 – Bromo – 2 – methylpropane
(c)
(an isomer of (a))

23. What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

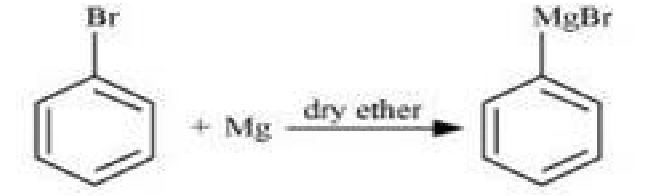
(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN.

Ans. (i) When n - butyl chloride is treated with alcoholic KOH, the formation of but - l - ene takes place. This reaction is a dehydrohalogenation reaction.

$$\underset{n-\text{Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{KOH(alc)/\Delta} \underset{\text{But-l-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

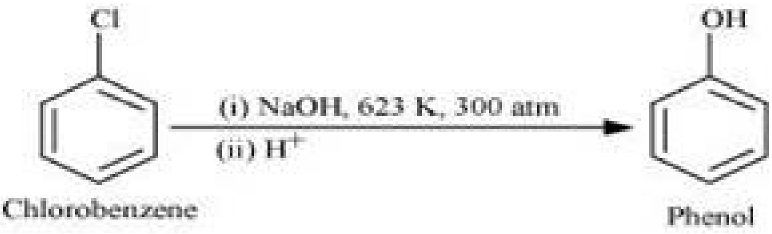
(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



Bromobenzene

Phenylmagensium bromide

(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + KCl$$

(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

$$\underset{\text{Methyl bromide}}{2\,CH_3-Br} + 2\,Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

(vi) When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide.

$$\underset{\text{Methyl chloride}}{CH_3-Cl} + KCN \xrightarrow[\text{Nucleophilic substitution}]{} \underset{\text{Methyl cyanide}}{CH_3-CN} + KCl$$