10 Haloalkanes and Haloarenes

Facts that Matter

- **Alkyl halides or haloalkanes:** Organic compounds in which one or more hydrogen atom of an alkane have been substituted by a halogen atom. For example, chloromethane, CH_3Cl, dibromoethane, CH_2BrCH_2Br, etc. Haloalkanes can be formed by direct reaction between alkanes and halogens using ultraviolet radiation. They are usually prepared by the reaction of an alcohol with a halogen carrier.
- **Reactions of haloalkanes involve:**
  (*i*) Nucleophilic substitution
  (*ii*) Elimination reaction
  (*iii*) Reaction with metals

  Nucleophilic substitution reactions are categorised as S_N1 and S_N2 on the basis of kinetic properties.

  A S_N2 reaction proceeds with stereochemical inversion while a S_N1 reaction proceeds with racemisation.

  Optically active molecule: It is a molecule that cannot be superimposed on its mirror image. It is also called chiral molecule.

  Asymmetric carbon: It is the carbon atom that is bonded to four different groups. It is also called chiral carbon.

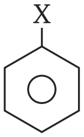
  Enantiomers: These are optical isomers that are mirror images of each other.

  Diastereoisomers: These are optical isomers that are not mirror images of each other.
- **Formation of Haloalkanes:**

$$RH + X_2 \longrightarrow R — X + HX$$

  (*i*) Halogen derivatives of alkanes are called haloalkanes. For e.g., $X — CH_3$
  (*ii*) Halogen derivatives of arenes are called haloarenes:

  E.g. $X — C_6H_5$

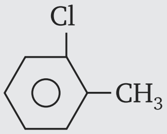
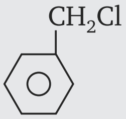


- (*a*) **Vicinal dihalides:** Halogen derivatives where the two halogen atoms are attached on the adjacent carbon atom.

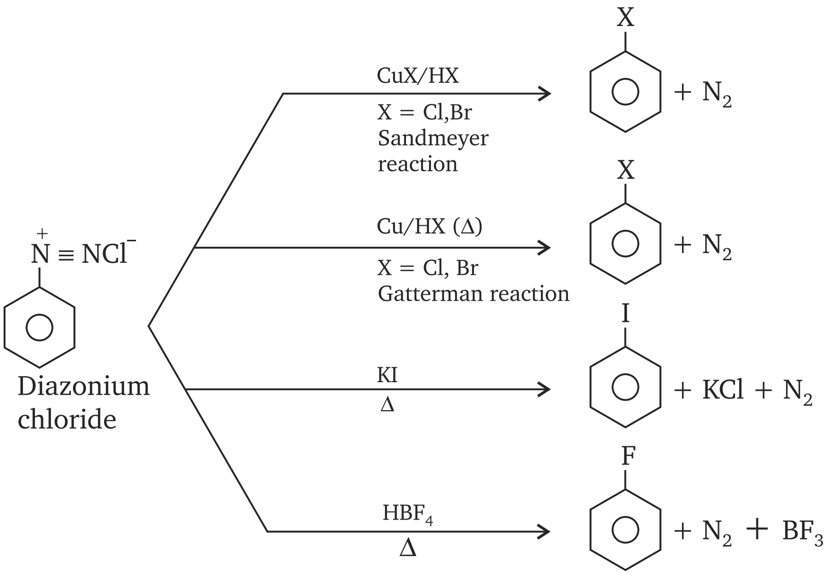
  E.g. $\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$

(*b*) **Geminal dihalide:** Where the two halogen atoms are attached to the same carbon atom. For e.g., CH_3CHBr_2

Nomenclature

Structure	Common Name	IUPAC Name
$CH_3CH_2CH(Cl)CH_3$	*Sec*-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	*Neo*-Pentyl bromide	1-Bromo–2, 2-dimethyl propane
$(CH_3)_3CBr$	*Tert*-Butyl bromide	2-Bromo –2 –methyl propane
CH_2–CHCl	Vinyl chloride	Chloroethane
CH_2–$CHCH_2Br$	Allyl bromide	3-Bromo propene
	*o*–Chlorotoluene	1-chloro-2-methylbenzene
	Benzyl chloride	α-Chlorotoluene/ Chloromethyl benzene

Preparation of Haloalkanes and Haloarenes



$$ROH \xrightarrow[ZnCl_2]{+HX} R-X + H_2$$

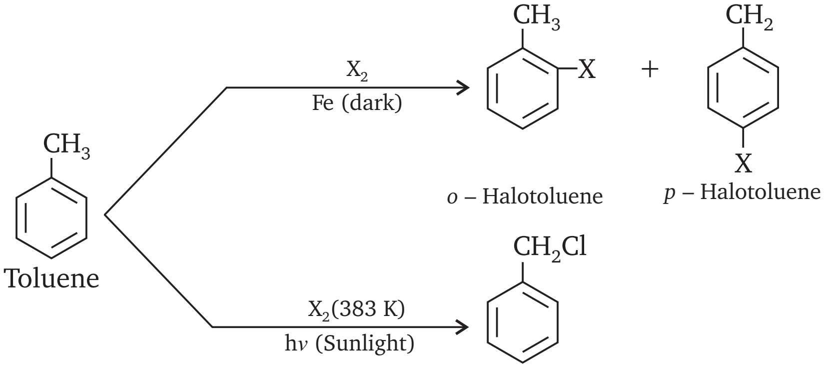
$$ROH \xrightarrow{+NaBr + H_2SO_4} R-Br + NaHSO_4 + H_2O$$

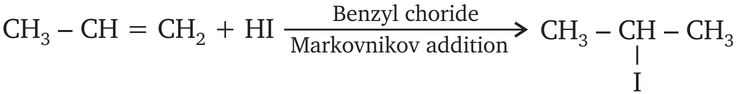
$$ROH \xrightarrow[(X = Cl, Br)]{+RX_3} 3R-X + H_3PO_3$$

$$ROH \xrightarrow{+PCl_5} R-Cl + POCl_3 + HCl$$

$$ROH \xrightarrow[X_2 = Br_2, I_2)]{Red\ P/X_2} R-X$$

$$ROH \xrightarrow{+SOCl_2} R-Cl + SO_2 + HCl$$





$$CH_3-CH=CH_2 + HI \xrightarrow[\text{Markovnikov addition}]{\text{Benzyl choride}} CH_3-\underset{\displaystyle I}{\underset{|}{CH}}-CH_3$$

2 – Iodopropane

Note: $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow[\text{(anti Markovnikov)}]{\text{Benzoyl peroxide}} \underset{\text{1 – Bromopropane}}{CH_3CH_2-CH_2Br}$

Important Name Reactions used for the prepration of Halogens:

$$R{-}X \xrightarrow[\text{Finkelstein Reaction}]{\text{NaI/Dry acetone}} R-I + NaX$$

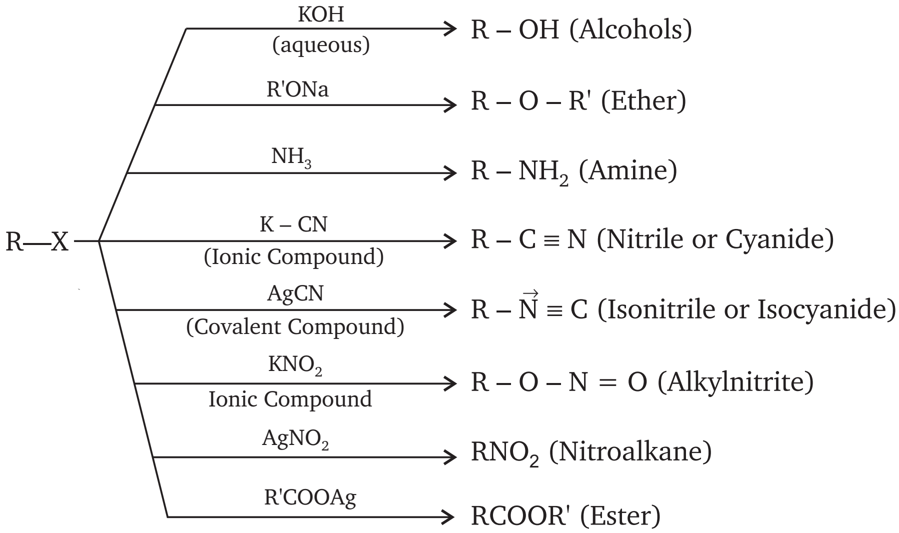
$$R{-}X \xrightarrow[\text{Swarts Reaction}]{AgF \text{ or } CoF_2} R-F + AgX$$

- **Racemic Mixture:** A mixture of equal amount of two enantiomers is called racemic mixture (*d* and *l*).
- **Racemisation:** The process of conversion of one enantiomer (+ or –) into a racemic mixture is called racemisation.

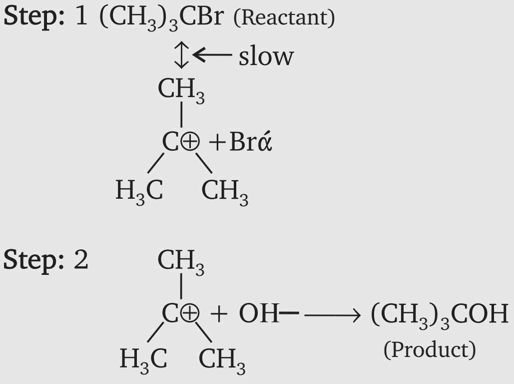
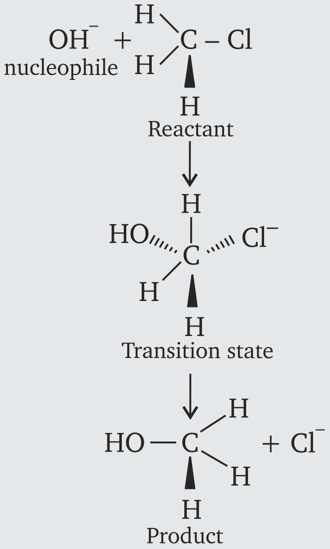
- **Retention of Configuration:** Preservation of the spatial arrangements of bond at an asymmetric centre during a chemical reaction.

Chemical Properties

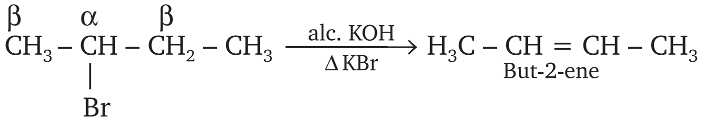
Nucleophilic Substitution in Haloalkanes (Important Reactions)



Mechanism of Nucleophilic Substitution Reactions:

S_N1	S_N2
1. Nucleophilic substitution is unimolecular.	1. Nucleophilic substitution is bimolecular.
2. It takes place in two steps.	2. It takes place in one step.
3. They are first order reactions.	3. They are mostly second order reactions.
4. It leads to racemisation	4. It leads to inversion of configuration.
	

Elimination Reaction:



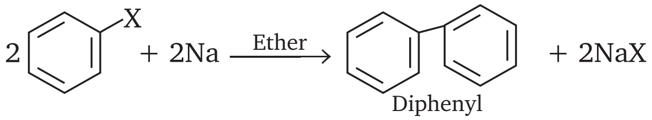
$$\overset{\beta}{CH_3}-\underset{\underset{Br}{|}}{\overset{\alpha}{CH}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[\Delta\ KBr]{alc.\ KOH} \underset{\text{But-2-ene}}{H_3C-CH=CH-CH_3}$$

- **Saytzeff's Rule:** When an alkyl halide is treated with alcoholic KOH it undergoes dehydrohalogenation reaction to give a product having more alkylated double bond.

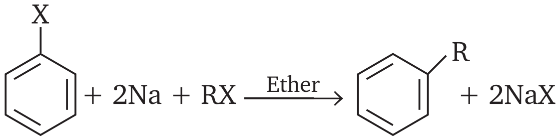
Wurtz Reaction:

$$R-X + 2Na + R-X \xrightarrow{\text{Ether}} R-R + 2NaX$$

Fittig Reaction:



Wurtz-Fittig Reaction:



Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds.

- **Dichloromethane**

  Applications:

  (*i*) Widely used as a solvent as a paint remover and as a processing solvent in the manufacture of drugs.

  (*ii*) It is also used in metal cleaning and as a finishing solvent.

  Harmful effects of dichloromethane

  (*i*) Methylene chloride can severely harm the human central nervous system.

  (*ii*) Exposure to lower level of methylene chloride in air can lead to slightly impaired hearing and vision.

  (*iii*) Higher level of methylene chloride in air causes dizziness, nausea, tingling and numbness in fingers and toes.

  (*iv*) In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin, direct contact with eyes can also burn the cornea.

- **Trichloromethane (Chloroform)**

  Applications:

  (*i*) Chloroform is employed as a solvent for fats, alkaloids and other substances.

  (*ii*) In the production of refrigerant, freon R-22.

  Harmful effects of chloroform

  (*i*) Breathing of even about 900 parts of chloroform per million parts of air for a short period of time can cause dizziness, fatigue and headache.

  (*ii*) Chronic chloroform exposure may cause damage to the liver and kidneys.

  (*iii*) Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas named carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air can be kept out.

- **Tri-iodomethane (Iodoform)**

  A yellow volatile solid sweet smelling haloform, made by the haloform reaction.

  Application:

  It was earlier used as an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

- **Tetrachloromethane (Carbon tetrachloride), CCl_4:**

  A colourless volatile liquid with a characteristic colour, virtually soluble in water but it is miscible with many organic liquids, such as ethanol and benzene.

  Applications:

  (*i*) Used in the manufacture of refrigerants and propellants, for example aerosol.

  (*ii*) In the synthesis of chlorofluorocarbons and other chemicals.

  (*iii*) It is widely used as a cleaning fluid.

  (*iv*) It is also used as a fire extinguisher.

  Harmful effects of CCl_4

  (*i*) Most common effects are dizziness, slight headache, nausea and vomiting, which can even cause permanent damage to the nerve cells.

  (*ii*) Exposure to CCl_4 can make the heart beat irregular or even stops it.

  (*iii*) When CCl_4 is released into the air, it rises upto the atmosphere and depletes the ozone layer. Depletion of ozone layer is believed to increase the human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorder.

- **Freons (CCl_2F_2)**

  The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.

  Properties:

  (*i*) They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.

  (*ii*) Freon–12 (CCl_2F_2) is one of the most common freons in industrial use.

  (*iii*) It is prepared by the action of antimony fluoride on carbon tetrachloride in the presence of antimony pentachloride.

  (*iv*) In stratosphere, freon is able to initiate the radical chain reactions that can upset the natural ozone balance.

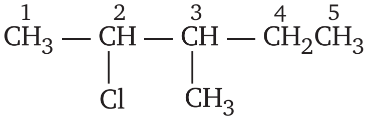
- ***p*, *p*' – Dichloro Diphenyl Trichloroethane (DDT):**
  - (*i*) It is the first chlorinated organic insecticide.
  - (*ii*) DDT is not metabolised very rapidly by animals, instead it is deposited and stored in the fatty tissues.
  - (*iii*) It is manufactured by heating a mixture of chloral and chlorobenzene in the presence of concentrated sulphuric acid.

NCERT IN-TEXT QUESTIONS SOLVED

10.1. 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.

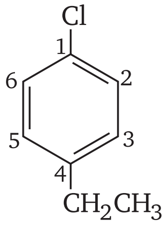
Ans. (*i*)



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

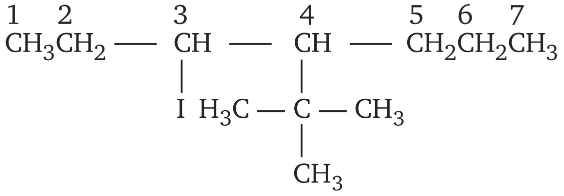
2 – Chloro–3–methylpentane

(*ii*)



1– Chloro–4–ethylbenzene

(*iii*)



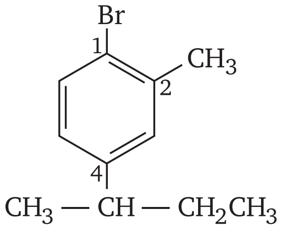
4-tert-Butyl-3-iodoheptane

(*iv*)

$$\overset{1}{BrCH_2}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2Br}$$

1, 4–Dibromobut–2–ene.

(*v*)



1 – Bromo–4–sec. butyl–2–methylbenzene

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

Ans. H_2SO_4 is an oxidising agent. It oxidises KI to HI and then to I_2. Thus, prevents the reaction between an alcohol and HI to form an alkyl iodide. To overcome this difficulty, a non-oxidising acid such as H_3PO_4 is used instead of H_2SO_4. For example,

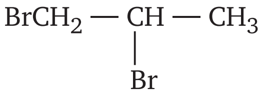
$$CH_3CH_2OH + KI + H_3PO_4 \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2-I} + KH_2PO_4 + H_2O$$

10.3. Write structures of different dihalogen derivatives of propane.

Ans.

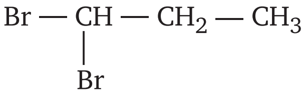
$$BrCH_2-CH_2-CH_2Br$$

1, 3–Dibromopropane



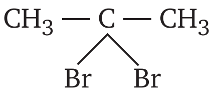
$$BrCH_2 - \underset{\underset{Br}{|}}{CH} - CH_3$$

1, 2– Dibromopropane



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

1, 1– Dibromopropane



2, 2– Dibromopropane

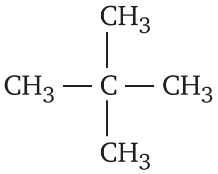
10.4. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(*i*) A single monochloride

(*ii*) Three isomeric monochlorides

(*iii*) Four isomeric monochlorides

Ans. (*i*)

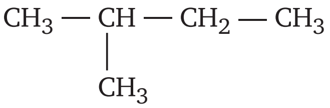


$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

All the hydrogen atoms are equivalent. Therefore, replacement of any one of them will give the same product.

(*ii*) $CH_3-CH_2-CH_2-CH_2-CH_3$

(*iii*)

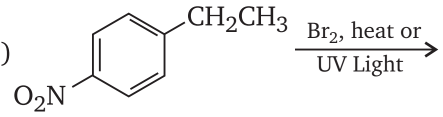


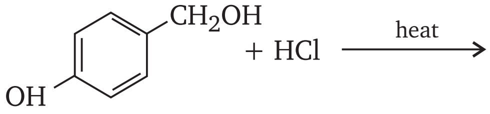
$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$$

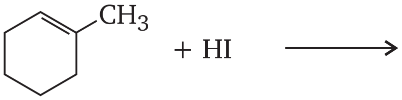
10.5. Draw the structures of major monohalo products in each of the following reactions:

(*i*)

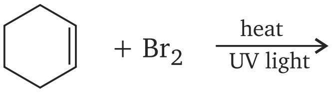
(*ii*)

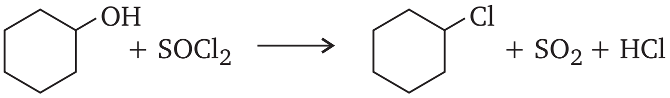


(*iii*) 

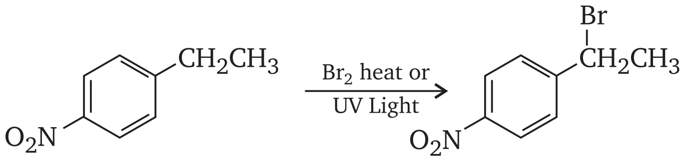
(*iv*) 

(*v*) $CH_3CH_2Br + NaI \longrightarrow$

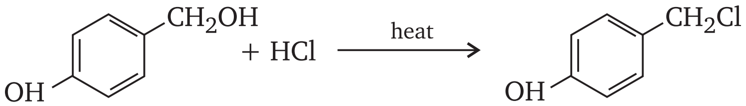
(*vi*) 

Ans. (*i*) 

Cyclohexanol Chlorocyclohexane

(*ii*) 

4 Ethylnitrobenzene 4 – (1′ –Bromoethylnitrobenzene)

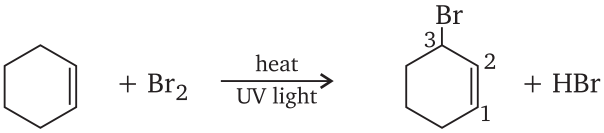
(*iii*) 

4–Hydroxymethylphenol 4–Chloromethylphenol

(*iv*) 

1–Methylcyclohexene 1 – Iodo–1–methylcyclohexane

(*v*) $\underset{\text{Bromoethane}}{CH_3CH_2-Br} + NaI \xrightarrow{\text{Oxyacetone, }\Delta} \underset{\text{Iodoethane}}{CH_3CH_2-I} + NaBr$

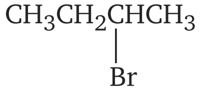
(*vi*) 

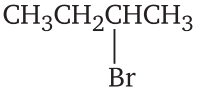
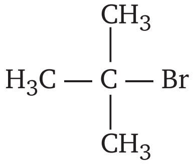
Cyclohexene 3-Bromocyclohexene

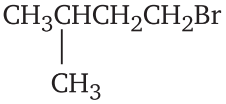
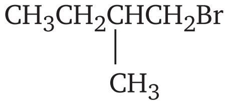
10.6. Arrange each set of compounds in order of increasing boiling points.
(*i*) Bromomethane, Bromoform, Chloromethane, Dibromomethane
(*ii*) 1–Chloropropane, Isopropyl chloride, 1–Chlorobutane

Ans. (*i*) Chloromethane < Bromomethane < Dibromomethane < Bromoform
Boiling point increases with increase in the molecular mass.
(*ii*) Isopropyl chloride < 1–Chloropropane < 1–Chlorobutane
Isopropyl chloride being a branched haloalkane has lower boiling point than 1-Chloropropane.

10.7. 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  $CH_3CH_2CH(Br)CH_3$

(*ii*)  $CH_3CH_2CH(Br)CH_3$ or  $(CH_3)_3C-Br$

(*iii*)  $CH_3CH(CH_3)CH_2CH_2Br$ or  $CH_3CH_2CH(CH_3)CH_2Br$

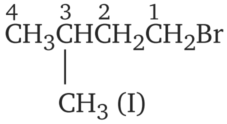
Ans. (*i*) $CH_3CH_2CH_2CH_2Br$ is a 1° alkyl halide while $CH_3CH_2 — CHBr — CH_3$ is a 2° alkyl halide. Since there will be some steric hindrance in 2° alkyl halides than in 1° alkyl halides.

Therefore, $CH_3CH_2CH_2CH_2Br$ will react faster than $CH_3CH_2CH(Br)CH_3$ by S_N2 mechanism.

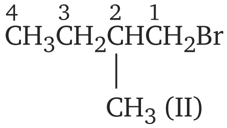
(*ii*) $CH_3CH_2 — CHBr — CH_3$ is a 2° alkyl halide while $(CH_3)_3C — Br$ is a 3° alkyl halide.

Since due to lesser steric hindrance a 2° alkyl halide it will react faster than a 3° alkyl halide. Therefore $CH_3CH_2CHBrCH_3$ will react faster than $(CH_3)_3CBr$ by S_N2 mechanism.

(*iii*)



$\overset{4}{C}H_3\overset{3}{C}H(CH_3)\overset{2}{C}H_2\overset{1}{C}H_2Br$ (I)

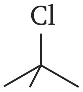
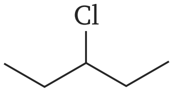
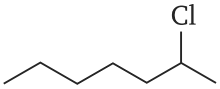
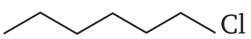


$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H(CH_3)\overset{1}{C}H_2Br$ (II)

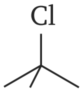
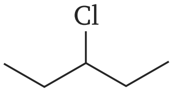
Both (I) and (II) are 2° alkyl halides. But in case of alkyl halide (II), the CH_3 group at C_2 is closer to Br atom while in alkyl halide (I) the CH_3 group at C_3 is a little away from Br atom. As a result, alkyl halide (II) will suffer greater steric hindrance than alkyl halide(I).

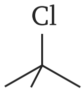
Therefore, $(CH_3)_2CHCH_2Br$ will react faster than $CH_3CH_2CH(CH_3)CH_2Br$ by S_N2 mechanism.

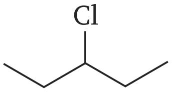
10.8. In the following pair of halogen compounds, which compound undergoes faster S_N1 reaction?

(*i*)  and  (*ii*)  and 

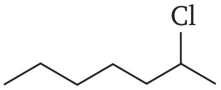
Ans. The reactivity towards S_N1 reaction is governed by the stability of carbocations.

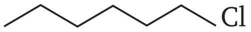
(*i*)  is a 3°alkyl halide  is a 2°alkyl halide

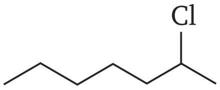
3° alkyl halide react faster than a 2° alkyl halide due to greater stability of 3° carbocation over 2° carbocation. Therefore 

will react faster than 

through S_N1 mechanism

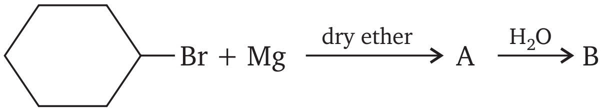
(*ii*) 

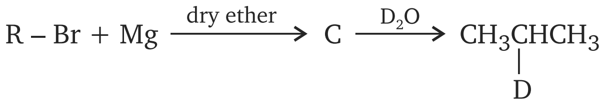
is a 2° alkyl halide and 

is a 1° alkyl halide. 2° alkyl halides react faster than 1° alkyl halides due to greater stability of 2° carbocation. So, 

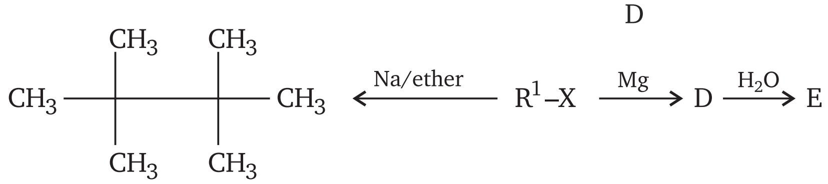
will react faster by S_N1 mechanism.

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



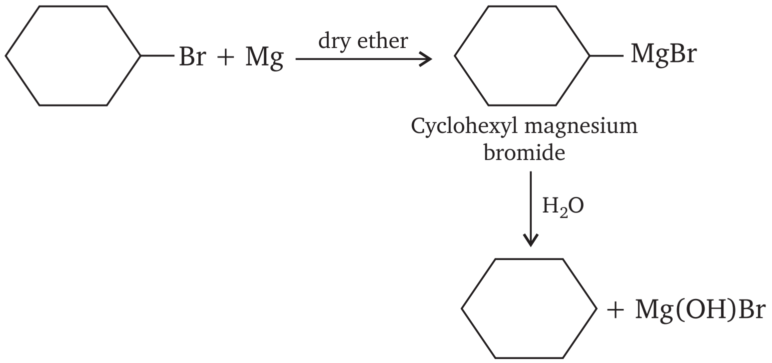


$$R-Br + Mg \xrightarrow{\text{dry ether}} C \xrightarrow{D_2O} CH_3\underset{\substack{|\\ D}}{C}HCH_3$$

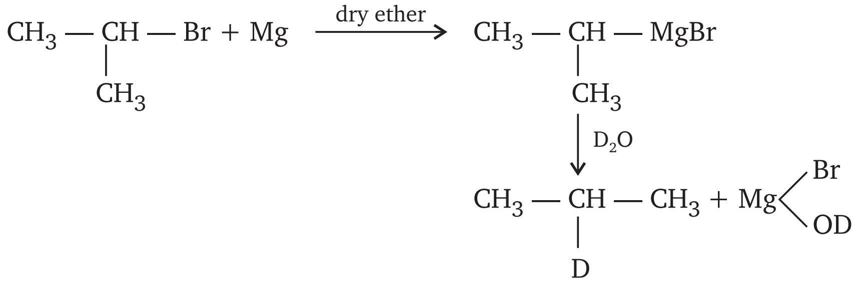


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xleftarrow{\text{Na/ether}} R^1-X \xrightarrow{Mg} D \xrightarrow{H_2O} E$$

Ans.



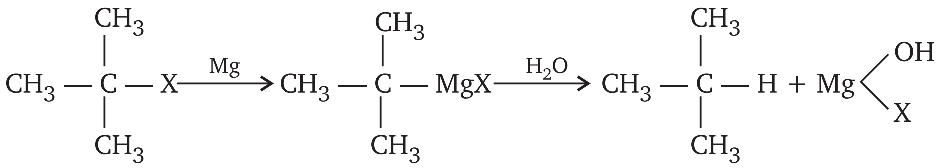
$$R-Br + Mg \xrightarrow{\text{dry ether}} RMgBr$$



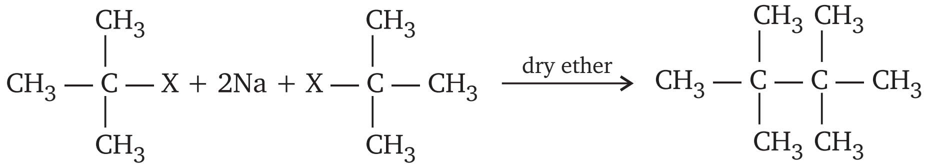
$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-Br + Mg \xrightarrow{\text{dry ether}} CH_3-\underset{\substack{|\\ CH_3}}{CH}-MgBr$$

$$\big\downarrow D_2O$$

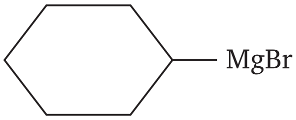
$$CH_3-\underset{\substack{|\\ D}}{CH}-CH_3 + Mg\left\langle\begin{matrix}Br\\ OD\end{matrix}\right.$$

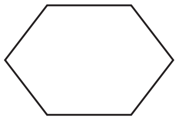


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X \xrightarrow{Mg} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-MgX \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + Mg\begin{matrix} OH \\ X \end{matrix}$$



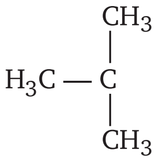
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X + 2Na + X-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{dry ether}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

A = 

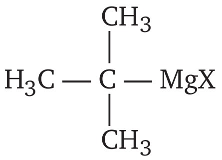
B = 

C = RMgBr

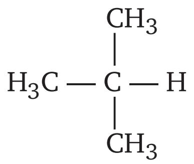
R = CH_3CHCH_3

R' = 

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

D = 

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

E = 

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

NCERT TEXTBOOK QUESTIONS SOLVED

10.1. 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*) 2-Chloro-3-methylbutane, 2° alkyl halide
(*ii*) 3-Chloro-4-methylhexane, 2° alkyl halide
(*iii*) 1-Iodo-2,2-dimethylbutane, 1° alkyl halide
(*iv*) 1-Bromo-3,3-dimethyl-1-phenylbutane, 2° benzylic halide
(*v*) 2-Bromo-3-methylbutane, 2° alkyl halide
(*vi*) 1-Bromo-2-ethyl-2-methylbutane, 1° alkyl halide
(*vii*) 3-Chloro-3-methylpentane, 3° alkyl halide

(*viii*) 3-Chloro-5-methylhex-2-ene, vinylic halide

(*ix*) 4-Bromo-4-methylpent–2-ene, alylic halide

(*x*) 1-Chloro-4-(2-methyl propyl)benzene, arylhalide.

(*xi*) 1-Chloromethyl-3(2,2-dimethyl propyl)benzene, 1° benzylic halide

(*xii*) 1-Bromo-2-(1–methylpropyl)benzene, aryl halide

10.2. Give the IUPAC name of the following compounds:

(*i*) $CH_3CH(Cl)CH(Br)CH_3$ (*ii*) $CHF_2CBrClF$

(*iii*) $ClCH_2C \equiv CCH_2Br$ (*iv*) $(CCl_3)_3CCl$

(*v*) $CH_3C(p\text{–}ClC_6H_4)_2CH(Br)CH_3$ (*vi*) $(CH_3)_3CCHCl = C_6H_4I\text{-}p$

Ans. (*i*) 2-Bromo-3-chlorobutane (*ii*) 1-Bromo-1-chloro-1,2,2–trifluoroethane

(*iii*) 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–dimethyl but-1-ene

10.3. Write the structures of the following organic halogen compounds:

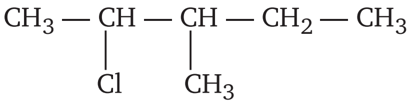
(*i*) 2-Chloro-3-methylpentane (*ii*) *p*-Bromochlorobenzene

(*iii*) 1-Chloro-4-ethylcyclohexane (*iv*) 2-(2′-Chlorophenyl)-1- iodooctane

(*v*) 2-Bromobutane (*vi*) 4-tert-Butyl-3-iodoheptane

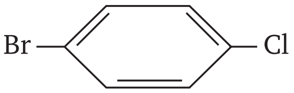
(*vii*) 1-Bromo-4-sec-butyl-2-methylbenzene (*viii*) 1, 4-Dibromobut-2-ene

Ans. (*i*)

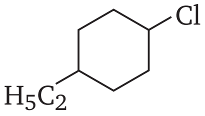


$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

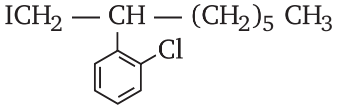
(*ii*)



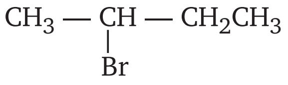
(*iii*)



(*iv*)

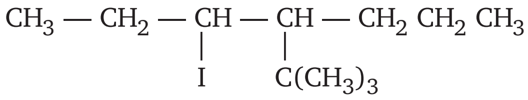


(*v*)



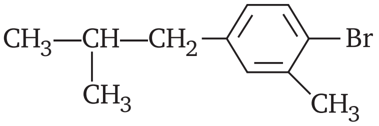
$CH_3-\underset{Br}{\underset{|}{CH}}-CH_2CH_3$

(*vi*)



$CH_3-CH_2-\underset{I}{\underset{|}{CH}}-\underset{C(CH_3)_3}{\underset{|}{CH}}-CH_2\ CH_2\ CH_3$

(*vii*)



(*viii*) $BrCH_2CH = CHCH_2Br$

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

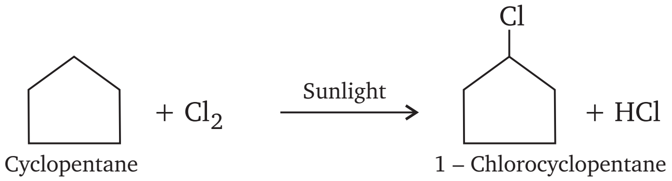
(*i*) CH_2Cl_2 (*ii*) $CHCl_3$ (*iii*) CCl_4

Ans. (*i*) CH_2Cl_2 has the highest dipole moment (1.60 D).

The dipole moment of CCl_4 is zero whereas that of $CHCl_3$ is 1.03 D. In CH_2Cl_2, the resultant of two C—Cl dipole moments is reinforced by the resultant of two C—H dipole moments.

10.5. 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. Since the hydrocarbon gives only one monochloro compound, it indicates that all the hydrogen atoms in the hydrocarbon chain are equivalent. Thus, the compound is cyclopentane.



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

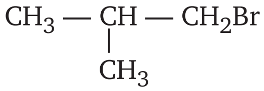
Ans.

$$CH_3CH_2CH_2CH_2Br$$

1 – Bromobutane

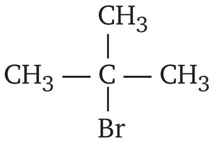
$$CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$$

2 – Bromobutane



$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$$

1 – Bromo –2– methylpropane



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

2 – Bromo – 2 methylpropane

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

(*i*) 1-butanol (*ii*) 1-chlorobutane (*iii*) but-1-ene

Ans. (*i*) $\underset{\text{1 – butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{P/I_2} \underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I}$

(*ii*) $\underset{\text{1 – chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + NaI \xrightarrow[\text{NaI}]{\text{Acetone}} \underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I} + NaCl$

(*iii*) $CH_3CH_2 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1 – bromobutane}}{CH_3CH_2CH_2CH_2Br}$

$$\text{Acetone}\ \Big\downarrow\ \text{NaI}$$

$$\underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I} + NaBr$$

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

Ans. Nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide group is a hybrid of two contributing structures and therefore it can act as a nucleophile in two different ways:

$$^{\ominus}C\equiv N \longleftrightarrow :C=N^{\ominus}$$

It can either attack through carbon atom to form cyanides or through N-atom to form isocyanides or carbylamines.

10.9. Which compound in each of the following pairs will react faster in S_N2 reaction with –OH? [*AI* 2014]

(*i*) CH_3Br or CH_3I (*ii*) $(CH_3)_3CCl$ or CH_3Cl

Ans. (*i*) Since I^- ion is a better leaving group than Br^- ion, therefore CH_3I will react faster than CH_3Br in S_N2 reaction with OH group.

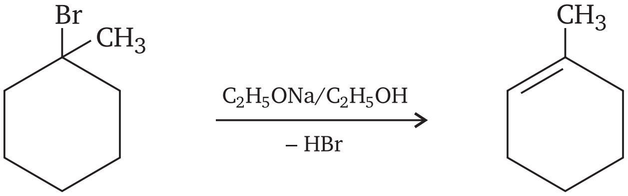
(*ii*) On the basis of steric grounds, 1° alkyl halides are more reactive than tert alkyl halides toward S_N2 reactions. Therefore, CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ by a S_N2 reaction with OH^- group.

10.10. 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

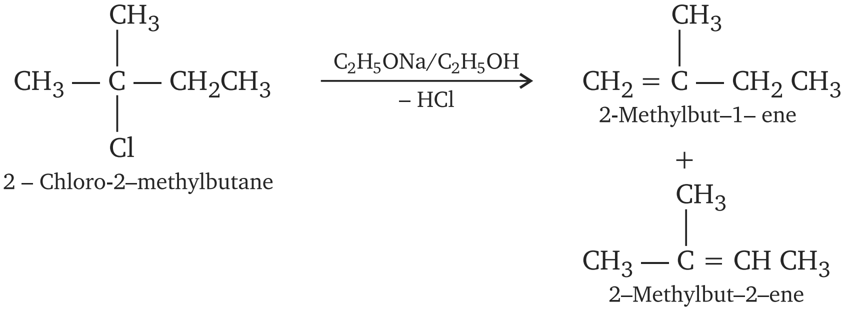
(*iii*) 2, 2, 3-Trimethyl-3-bromopentane

Ans. (*i*)



1–Methyl cyclohexene

(*ii*)



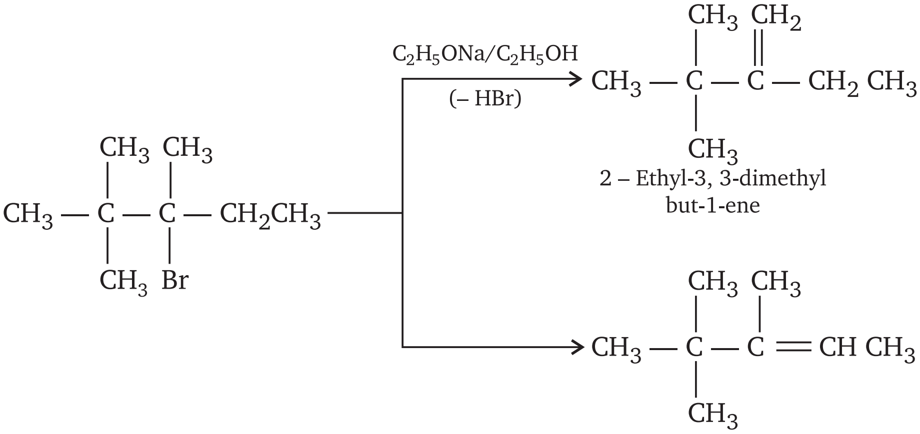
2 – Chloro-2–methylbutane

2-Methylbut–1– ene

2–Methylbut–2–ene

$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow[-\,HCl]{C_2H_5ONa/C_2H_5OH} CH_2=\overset{CH_3}{C}-CH_2\,CH_3 + CH_3-\overset{CH_3}{C}=CH\,CH_3$$

(*iii*)



2 – Ethyl-3, 3-dimethyl but-1-ene

3, 4, 4 -Trimethylpent -2-ene

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow[(-\,HBr)]{C_2H_5ONa/C_2H_5OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_2}{\overset{\|}{C}}-CH_2\,CH_3 \;+\; CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{C}=CH\,CH_3$$

10.11. 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*)

$$CH_3CH_2OH \xrightarrow{PCl_5} CH_3\,CH_2Cl + HC \equiv C^-\,Na^+ \longrightarrow HC \equiv C — CH_2 — CH_3$$

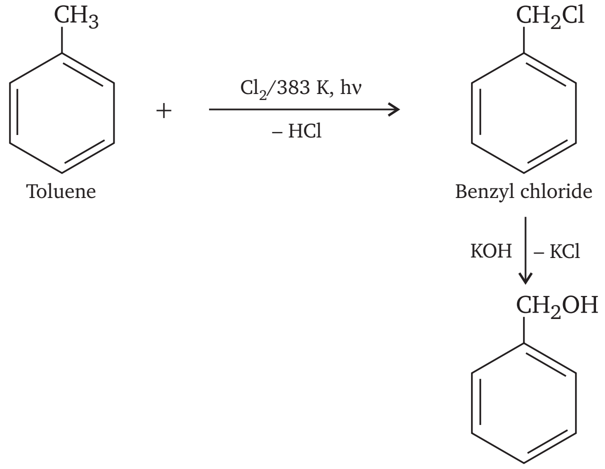
(*ii*)

$$\underset{\text{Ethane}}{CH_3—CH_3} + Br_2 \xrightarrow[-\text{ HBr}]{520 - 670\text{ K}} CH_3CH_2 — Br \xrightarrow[\text{–HBr}]{\text{KOH (alc)}/\Delta} CH_2 = CH_2 \xrightarrow{Br_2/CCl_4} \underset{\text{1,2, Dibromoethane}}{Br\,CH_2 — CH_2Br} \xrightarrow[\text{–HBr}]{\text{KOH alc.}/\Delta} \underset{\text{Bromoethene}}{CH_2 = CHBr}$$

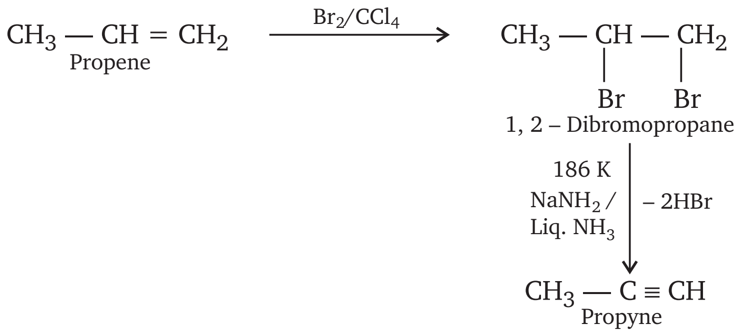
(*iii*)

$$\underset{\text{Propene}}{CH_3 — CH = CH_2} \xrightarrow[\text{peroxide effect}]{HBr/RCOOR} \underset{\text{1, Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[-\text{ AgBr}]{AgNO_2,\ C_2H_5OH/H_2O} \underset{1 - \text{Nitropropane}}{CH_3CH_2CH_2NO_2}$$

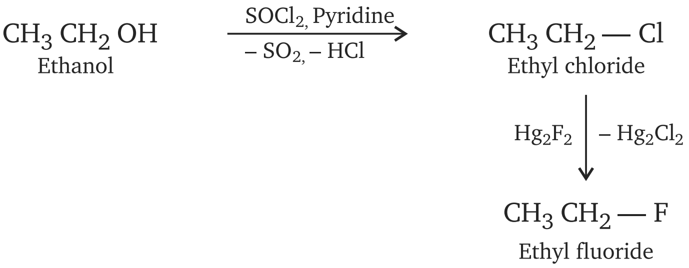
(*iv*)



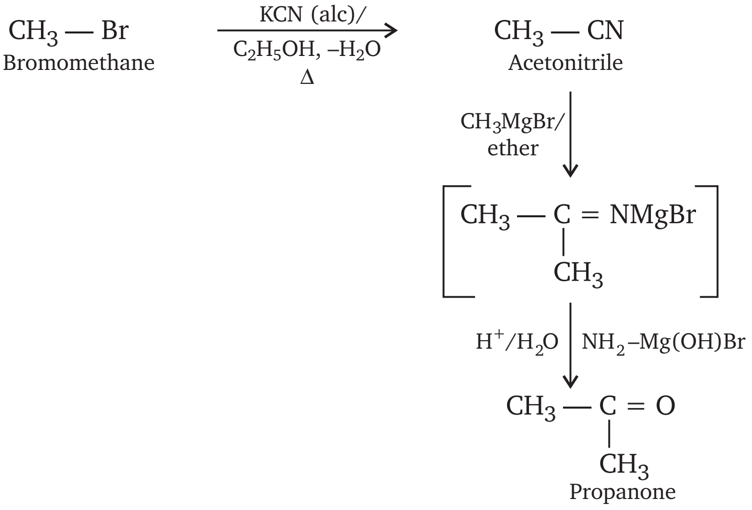
(*v*)


$CH_3-CH=CH_2$
Propene
Br_2/CCl_4
$CH_3-CH(Br)-CH_2(Br)$
1, 2 – Dibromopropane
186 K
$NaNH_2$ / Liq. NH_3
– 2HBr
$CH_3-C\equiv CH$
Propyne

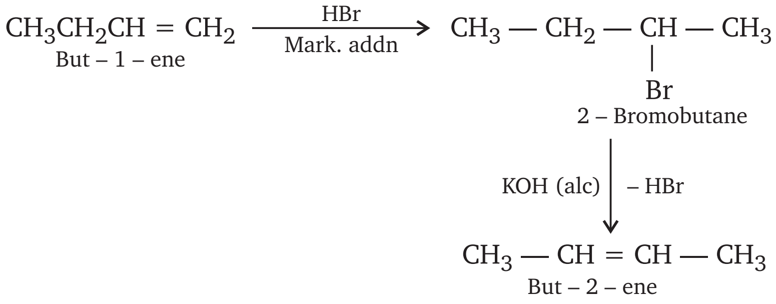
(*vi*)


$CH_3\,CH_2\,OH$
Ethanol
$SOCl_2$, Pyridine
$-SO_2$, – HCl
$CH_3\,CH_2-Cl$
Ethyl chloride
Hg_2F_2
$-Hg_2Cl_2$
$CH_3\,CH_2-F$
Ethyl fluoride

(*vii*)


CH_3-Br
Bromomethane
KCN (alc)/
C_2H_5OH, $-H_2O$
Δ
CH_3-CN
Acetonitrile
CH_3MgBr/ ether
$[CH_3-C(CH_3)=NMgBr]$
H^+/H_2O
$NH_2-Mg(OH)Br$
$CH_3-C(CH_3)=O$
Propanone

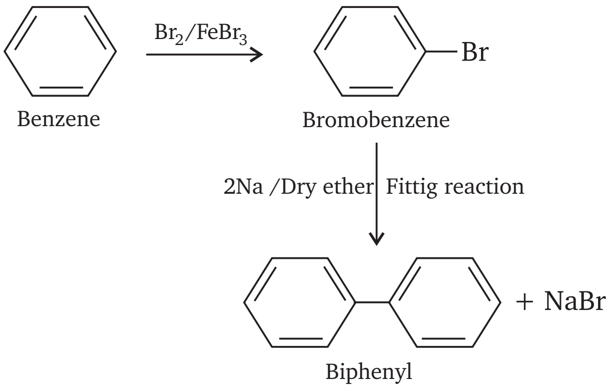
(*viii*)


$CH_3CH_2CH=CH_2$
But – 1 – ene
HBr
Mark. addn
$CH_3-CH_2-CH(Br)-CH_3$
2 – Bromobutane
KOH (alc)
– HBr
$CH_3-CH=CH-CH_3$
But – 2 – ene

(*ix*) $\underset{\text{1 – Chlorobutane}}{2CH_3CH_2CH_2CH_2Cl} + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}}$

$$\underset{n\text{ – octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaCl$$

(*x*)



10.12. 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 is stabilised by resonance and there is a +ve charge on 'Cl' in 3 out of 5 resonating structures, therefore it has lower dipole moment than cyclohexyl chloride in which there is no such +ve charge on the 'Cl'–atom.

(*ii*) Alkyl halides cannot form H–bond with water molecules and also cannot break H–bonds between the water molecules, therefore they are immiscible with water.

(*iii*) Grignard reagents react with H_2O to form alkanes. Therefore, they are prepared under anhydrous conditions.

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

Ans. Uses of freon–12

(*i*) For aerosol propellants

(*ii*) In refrigeration and air conditioning

Uses of DDT:

(*i*) As an insecticide

(*ii*) It is also used as an effective tool against malaria

Uses of CCl_4

(*i*) In the manufacture of refrigerants and propellants for aerosol.

(*ii*) In the synthesis of chlorofluorocarbons and other chemicals.

(*iii*) Widely used as a cleaning fluid and fire extinguisher.

Uses of Iodoform:

(*i*) Employed as a solvent for fats, alkaloids, iodine and other substances.

(*ii*) Used to manufacture pharmaceuticals.

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

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

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

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

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

(*v*) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

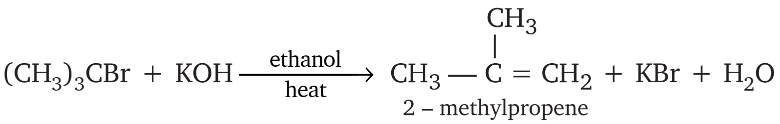
(*vi*) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(*vii*) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$

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

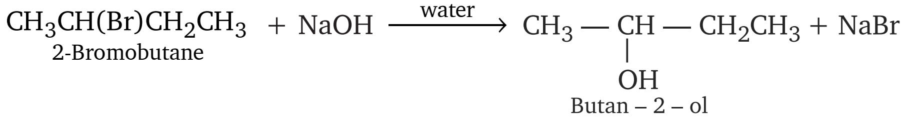
Ans. (*i*) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}} \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I} + NaCl$

(*ii*)



$(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}} \underset{\text{2 – methylpropene}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} + KBr + H_2O$

(*iii*)



$\underset{\text{2-Bromobutane}}{CH_3CH(Br)CH_2CH_3} + NaOH \xrightarrow{\text{water}} \underset{\text{Butan – 2 – ol}}{CH_3 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_2CH_3} + NaBr$

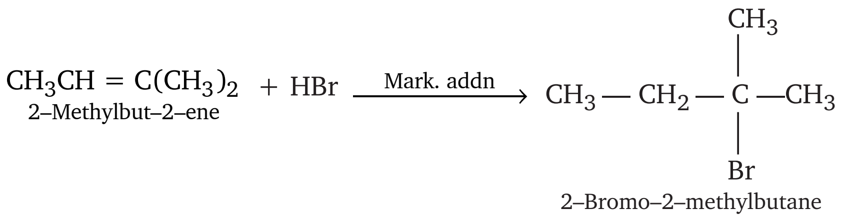
(*iv*) $\underset{\text{Bromoethane}}{CH_3CH_2Br} + KCN \xrightarrow{\text{aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3CH_2 - CN} + KBr$

(*v*) $\underset{\text{Sod. phenoxide}}{C_6H_5ONa} + C_2H_5Cl \xrightarrow[\text{synthesis}]{\text{Williamson's}} \underset{\text{Phenetole}}{C_6H_5 - O - C_2H_5} + NaCl$

(*vi*) $\underset{\text{Propan–1–ol}}{CH_3CH_2CH_2OH} + SOCl_2 \xrightarrow[\text{Substitution}]{\text{Nucleophilic}} \underset{\text{1–Chloropropane}}{CH_3CH_2CH_2Cl} + HCl + SO_2$

(*vii*) $\underset{\text{But –1–ene}}{CH_3CH_2CH = CH_2} + HBr \xrightarrow{\text{peroxide}} \underset{\text{1–Bromobutane}}{CH_3CH_2CH_2CH_2Br}$

(*viii*)

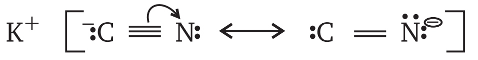


$\underset{\text{2–Methylbut–2–ene}}{CH_3CH = C(CH_3)_2} + HBr \xrightarrow{\text{Mark. addn}} \underset{\text{2–Bromo–2–methylbutane}}{CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_3}$

10.15. Write the mechanism of the following reaction:

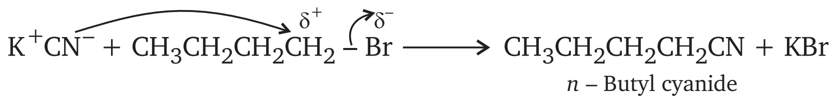
$$n\text{BuBr} + \text{KCN} \xrightarrow{\text{EtOH–H}_2\text{O}} n\text{BuCN}$$

Ans. KCN is a resonance hybrid of the following two contributing structures:



$$\text{K}^+ \left[{}^{-}\!:\!\text{C} \equiv \text{N}: \longleftrightarrow :\!\text{C} = \ddot{\text{N}}\!:^{-} \right]$$

CN^- ion is an ambident nucleophile. Therefore, it can attack the carbon atom of C–Br bond in *n*–BuBr either through C–atom or N–atom. Since C–C bond is stronger than C–N bond, therefore attack occurs through C–atom to form *n*–butyl cyanide as follows:



$$\text{K}^+\text{CN}^- + \text{CH}_3\text{CH}_2\text{CH}_2\overset{\delta^+}{\text{CH}_2} - \overset{\delta^-}{\text{Br}} \longrightarrow \underset{n\text{ – Butyl cyanide}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}} + \text{KBr}$$

10.16. Arrange the compounds of each set in order of reactivity towards S_N2 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. Due to steric reasons, the order of reactivity in S_N2 reactions follows the order: $1° > 2° > 3°$. Therefore, the order of reactivity of the given alkyl bromides are:

(*i*) 2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(*ii*) 2-Bromo-2-methylbutane < 3-Bromo-2-methylbutane < 1-Bromo-3-methylbutane

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

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

Ans. In $C_6H_5CH_2Cl$ carbocation is stabilised by the resonance effect of one of the phenyl group, whereas in $C_6H_5CHClC_6H_5$ the carbocation formed will be stabilised by the resonance effect of two phenyl groups. That is why $C_6H_5CHClC_6H_5$ is more easily hydrolysed.

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

Ans. The *p*–isomer being more symmetrical fits closely in the crystal lattice and thus has stronger intermolecular forces of attraction than those of o–and m–isomers. Since during melting or dissolution the crystal lattice breaks, therefore a larger amount of energy is needed to melt or dissolve the *p*–isomer than the corresponding o–and m–isomers. In other words, the melting point of *p*–isomer is higher and its solubility is lower than the corresponding *o*–and *m*–isomers.

10.19. How following conversions can be carried out?

(*i*) Propene to propan-1-ol

(*ii*) Ethanol to but-1-yne

(*iii*) 1-Bromopropane to 2-bromopropane

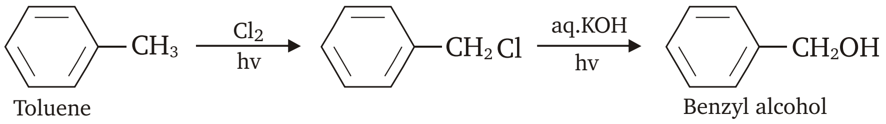
(*iv*) Toluene to benzyl alcohol

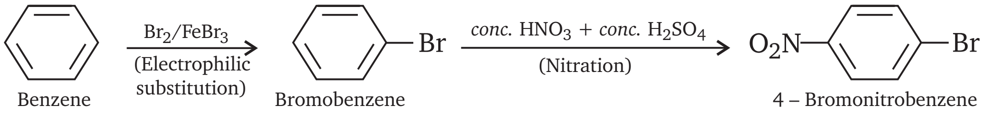
(*v*) Benzene to 4-bromonitrobenzene
(*vi*) Benzyl alcohol to 2-phenylethanoic acid
(*vii*) Ethanol to propanenitrile
(*viii*) Aniline to chlorobenzene
(*ix*) 2-Chlorobutane to 3, 4-dimethylhexane
(*x*) 2-Methyl-1-propene to 2-Chloro-2-methylpropane
(*xi*) Ethyl chloride to propanoic acid
(*xii*) But-1-ene 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 phenyl isocyanide.

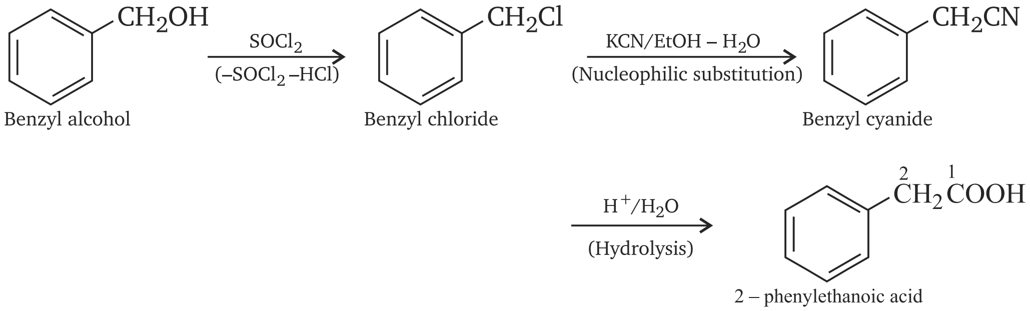
Ans. (*i*) $\underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow[\text{(Anti–Mark. addn.)}]{\text{HBr/peroxide}} \underset{\text{1 – Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Hydrolysis)}]{\text{Aq. KOH, }\Delta} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$

(*ii*) $\underset{\text{Ethanol}}{CH_3CH_2OH} + HCl \longrightarrow CH_3CH_2Cl \xrightarrow[-H_2O]{HC\equiv CNa} \underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH} + NaCl$

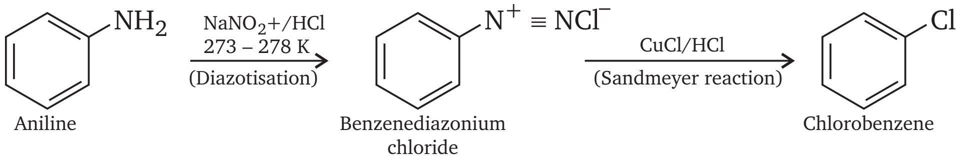
(*iii*) $\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc), }\Delta} \underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow[\text{(Mark. addn.)}]{\text{HBr}} \underset{\text{2–Bromopropane}}{CH_3 — CHBr — CH_3}$

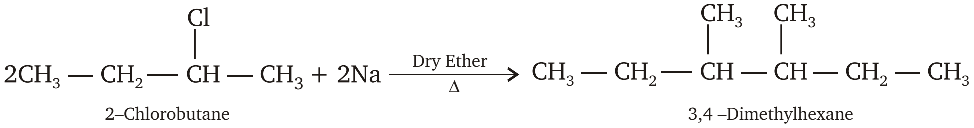
(*iv*) 

(*v*) 

(*vi*) 

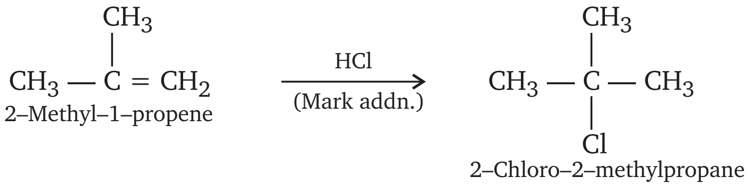
(*vii*) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PBr_3} \underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN, EtOH – }H_2O} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$

(viii) 

(ix) 

$$2CH_3-CH_2-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3 + 2Na \xrightarrow[\Delta]{\text{Dry Ether}} CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$$

2–Chlorobutane 3,4 –Dimethylhexane

(x) 

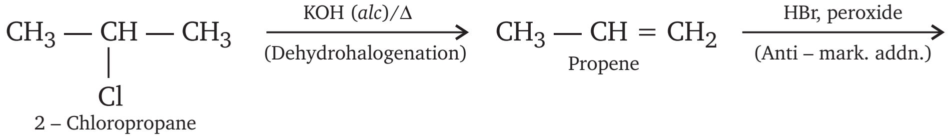
$$\underset{\text{2–Methyl–1–propene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} \xrightarrow[\text{(Mark addn.)}]{HCl} \underset{\underset{\displaystyle Cl}{|}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3}$$

2–Chloro–2–methylpropane

(xi) $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{(Nucleophilic substitution)}]{KCN,\ EtOH - H_2O} \underset{\text{Propanenitrile}}{CH_3CH_2CN} \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$

(xii) $\underset{\text{But – 1 – ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{(Anti – Mark. addn.)}]{HBr/RCOOR} \underset{\text{1 – Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{(Finkelstein reaction)}]{\text{NaI, acetone}}$

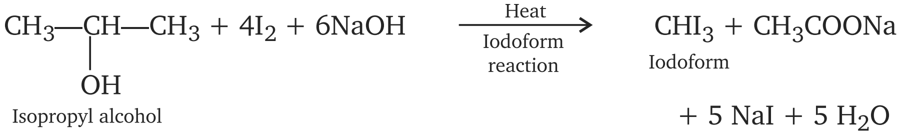
$\underset{\text{1–Butyliodide}}{CH_3CH_2CH_2CH_2I}$

(xiii) 

$$\underset{\underset{\displaystyle Cl}{|}}{CH_3-CH-CH_3} \xrightarrow[\text{(Dehydrohalogenation)}]{KOH\ (alc)/\Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{(Anti – mark. addn.)}]{\text{HBr, peroxide}}$$

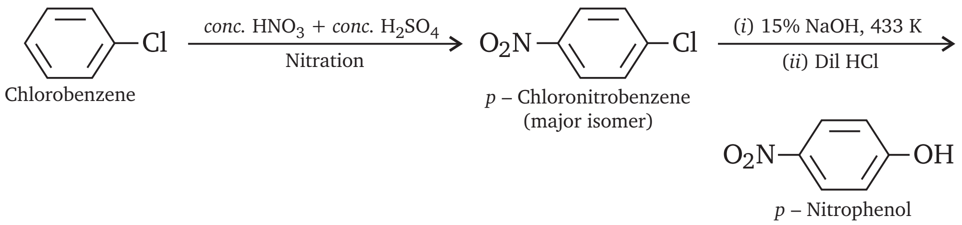
2 – Chloropropane

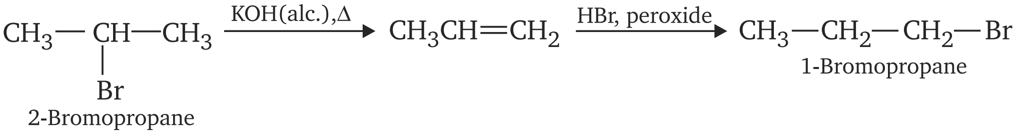
$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Nucleophilic substitution)}]{KOH\ (aq)/\Delta} \underset{\text{1 – Propanol}}{CH_3CH_2CH_2OH}$

(xiv) 

$$\underset{\underset{\displaystyle OH}{|}}{CH_3-CH-CH_3} + 4I_2 + 6NaOH \xrightarrow[\text{Iodoform reaction}]{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 5\ NaI + 5\ H_2O$$

Isopropyl alcohol

(xv) 

(xvi) 

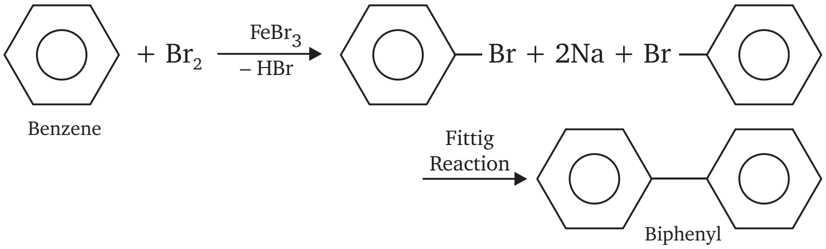
$$\underset{\underset{\displaystyle Br}{|}}{CH_3-CH-CH_3} \xrightarrow{KOH(alc.),\Delta} CH_3CH=CH_2 \xrightarrow{\text{HBr, peroxide}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

2-Bromopropane

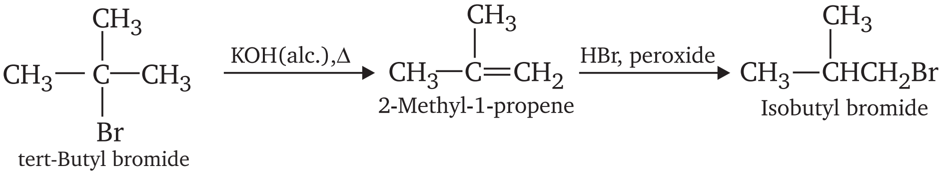
(*xvii*) $2CH_3CH_2-Cl + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether, }\Delta} CH_3CH_2-CH_2CH_3 + 2\,NaCl$

Chloroethane Butane

(*xviii*)



(*xix*)



$$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{KOH(alc.),\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{HBr,\ peroxide} CH_3-\overset{\overset{CH_3}{|}}{C}HCH_2Br$$

tert-Butyl bromide 2-Methyl-1-propene Isobutyl bromide

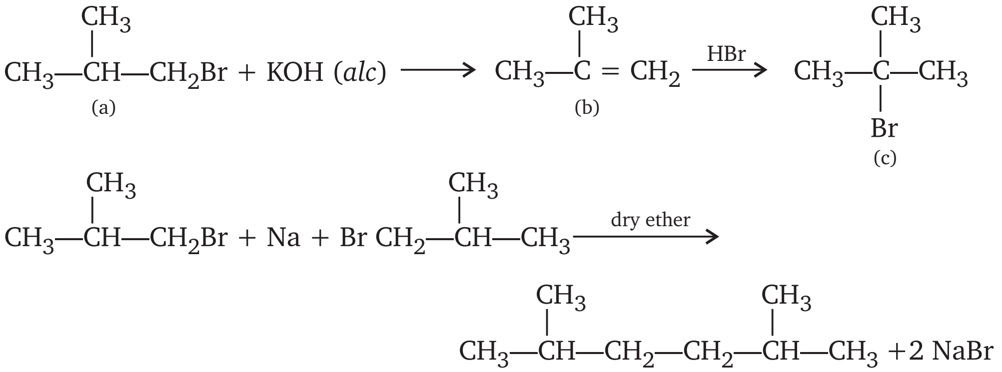
(*xx*) $C_6H_5-NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\text{Warm}} C_6H_5NC + 3\,KCl + 3\,H_2O$

10.20. 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 aqueous solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile brings about a substitution reaction of alkyl halides to form alcohols. In aqueous solution, OH^- ions are highly hydrated. This solvation process reduces the basic character of OH^- ions which therefore fails to abstract a hydrogen atom from the β–carbon of the alkyl chloride to form an alkene. In contrast, an alcoholic solution of KOH contains alkoxide (RO^-) ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

10.21. 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.



$$\underset{(a)}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Br} + KOH\ (alc) \longrightarrow \underset{(b)}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} \xrightarrow{HBr} \underset{(c)}{CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Br + Na + Br\,CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow{\text{dry ether}}$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3 + 2\,NaBr$$

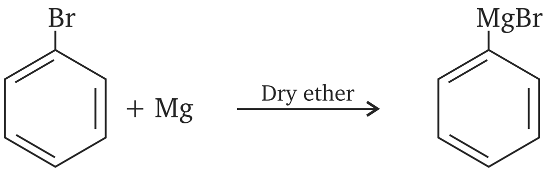
$$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{\text{dry ether}} \underset{\substack{n-\text{Octane }(C_8H_{18})\\ \text{(d)}}}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3}$$

10.22. What happens when

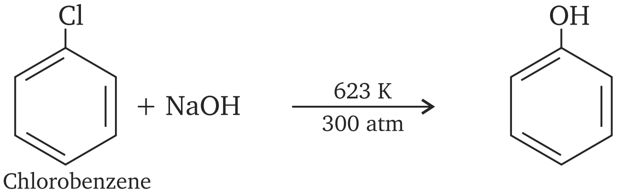
(*i*) *n*–butyl chloride is treated with alcoholic KOH
(*ii*) bromobenzene is treated with Mg in presence of dry ether
(*iii*) chlorobenzene is subjected to hydrolysis
(*iv*) ethyl chloride is treated with aqueous KOH
(*v*) methyl bromide is treated with sodium in presence of dry ether
(*vi*) methyl chloride is treated with KCN?

Ans. (*i*) $\underset{n-\text{butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + KOH\text{ (alc)} \longrightarrow \underset{\text{But–1–ene}}{CH_3—CH_2—CH = CH_2} + KCl + H_2O$

(*ii*)



(*iii*)



(*iv*) $C_2H_5Cl + aq.\ KOH \longrightarrow C_2H_5OH + KCl$

(*v*) $2CH_3Br + 2Na \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Ethane}}{CH_3—CH_3} + 2NaBr$

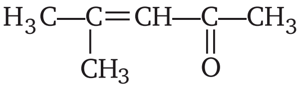
(*vi*) Methyl cyanide is formed by nucleophilic substitution reaction as:

$CH_3Cl + KCN \longrightarrow \underset{\text{Methyl cyanide}}{CH_3C \equiv N} + KCl$

ADDITIONAL QUESTIONS SOLVED

Q.1 Write the structure of:
4-methylpent-3-en-2-one
[*CBSE Sample Paper* (II) 2009]

Ans.



$H_3C—\underset{\underset{CH_3}{|}}{C}=CH—\underset{\underset{O}{||}}{C}—CH_3$

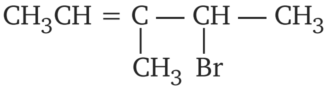
Q2. Write balanced chemical equations for the following:

(*i*) When chloroform is oxidised by air
(*ii*) Chloroform reacts with chlorine
[*CBSE* 2007]

Ans. (*i*) $\underset{\text{Chloroform}}{2\,CHCl_3} + O_2 \longrightarrow \underset{\text{Phosgene}}{2\,COCl_2} + 2HCl$

(*ii*) $\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$

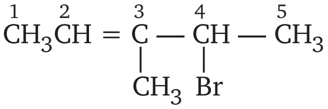
Q3. Give the IUPAC name of the following organic compound.



$$CH_3CH = \underset{CH_3}{\underset{|}{C}} - \underset{Br}{\underset{|}{CH}} - CH_3$$

[CBSE Sample Paper (II) 2008]

Ans.



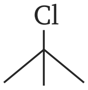
$$\overset{1}{C}H_3\overset{2}{C}H = \underset{CH_3}{\underset{|}{\overset{3}{C}}} - \underset{Br}{\underset{|}{\overset{4}{C}H}} - \overset{5}{C}H_3$$

4–Bromo–3–methylpent–2–ene

Q4. In each of the following pair of compounds, identify the compound which will undergo S_N1 reaction.

[*CBSE Sample Paper* (III) 2008, 2009]

(*i*)



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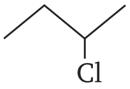
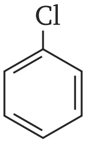


(*ii*)



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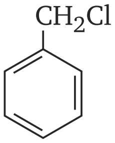
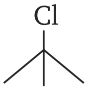


Ans. (*i*) Since 3° carbocation are more stable than 2° carbocation, therefore

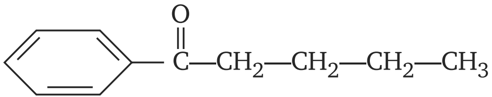


will react faster.

(*ii*) Benzyl chloride readily forms benzyl cation which is stabilized by resonance. Thus, benzyl chloride undergoes S_N1 reaction faster than chlorobenzene.

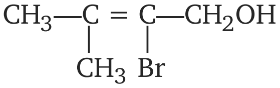
Q5. Write the structural formula of 1-pheny pentan-1-one. [*AI CBSE* 2009]

Ans.



1–phenyl pentan–1–one.

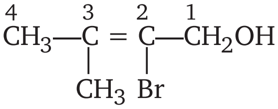
Q6. Give the IUPAC name of the following compound:



$$CH_3-\underset{CH_3}{\underset{|}{C}} = \underset{Br}{\underset{|}{C}}-CH_2OH$$

[*CBSE* 2009]

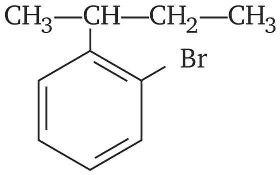
Ans.



$$\overset{4}{C}H_3-\underset{CH_3}{\underset{|}{\overset{3}{C}}} = \underset{Br}{\underset{|}{\overset{2}{C}}}-\overset{1}{C}H_2OH$$

2 – bromo – 3 –methylbut – 2 – en – 1 –ol

Q7. Write the IUPAC name of



[*AI* 2008]

Ans. IUPAC name:1-Bromo–2–sec. butyl–benzene

Q8. Write the IUPAC name of

$ClCH_2C \equiv CCH_2Br$ [*AI* 2008]

Ans. $Cl\overset{4}{C}H_2\overset{3}{C}\equiv\overset{2}{C}\overset{1}{C}H_2Br$

IUPAC name: 1-Bromo-4-Chlorobut-2-yne.

Q9. Which is a better nucleophile, a bromide ion or an iodide ion?

Ans. Iodide ion, because of its bigger size and lower electronegativity.

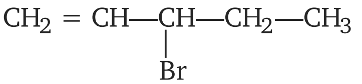
Q10. What condition is to be satisfied for a compound to be chiral?

Ans. Its mirror image should be non–superimposable.

Q11. What is a racemic modification?

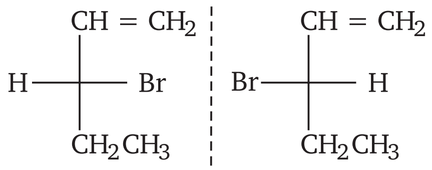
Ans. A 50:50 mixture of two enantiomers of any optically active compound is called a racemic mixture. It is always optically inactive.

Q12. Identify the presence of chirality if any, in the following molecule 3-bromo-pent-1-ene. How many sterioisomers are possible for those containing chiral centres? [*CBSE* 2004]

Ans. 

$CH_2 = CH—\underset{\displaystyle|\atop\displaystyle Br}{CH}—CH_2—CH_3$

3–Bromopent–1–ene.



It has 2 Sterioisomers.

Q13. Out of chlorobenzene and chloromethane, which is more reactive towards nucleophilic substitution reaction?

Ans. Chloromethane being an alkyl halide is more reactive than chlorobenzene which is an aryl halide.

Q14. Give the IUPAC name of $C_6H_5CH_2CH_2Cl$.

Ans. 1–Chloro–2 phenylethane

Q15. Give one example (with equation) of Wurtz–Fittig reaction.

Ans. $C_6H_5Cl + 2Na + ClCH_3 \xrightarrow{\text{Dry ether}} C_6H_5\,CH_3 + 2NaCl$

Q16. What is a plane polarised light?

Ans. A beam of light which has vibrations in only one plane is called a plane polarised light.

Q17. Explain why aryl halides are extremely less reactive towards nucleophilic substitution reactions.

Ans. It is due to resonance in aryl halides in the C–X bond, due to which it acquires a double bond character which makes it difficult to substitute halogen.

Q18. Arrange the following in increasing order of the property indicated:

Bromomethane, Bromoform,
Chloromethane, Dibromomethane
(Boiling point)

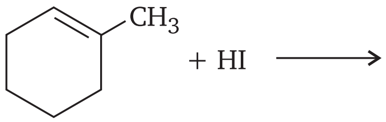
Ans. Chloromethane < Bromomethane < Dibromomethane < Bromoform.

Q19. Haloalkanes are only very slightly soluble in water explain.

Ans. This is because haloalkanes are unable to form hydrogen bond with water.

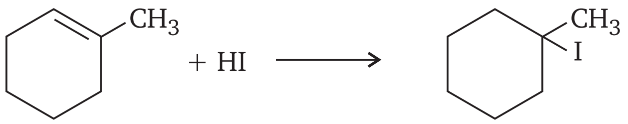
II. Short Answer Type Questions (2 or 3 Marks)

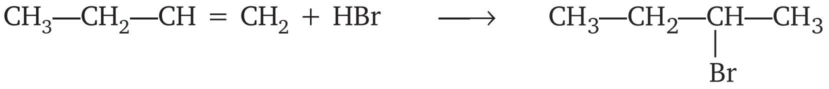
Q1. Complete the following reaction equations:

(*i*) 

(*ii*) $CH_3CH_2CH = CH_2 + HBr \longrightarrow$

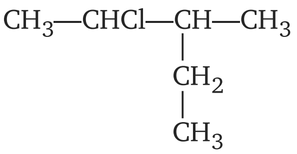
[*AI CBSE* 2009]

Ans. (*i*) 

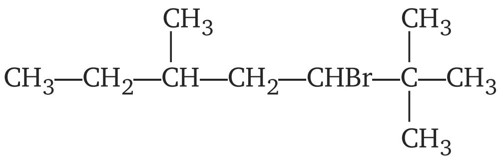
(*ii*) 

$CH_3—CH_2—CH = CH_2 + HBr \longrightarrow CH_3—CH_2—\underset{\displaystyle|\atop\displaystyle Br}{CH}—CH_3$

Q2. Write the IUPAC names of the following compounds:

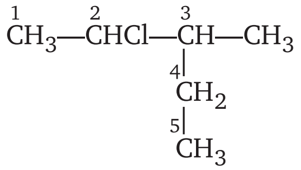
(*i*) 

$CH_3—CHCl—\underset{\displaystyle|\atop{\displaystyle CH_2\atop{\displaystyle|\atop\displaystyle CH_3}}}{CH}—CH_3$

(*ii*) 

$CH_3—CH_2—\overset{\displaystyle CH_3\atop\displaystyle|}{CH}—CH_2—CHBr—\overset{\displaystyle CH_3\atop\displaystyle|}{\underset{\displaystyle|\atop\displaystyle CH_3}{C}}—CH_3$

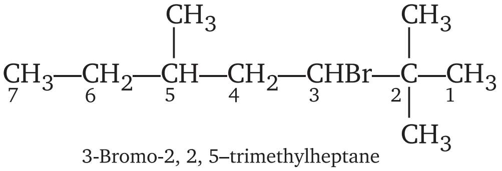
Ans. (*i*)



$$\overset{1}{CH_3}-\overset{2}{CHCl}-\overset{3}{\underset{\substack{4\,|\\ CH_2\\ 5\,|\\ CH_3}}{CH}}-CH_3$$

2-chloro-3-methylpentane

(*ii*)



$$\underset{7}{CH_3}-\underset{6}{CH_2}-\underset{5}{\overset{\substack{CH_3\\ |}}{CH}}-\underset{4}{CH_2}-\underset{3}{CHBr}-\underset{\substack{2\,|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}-\underset{1}{CH_3}$$

3-Bromo-2, 2, 5–trimethylheptane

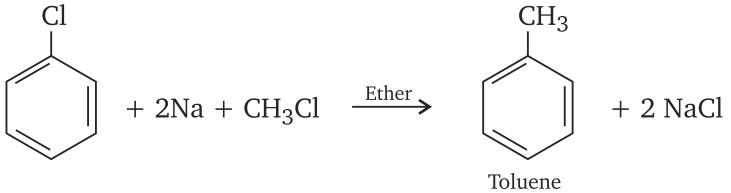
Q3. Give one example of each of the following reactions:

(*i*) Wurtz Reaction (*ii*) Wurtz – Fittig reaction. [*CBSE* 2007]

Ans. (*i*) **Wurtz Reaction:** It converts alkyl halides into alkane. Example:

$$CH_3Cl + 2Na + CH_3Cl \xrightarrow{\text{Dry ether}} 2NaCl + C_2H_6$$

(*ii*) **Wurtz-Fittig reaction:** It converts an aryl halide and alkyl halide into the corresponding hydrocarbon.



Q4. (*i*) What happens when iodoform is heated with silver powder? Write the chemical equation.

(*ii*) Out of ethyl bromide and ethyl chloride which has higher boiling point and why?

Ans. (*i*) When iodoform is heated with silver powder, acetylene (ethyne) is formed.

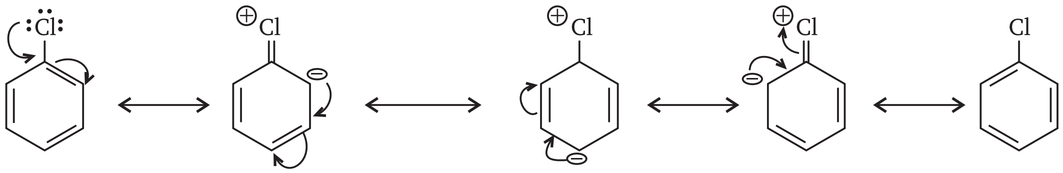
$$CH_3I + 6Ag + CH_3I \longrightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6AgI$$

(*ii*) The boiling point of ethyl bromide is higher due to greater magnitude of the van der Waals' forces which depends upon molecular size of the halogen atom.

Q5. Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

Ans. Haloarenes are much less reactive than haloalkanes towards the nucleophilic substitution reactions due to the following reasons:

(*i*) **Resonance effect:** In haloarenes the electron pair on the halogen atom is in conjugation with the π–electrons of the ring and the following resonating structures are possible.



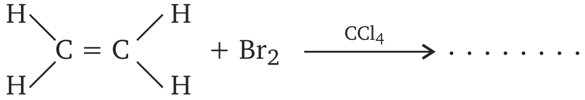
C – Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than in case of haloalkanes and therefore, they are less reactive towards nucleophilic substitution reaction.

(*ii*) The C – Cl bond length in haloalkane is 177 pm while in haloarene is 169 pm. Since it is difficult to break shorter bond than a longer bond. Therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

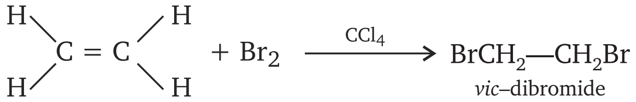
(*iii*) Phenyl cation is less stable than the alkyl carbocation.

Q6. Complete the following reaction equations:

(*i*) $C_6H_5N_2Cl + KI \longrightarrow$ . . . .

(*ii*)  [*CBSE* 2008]

Ans. (*i*) $C_6H_5\overset{+}{N}_2\,Cl^- + KI \longrightarrow C_6H_5I + KCl + N_2$

(*ii*) 

Q7. Point out the difference between:

(*i*) Chirality and chiral centre.

(*ii*) Diastereoisomers and Enantiomers. [*Foreign* 2004]

Ans. (*i*) **Chirality:** The phenomena of a molecule containing a carbon atom attached to four different atoms or groups of atom and thus making the mirror image of the molecule non-superimposible on the molecule is called chirality.

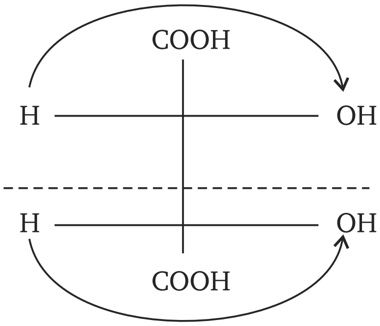
Chiral centre: The carbon atom which is attached to four different atoms or groups of atoms is called the chiral centre.

(*ii*) **Diastereoisomers:** Those pairs of stereoisomers which are not mirror images of each other and differ in optical rotation.

Enantiomers: They are non-superimposable mirror images of molecules with each other. They have optical rotation equal in magnitude but opposite in sign.

Q8. Does the presence of two chiral carbon atoms always make the molecule optically active? Explain giving an example. [*AI* 2004]

Ans. No the presence of two chiral carbon atoms not always make the molecule optically active. For example, *meso* tartaric acid is optically inactive because if upper half of molecule rotates the plane–polarised light towards the left, then lower half rotate it towards the right, such that net optical rotation is zero due to internal compensation.



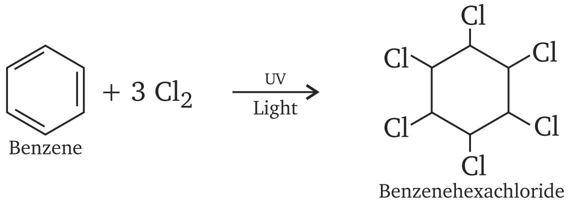
Optically inactive meso–tartaric acid.

Q9. Write the structure of the main product:

(*i*) Chlorination of benzene in the presence of UV light (*ii*) Propene is treated with HBr in presence of benzoyl peroxide

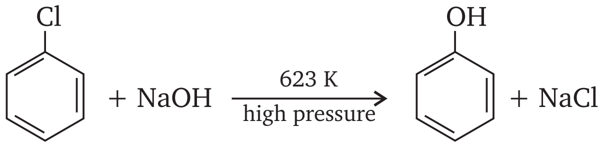
(*iii*) Chlorobenzene is treated with NaOH at 623 K and high pressure

Ans. (*i*)



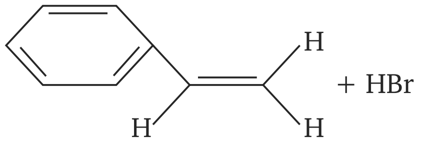
(*ii*) $\underset{\text{Propene}}{CH_3—CH = CH_2} + HBr \xrightarrow[\text{peroxide}]{\text{Benzoyl}} \underset{\text{1 – Bromopropane}}{CH_3CH_2CH_2Br}$

(*iii*)



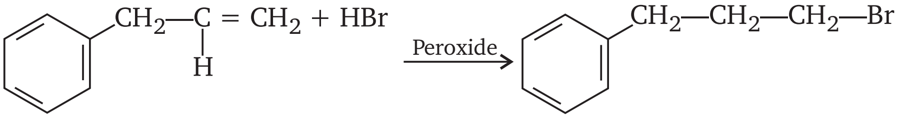
Q10. Write the products of the following reactions:

(*i*)



(*ii*) $CH_3—CH_2—CH = CH_2 + HCl$

Ans. (*i*)

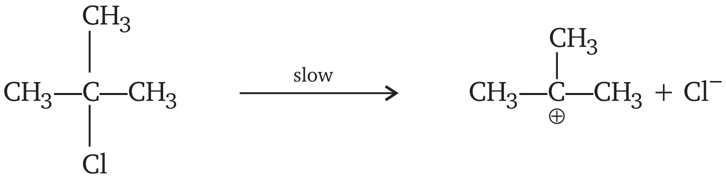


(*ii*) $CH_3CH_2CH{=}CH_2 + HCl \longrightarrow CH_3CH_2CHClCH_3$

Q11. Discuss the mechanism of S_N1 reaction of haloalkanes.

Ans. Tertiary halides undergo S_N1 mechanism. It is a two-step process. First step involves the formation of carbocation:

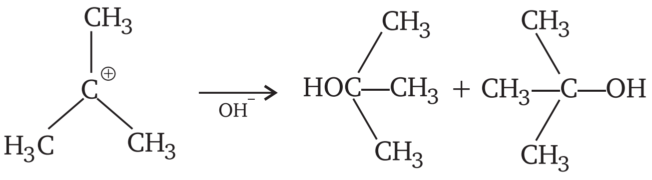
Ist Step:



$$CH_3—\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3 \xrightarrow{\text{slow}} CH_3—\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}—CH_3 + Cl^-$$

In the second step, the carbocation is attacked by the nucleophile to complete the substitution reaction.

IInd Step:



Q12. Account for the following:

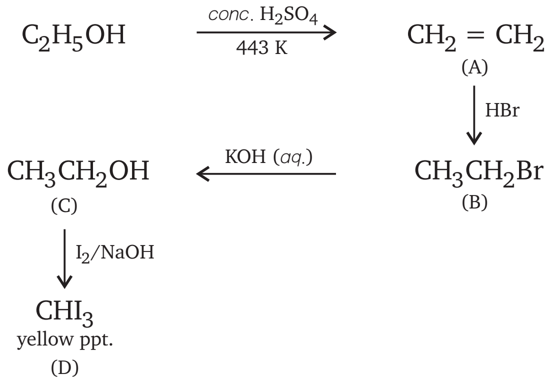
The treatment of an alkyl chloride with aqueous KOH leads to the formation of alcoholic whereas in the presence of alcoholic KOH, alkene is the major product.

Ans. Aqueous KOH gives OH^- ions which can replace Cl^- ions and carry out the nucleophilic substitution reaction, whereas *alc.* KOH gives $C_2H_5O^-$ which is a stronger nucleophile and abstracts H^+ from the β carbon atom and carry out the elimination reaction, thus leading to the formation of an alkene.

Q13. Identify the compounds A, B, C and D in the following sequence of reactions:

$$C_2H_5OH \xrightarrow[443\text{ K}]{conc.\ H_2SO_4} A \xrightarrow{HBr} B \xrightarrow[443\text{ K}]{KOH\ (aq)} C \xrightarrow{I_2,\ NaOH} D$$

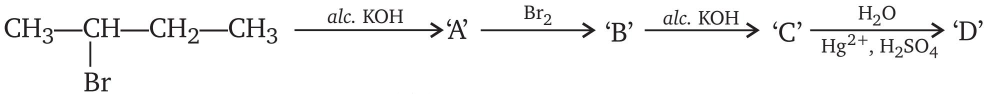
Ans.



$$C_2H_5OH \xrightarrow[443\text{ K}]{conc.\ H_2SO_4} \underset{(A)}{CH_2=CH_2}$$

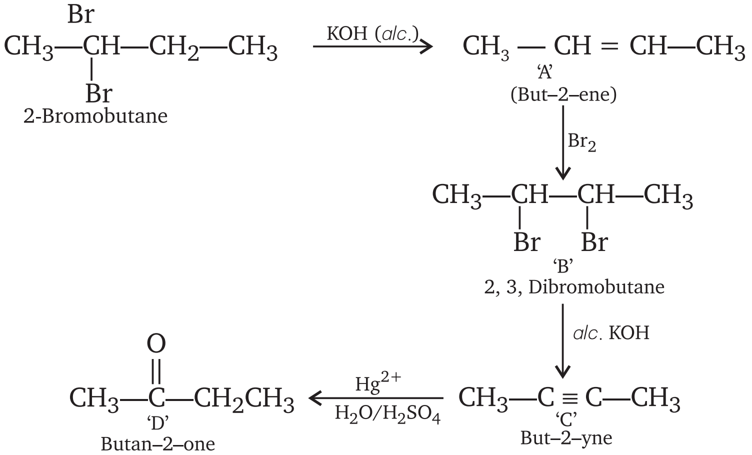
$$\underset{(A)}{CH_2=CH_2} \xrightarrow{HBr} \underset{(B)}{CH_3CH_2Br} \xrightarrow{KOH\ (aq.)} \underset{(C)}{CH_3CH_2OH} \xrightarrow{I_2/NaOH} \underset{\substack{\text{yellow ppt.}\\(D)}}{CHI_3}$$

Q14. Write the structural formula of the organic compounds 'A', 'B', 'C' and 'D' in the following sequence of reaction.



$$CH_3-\underset{\substack{|\\Br}}{CH}-CH_2-CH_3 \xrightarrow{alc.\ KOH} \text{'A'} \xrightarrow{Br_2} \text{'B'} \xrightarrow{alc.\ KOH} \text{'C'} \xrightarrow[Hg^{2+},\ H_2SO_4]{H_2O} \text{'D'}$$

Ans.

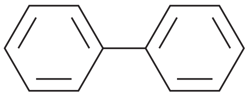


$$\underset{\text{2-Bromobutane}}{CH_3-\underset{\substack{|\\Br}}{CH}-CH_2-CH_3} \xrightarrow{KOH\ (alc.)} \underset{\substack{\text{'A'}\\\text{(But–2–ene)}}}{CH_3-CH=CH-CH_3}$$

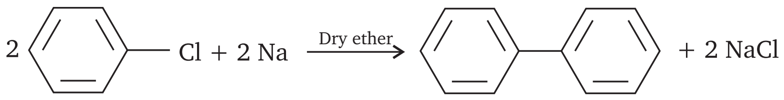
$$\xrightarrow{Br_2} \underset{\substack{\text{'B'}\\\text{2, 3, Dibromobutane}}}{CH_3-\underset{\substack{|\\Br}}{CH}-\underset{\substack{|\\Br}}{CH}-CH_3} \xrightarrow{alc.\ KOH} \underset{\substack{\text{'C'}\\\text{But–2–yne}}}{CH_3-C\equiv C-CH_3} \xrightarrow[H_2O/H_2SO_4]{Hg^{2+}} \underset{\substack{\text{'D'}\\\text{Butan–2–one}}}{CH_3-\overset{\substack{O\\\|}}{C}-CH_2CH_3}$$

Q15. Write the structure of diphenyl. How is it prepared from chlorobenzene?

Ans.

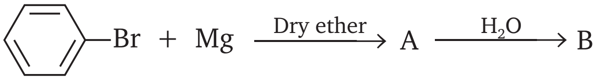


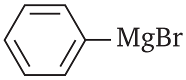
Diphenyl



Diphenyl

Q16. Identify A and B in the following:



Ans. A =  B = 

Q17. Give the IUPAC names of the following:

(*a*) $Cl - CH_2C \equiv C - CH_2 - Br$ (*b*) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

Ans. (*a*) 1-Bromo-4-chlorobut-2-yne

(*b*) 3-chloro-4-methylhexane

Q18. Write the general form of reactions:

(*a*) Wurtz reaction (*b*) Swarts reaction

Ans. (*a*) $R - X + 2Na + R - X \xrightarrow{\text{Dry Ether}} R - R + 2NaX$

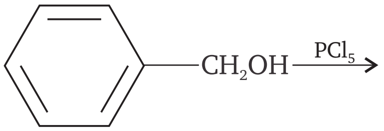
(*b*) $R - Br + AgF \longrightarrow RF + AgBr$

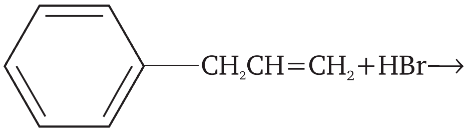
Q19. Which halogen compound in each of the following pairs will react faster in S_N2 reaction: (*CBSE* 2014)

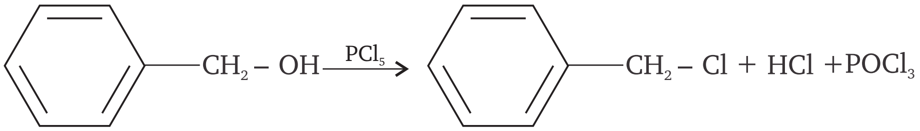
(*i*) CH_3Br Or CH_3I (*ii*) $(CH_3)_3C–Cl$ or $CH_3 - Cl$

Ans. (*i*) CH_3I (*ii*) CH_3Cl

Q.20. Draw the structure of major monohalo products in each of the following ractions: (CBSE 2014)

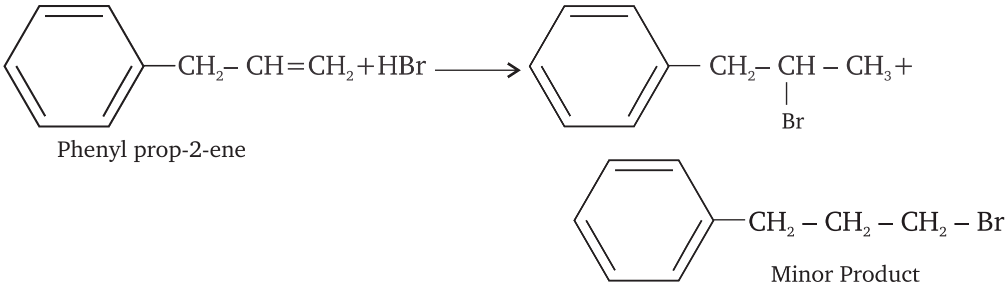
(*i*) 

(*ii*) 

Ans. (*i*) 

Benzyl alcohol

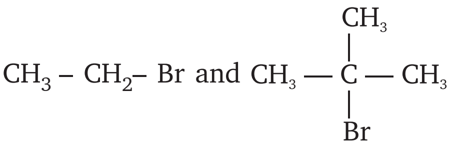
Benzyl chloride

(*ii*) 

Phenyl prop-2-ene

Minor Product

Q.21. Which would undergo S_NI reaction faster in the following pair and why? (*CBSE* 2014)



$CH_3 - CH_2 - Br$ and $CH_3 - \underset{Br}{\overset{CH_3}{C}} - CH_3$ (*CBSE* 2015)

Ans. 3° carbocation > 2° carbocation>1° carbocation > CH_3^+. Therefore, the reactivity of alkyl halides towards S_Nl ractions decreases in the same order.

Among the given compounds bromoethane is a primary alkyl halide which forms a 1° carbocation intermediate in the S_Nl reaction. The other compound is 2-chloro 2-methylpropane which is a tertiary alkyl halide which forms a tertiary carbocation intermediate in the S_Nl reaction.

Hence, 2-bromo-2-methylpropane undergoes an S_Nl reaction faster than bromoethane.

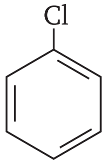
III. Long Answer Type Questions (5 Marks)

Q1. What are haloarenes? How are they classified? Give one method each for the preparation of nuclear and side chain substituted haloarenes.

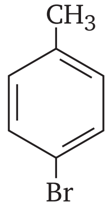
Ans. Haloarenes: The replacement of hydrogen atom(*s*) in an aromatic hydrocarbon chain by the halogen atom(*s*) which results in the formation of aryl halide (haloarene). Haloarenes contain halogen atom(*s*) attached to the sp^2 hybridised carbon atom(*s*) of an aryl group.

They are classified as:

(*i*) **Nuclear halogen derivatives:** Halogen derivatives of aromatic hydrocarbons in which the halogen atom (F, Cl, Br, or I) is directly attached to an aromatic ring are called aryl halides. Some examples of aryl halides are:

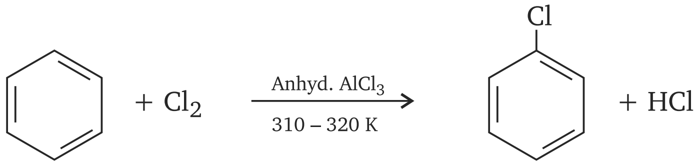


Chlorobenzene



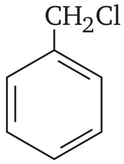
p–bromotoluene

Preparation: They are prepared by direct halogenation of aromatic hydrocarbons.

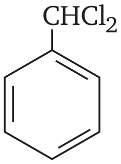


Chlorobenzene

(*ii*) **Side chain halogen derivatives:** Halogen derivatives of aromatic hydrocarbons in which the halogen atom is linked to one of the carbon atoms of the side chain carrying the aryl group are called aryl halides. For example,

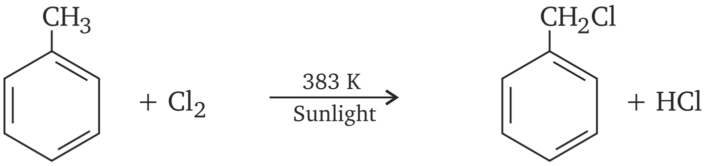


Benzyl chloride
Chlorophenylmethane



Benzal chloride
1, 1–Dichloro–1–phenylmethane

Preparation: By the direct halogenation of a suitable arene.



Toluene

Benzyl chloride

Q2. (*a*) How will you bring about the following conversions:

(*i*) Ethene to Bromoethene? (*ii*) Toluene to Benzene?

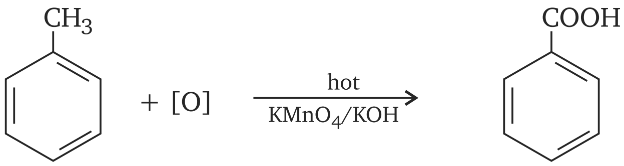
(*b*) What happens when:

(*i*) Propene is treated with HBr in the presence of peroxide?

(*ii*) Benzene is treated with methyl chloride in the presence of $AlCl_3$?

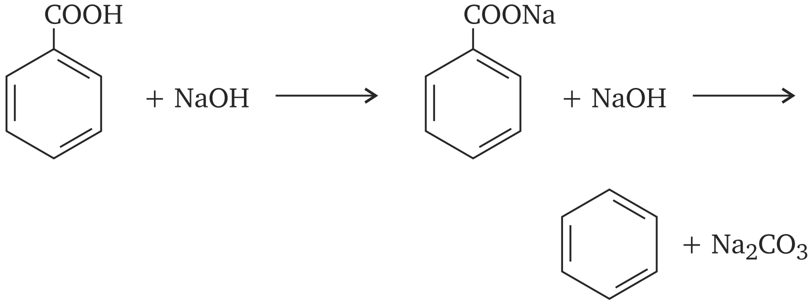
Ans. (*a*) (*i*) $\underset{\text{Ethene}}{CH_2 = CH_2} + Br_2 \xrightarrow[\text{Sunlight}]{\text{heat}} \underset{\text{Bromoethene}}{CH_2 = CHBr}$

(*ii*)



Benzoic acid

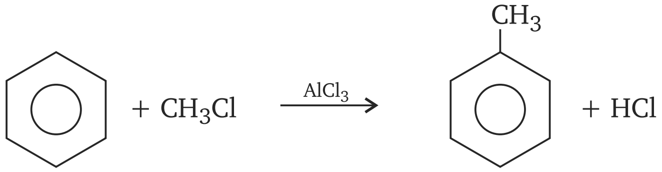
Then,



Benzene

(*b*) (*i*) $\underset{\text{Propene}}{CH_3CH = CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1 – Bromopropane}}{CH_3CH_2CH_2Br}$

(*ii*)



Benzene

Toluene

Q3. Give the names of the predominant products obtained when bromoethane is treated with following:

(*i*) An aqueous Alkali (*ii*) Sodium metal in dry ether

(*iii*) An alcoholic potassium hydroxide solution (*iv*) Magnesium followed by ethanol

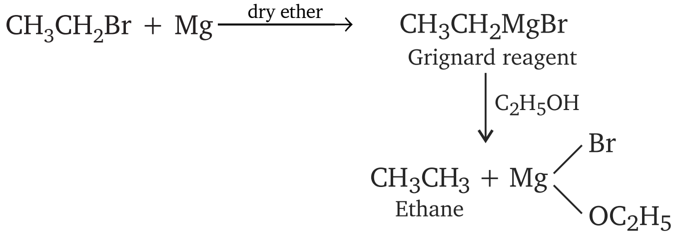
(*v*) Aminoethane

Ans. (*i*) $CH_3CH_2Br \xrightarrow{aq.\ KOH/NaOH} \underset{\text{Ethanol}}{CH_3CH_2OH} + KBr$

(*ii*) $2CH_3CH_2Br \xrightarrow{Na/ether} CH_3CH_2CH_2CH_3 + 2NaBr$

(*iii*) $CH_3CH_2Br \xrightarrow{Alcoholic\ KOH} \underset{\text{Ethene}}{CH_2 = CH_2} + KBr + H_2O$

(*iv*)



$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr} \xrightarrow{C_2H_5OH} \underset{\text{Ethane}}{CH_3CH_3} + Mg\begin{matrix} Br \\ OC_2H_5 \end{matrix}$$

(*v*) $CH_3CH_2Br + C_2H_5NH_2 \longrightarrow \underset{\text{Diethylamine}}{(C_2H_5)_2NH} + HBr$

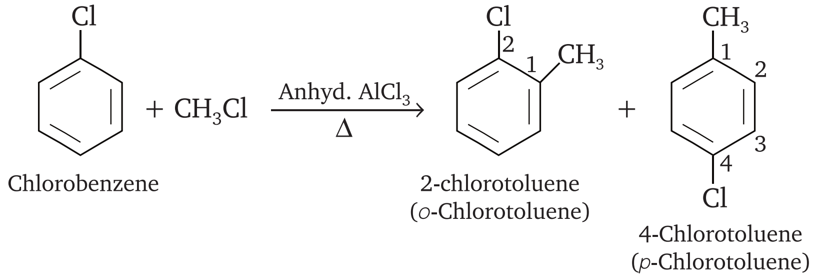
Q.4. How do you convert the following:

(*i*) Prop-1-ene to 1-fluoroproane (*ii*) Chlorobenzene to 2-chlorotoluene

(*iii*) Ethanol to propanenitrile

Ans. (*i*) $\underset{\text{Prop-1-ene}}{CH_3 - CH = CH_2} + HI \xrightarrow{\text{Peroxide}} \underset{\text{1-Iodopropane}}{CH_3 - CH_2 - CH_2 - I}$

(*ii*)



(*iii*) $\underset{\text{Ethanol}}{CH_3 - CH_2 - OH} + KBr \xrightarrow{H_2SO_4} \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} \xrightarrow[-KBr]{\text{Reflux with KCN in alcohol}} \underset{\text{Propanenitrile}}{CH_3 - CH_2 - CN}$

Or

Write the main products when

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

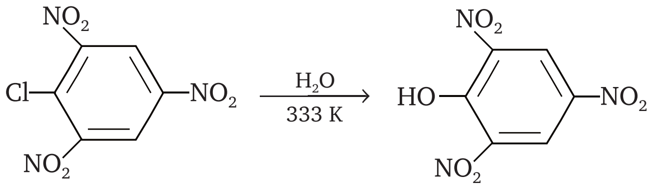
(*ii*) 2,4,6-trinitrochlorobenzene is subject to hydrolysis.

(*iii*) methl chloride is treated with AgCN.

Ans. (*i*) When *n*-butyle chloride is treated with alcoholic KOH, but-1-ene is formed:

$$CH_3 - CH_2 - CH_2 - CH_2 - Cl + alc.\ KOH \longrightarrow \underset{\text{But - 1 - ene}}{CH_3 - CH_2 - CH = CH_2} + KCl + H_2O$$

(*ii*) 2,4,6,trinitrochlorobenzene under mild hydrolysis conditions (H_2O/323 K) gives 2,4,6,-trinitrophenol or picric acid



2,4,6-trinitrochlorobenzene   2,4,6-Trinitrophenol (Picric acid)

(*iii*) When methyl chloride is treated with AgCN, methyl cyanide is formed:

$$CH_3 - Cl \quad + \quad AgCN \quad \rightarrow \quad CH_3 - C \equiv N \quad + \quad AgCl$$

Methyl chloride   Methyl cyanide

IV. Value-Based Questions

Q1. Abhishek decided to visit his village during summer holidays with his friends, where his grandparents were staying. One day, while going for a walk they happened to hear the farmers discussing about how the pests have destroyed their crops, which caused a great loss, inspite of spraying pesticides. One of them suggested that they must use DDT to have better control on pests and others agreed. On hearing this Abhishek and his friends were worried and they convinced the farmers against the usage of DDT.

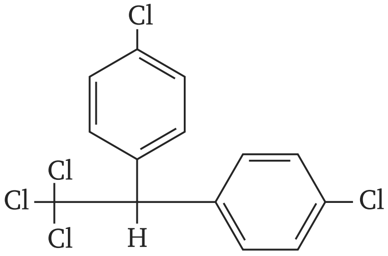
(*a*) Write expansion of DDT, and its structure.

(*b*) Why were Abhishek and his friends worried about the use of DDT?

(*c*) What are the values that can be learnt from the action of Abhishek and his friends?

Ans. (*a*) Dichlorodiphenyltrichloromethane

Structure of DDT:



(*b*) DDT is highly toxic and is a stable compound. Its residue accumulates in the environment which can be toxic for living beings.

(*c*) Self awareness and Environmental conservation.

Q2. A case study states that Chlorofluorocarbons (CFCs) and gas emitted from the exhaust system of supersonic aeroplanes might be slowly depleting-the concentration of the ozone layer in the upper atmosphere.

(*a*) Name the gases emitted by the exhaust of supersonic jet aeroplanes.

(*b*) Write the chemical reactions involved in the ozone layer depletion.

(*c*) Mention the values that are learnt by the students in this case study.

Ans. (*a*) Freons and gases like Nitric oxide

(*b*) $NO + O_3 \longrightarrow NO_2 + O_2$

$NO_2 + O \longrightarrow NO + O_2$

$CF_2Cl_2 \xrightarrow{\text{light}} CF_2Cl^{\bullet} + Cl^{\bullet}$

$CFCl_3 \longrightarrow CFCl_2^{\bullet} + Cl^{\bullet}$

$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$

$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$

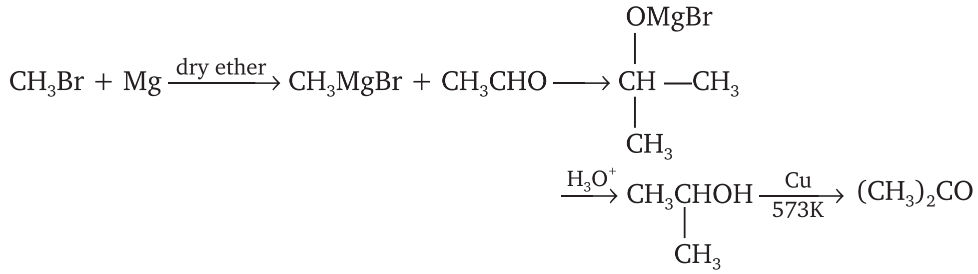
(*c*) Environmental conservation

V. HOTS Questions

Q1. Do the following conversions:

(*i*) Methyl bromide to acetone (*ii*) Benzyl alcohol to 2-phenylacetic acid

Ans. (*i*)



$$CH_3Br + Mg \xrightarrow{\text{dry ether}} CH_3MgBr + CH_3CHO \longrightarrow \underset{CH_3}{\overset{OMgBr}{CH}}-CH_3 \xrightarrow{H_3O^+} \underset{CH_3}{CH_3CHOH} \xrightarrow[573K]{Cu} (CH_3)_2CO$$

(*ii*) $C_6H_5CH_2OH + SOCl_2 \longrightarrow C_6H_5CH_2Cl + KCN \longrightarrow C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$

Q2. How will you distinguish between the following pairs of compounds:

(*i*) Chloroform and carbon tetrachloride.

(*ii*) Benzyl alcohol and chlorobenzene.

Ans. (*i*) On heating chloroform and carbon tetrachloride with aniline and ethanoic acid and potassium hydroxide separately chloroform forms a pungent smelling isocyanide compound but carbon tetrachloride does not form this compound.

(*ii*) On adding sodium hydroxide and silver nitrate to both of the compounds, benzyl chloride forms as a white precipitate but chlorobenzene does not form any white precipitate.

Q3. Give reasons for the following:

(*i*) Ethyl iodide undergoes S_N2 reactions faster than ethyl bromide.

(*ii*) (±) 2–Butanol is optically inactive.

(*iii*) C—X bond length in halobenzene is smaller than C—X bond length in CH_3–X.

Ans. (*i*) Because in ethyl iodide, iodide (I^-) act as the best leaving group among all the halide ions. Rate of S_N2 reaction $\propto$ ability of leaving group.

(*ii*) (±) 2–butanol is a racemic mixture which is optically inactive due to the external compensation.

(*iii*) Due to resonance in halobenzene, it has smaller bond length value as compared to CH_3–X.