10 Haloalkanes and Haloarenes

LESSON AT A GLANCE

- **Alkyl halides or haloalkanes:** Organic compounds in which one or more hydrogen atoms of an alkane have been substituted by 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 made by reaction of an alcohol with a halogen carrier.
- **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 a carbon that is bonded to four different groups. It is also called chiral carbon.
- **Enantiomers:** These are optical isomers that are mirror images.
- **Diastereoisomers:** These are optical isomers that are not mirror images.
- **Racemic mixture:** A mixture of equal quantities of the *d*- and *l*- forms of an optically active compound. This is denoted by the prefix *dl* (*e.g.*, *dl*-lactic acid). A recemic mixture shows no optical activity.
- **Meso Compound:** It is a compound that has more than one asymmetric carbon and that is superimposable on its mirror image.
- **Haloalkanes:** Haloalkanes are the compounds in which a halogen is bonded to an alkyl group.

  These are classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present as mono, di-, tri, tetrahaloalkanes *etc.*

- **Polarimeter:** Optical activity of a compound is detected and measured by means of a polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarised light is rotated through a certain number of degrees either to the right (clockwise) or to the left (anticlockwise).
- **Dextrorotatory:** The compound which rotates the plane of polarised light to the right (clockwise) is said to be Dextrorotatory. It is indicated by the sign (+).
- **Laevorotatory:** The compound which rotates the plane of polarised light to the left (anticlockwise) is said to be Laevorotatory. It is indicated by the sign (–).
- **Plane of symmetry:** A plane which divides an object into two symmetrical halves is said to be plane of symmetry. For example, a person's hat has a plane of symmetry. A person's hand or gloves lack plane of symmetry.
- **Asymmetric molecule:** In all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.
- **Symmetrical objects:** Those objects whose projections are superimposable on their mirror images are symmetrical objects. *e.g.*, a sphere, a cube, a cone, all are identical to their mirror images.
- **Chirality:** The property of existing in left and right-handed structural forms. The necessary condition for a molecule to exhibit optical isomerism is that it should be dissymmetric.
- **Enantiomers:** The non-superimposable mirror image forms of a chiral molecule are called Enantiomers. They represent two optical isomers (+) and (–). Their opposite rotatory powers are due to the opposite arrangements of groups around the asymmetric carbon atom.
- **Wurtz reaction:** Alkyl halides react with sodium in dryether to give hydrocarbons containing double the number of carbon atoms present in the halide.

$$2RX + 2Na \longrightarrow R - R + 2NaX$$

- **Trichloromethane (Chloroform)**
  Applications:
  (*i*) Chloroform is employed as a solvent for fats, alkaloids and other substances,
  (*ii*) In the production of freon refrigerant R – 22.
- **Tri-iodomethane (Iodoform)**
  Uses
  (*i*) A yellow volatile solid sweet smelling haloform, made by the haloform reaction.
  (*ii*) It was used earlier as an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.
- **Tetra chloromethane (Carbontetrachloride) CCl_4:** A colourless volatile liquid with a characteristic colour, virtually soluble in water but miscible with many organic liquids, such as ethanol and benzene.
- **Freons (CCl_2F_2):** The chlorofluoro compounds of methane and ethane are collectively known as freons.

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) $p\text{-}ClC_6H_4CH_2CH(CH_3)_2$
(xi) $m\text{-}ClCH_2C_6H_4CH_2C(CH_3)_3$
(xii) $o\text{-}BrC_6H_4CH(CH_3)CH_2CH_3$

Ans. (*i*) 2-Chloro-3-methylbutane (Secondary alkyl halide)
(*ii*) 3-Chloro-4-methylhexane (Secondary alkyl halide)
(*iii*) 1-Iodo-2, 2-dimethylbutane (Primary alkyl halide)

(*iv*) 1-Bromo-3, 3-dimethyl-1-phenylbutane (Benzylic secondary halide)

(*v*) 2-Bromo-3-methylbutane (Secondary alkyl halide)

(*vi*) 1-Bromo-2-ethyl-2-methylbutane (Primary alkyl halide)

(*vii*) 3-Chloro-3-methylpentane (Tertiary alkyl halide)

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

(*ix*) 4-Bromo-4-methylpent-2-ene (Allyl halide)

(*x*) 2-Methyl-1- (4-chlorophenyl) propane (Aryl halide)

(*xi*) 1-(3-Chloromethylphenyl)-2, 2-dimethylpropane (Benzylic primary halide)

(*xii*) 2-(2-Bromophenyl) butane (Aryl halide)

10.2 *Give the IUPAC names 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) $(CH_3)_3CCH{=}C(Cl)C_6H_4I\text{-}p$

Ans. (*i*) 2-Bromo-3-Chlorobutane

(*ii*) 1-Bromo-1-Chloro-1, 2, 2-trifluoroethane

(*iii*) 1-Bromo-4-Chlorobut-2-yne

(*iv*) 1, 1, 1, 2, 3, 3, 3-Heptachloro-2-(trichloromethyl) propane

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

(*vi*) 1-Chloro-3, 3-dimethyl-1-(4-iodophenyl) 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

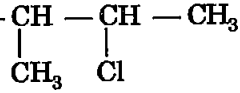
(v) Perfluorobenzene

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

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

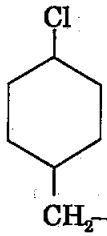
(viii) 1,4-Dibromobut-2-ene

Ans. (*i*)

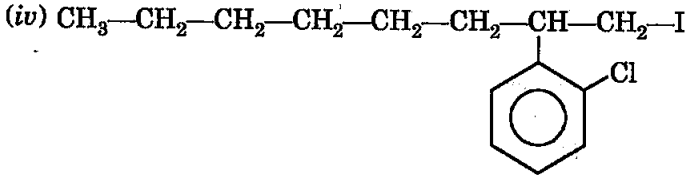


(*ii*)

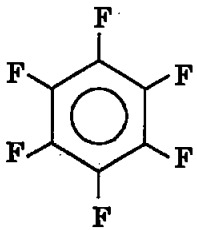
(*iii*)



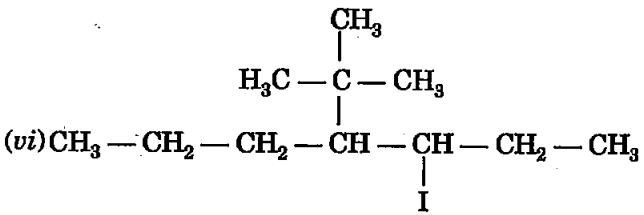
(*iv*)



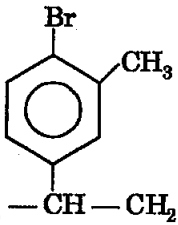
(*v*)



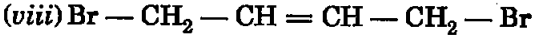
(*vi*)



(*vii*)



(*viii*)



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

(i) CH_2Cl_2

(ii) $CHCl_3$

(iii) CCl_4

Ans. $CHCl_3$ has the highest dipole moment.

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. Molecular formula C_5H_{10} indicates that it can be either an alkene or a cyclic hydrocarbon. Since it does not react with chlorine in dark so it cannot be an alkene. It gives only a single monochloro derivative. It shows that it is cyclic hydrocarbon in which all the hydrogen atoms are identical. it can be only cyclopentane.

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

Ans. The four possible isomers for the compound having formula C_4H_9Br are as follows:

(i) $CH_3 - CH_2 - CH_2 - CH_2 - Br$ (1-Bromobutane)

(ii) $CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$ (2-Bromobutane)

(iii) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - Br$ (1-Bromo-2-methylpropane)

(iv) $CH_3 - \underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$ (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)* $\underset{\text{1-Butanol}}{CH_3 - CH_2 - CH_2 - CH_2 - OH} \xrightarrow{\text{red P} + I_2} \underset{\text{1-Iodobutane}}{CH_3 - CH_2 - CH_2 - CH_2 - I}$

(ii) $\underset{\text{1-Chlorobutane}}{CH_3 - CH_2 - CH_2 - CH_2 - Cl} + NaI \xrightarrow[\text{reflux}]{\text{acetone}} CH_3 - CH_2 - CH_2 - CH_2 - I + NaCl$

(*iii*) $CH_3-CH_2-CH=CH_2 + HBr \xrightarrow{\text{peroxide}}$

But-1-ene

$CH_3-CH_2-CH_2-CH_2-Br$

1-Bromobutane

$CH_3-CH_2-CH_2-CH_2-Br + NaI \xrightarrow[\text{reflux}]{\text{acetone}} CH_3-CH_2-CH_2-CH_2-I$

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

Ans. Those species, which can attack as nucleophile from more than one centres, are known as ambident nucleophiles. Such as cyanide ion has a pair of electron at carbon as well as at nitrogen and can use any of these electron pairs, depending upon the reaction conditions.

$$\ddot{C}\equiv N:^{\ominus}$$

10.9 *Which compound in each of the following pairs will react faster in S_N2 reaction with ^-OH?*

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

Ans. (*i*) CH_3I

(*ii*) CH_3Cl

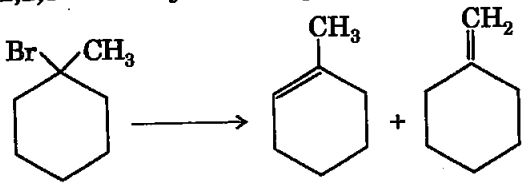
10.10 *Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:*

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane

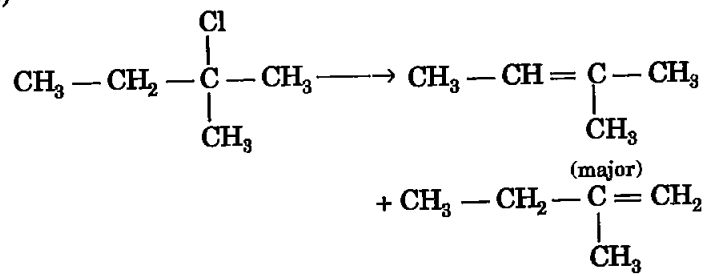
(iii) 2,2,3-Trimethyl-3-bromopentane.

Ans. (*i*)

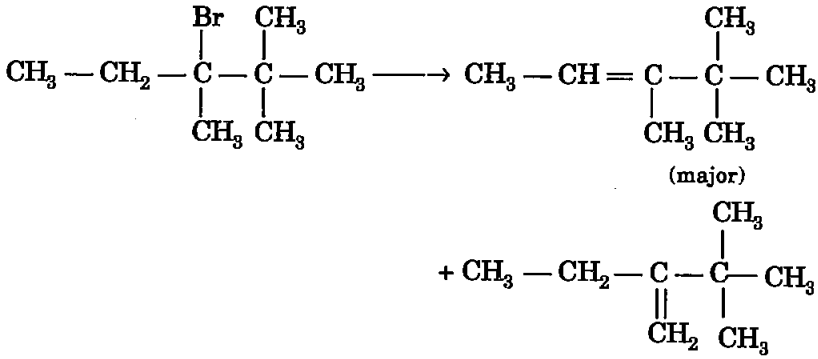


(major)

(*ii*)



(*iii*)



(major)

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*) $CH_3-CH_2-OH \xrightarrow{HBr} CH_3-CH_2-Br$

Ethanol

$\xrightarrow{HC\equiv C^-\,Na^+} CH_3-CH_2-C\equiv CH$

But-1-yne

(*ii*) $CH_3-CH_3 + Br_2 \xrightarrow{h\nu} CH_3-CH_2-Br$

Ethane

$\xrightarrow[\Delta]{\text{alc. KOH}} CH_2=CH_2 + Br_2 \longrightarrow CH_2(Br)-CH_2(Br)$

Ethene

$\xrightarrow{\text{alc. KOH}} CH_2=CH-Br$

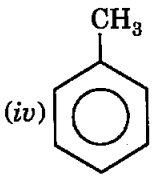
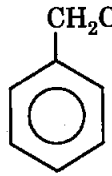
Bromoethene

(*iii*) $CH_3—CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3—CH_2—CH_2—Br$

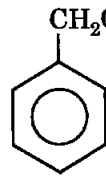
Propene

$\xrightarrow{AgNO_2} CH_3—CH_2—CH_2—NO_2$

1- Nitropropane

(*iv*)  $+ Cl_2 \xrightarrow{h\nu}$ 

Toluene

$\xrightarrow{\text{NaOH solution}}$ 

Benzyl alcohol

(*v*) $CH_3—CH=CH_2 + Br_2 \longrightarrow CH_3—\underset{Br}{\underset{|}{CH}}—\underset{Br}{\underset{|}{CH_2}}$

Propene

$\xrightarrow{NaNH_2/\text{ liq. } NH_3} CH_3—C\equiv CH$

Propyne

(*vi*) $CH_3—CH_2—OH + SOCl_2 \longrightarrow CH_3—CH_2—Cl$

Ethanol

$\xrightarrow{AgF} CH_3—CH_2—F$

Ethyl fluoride

(*vii*) $CH_3—Br \xrightarrow{CH\equiv C^{\ominus}\ Na^{\oplus}} CH_3—C\equiv CH$

Bromomethane

$\xrightarrow{H_2O/H_2SO_4/Hg^{2+}} CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

Propanone

(*viii*) $CH_3-CH_2-CH=CH_2 + HBr \longrightarrow$

But-1-ene

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

$\xrightarrow[\text{alc. KOH}]{\Delta}$

$CH_3-CH=CH-CH_3$

But-2-ene

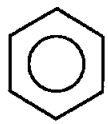
(*ix*) $CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[\text{dry ether}]{Na}$

1-Chlorobutane

$CH_3-(CH_2)_6-CH_3$

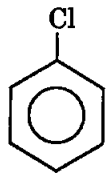
n-Octane

(*x*)

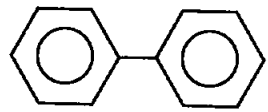


Benzene

$\xrightarrow{Cl_2/FeCl_3}$



$\xrightarrow{Na}$



Diphenyl

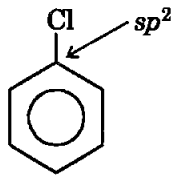
10.12 *Explain why:*

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

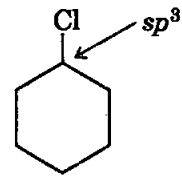
(ii) alkyl halides, though polar, are immiscible with water?

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

Ans. (*i*) In both the compounds, C—Cl bond is polar due to high electronegativity of chlorine. But in case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So the net dipole moment is lower in chlorobenzene.



Chlorobenzene



Cyclohexyl chloride

(*ii*) Alkyl halides are polar but are insoluble in water because they are not able to form the hydrogen bonds with water molecules.

(*iii*) Grignard reagents react with water to form alkanes.

$$R-Mg-X + H_2O \longrightarrow R-H + Mg\begin{matrix}X\\OH\end{matrix}$$

So, they must be prepared under anhydrous conditions because any water present will react with Grignard reagents.

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

Ans. Uses of freon 12

(*i*) For aerosol propellants.

(*ii*) Refrigeration and air conditioning.

Uses of DDT:

(*i*) As insecticide.

Uses of CCl_4

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

(*ii*) In the synthesis of chloroform carbons 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 substance.

(*ii*) Used to manufacture pharmaceuticals.

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

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

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

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

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

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

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

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

Ans. (i) $CH_3 - CH_2 - CH_2 - Cl + NaI \xrightarrow[heat]{acetone} CH_3 - CH_2 - CH_2 - I$

(ii) $(CH_3)_3C - Br + KOH \xrightarrow[heat]{ethanol} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2$

(iii) $CH_3 - \underset{\displaystyle Br}{\overset{\displaystyle |}{CH}} - CH_2 - CH_3 + NaOH \xrightarrow{water} CH_3 - \underset{\displaystyle OH}{\overset{\displaystyle |}{CH}} - CH_2 - CH_3$

(iv) $CH_3 - CH_2 - Br + KCN \xrightarrow{aq.\ ethanol} CH_3 - CH_2 - CN$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow C_6H_5 - O - C_2H_5$

(vi) $CH_3 - CH_2 - CH_2 - OH + SOCl_2 \longrightarrow CH_3 - CH_2 - CH_2 - Cl$

(vii) $CH_3 - CH_2 - CH = CH_2 + HBr \xrightarrow{peroxide} CH_3 - CH_2 - CH_2 - CH_2 - Br$

(viii) $CH_3 - CH = C(CH_3)_2 + HBr \longrightarrow CH_3 - CH_2 - \underset{\displaystyle Br}{\overset{\displaystyle |}{C}}(CH_3)_2$

10.15 *Write the mechanism of the following reaction:*

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

Ans. This reaction follows S_N2 type of mechanism

$$KCN \xrightarrow{EtOH - H_2O} K^+ + \overset{\ominus}{C}N$$

$$CH_3-CH_2-CH_2-CH_2-Br + \overset{\ominus}{C}N \longrightarrow CH_3-CH_2-CH_2-CH_2-CN + Br^-$$

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. The increasing order of reactivity towards S_N2 displacement:

(*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. $C_6H_5CHCl\,C_6H_5$ is more easily hydrolysed by aqueous KOH.

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

Ans. *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers because it is more symmetrical and packing is better in solid form.

10.19 *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-buty iodide

(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)* $CH_3—CH=CH_2 \xrightarrow{B_2H_6} (CH_3—CH_2—CH_2—)_3B$
Propene

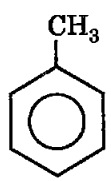
$(CH_3—CH_2—CH_2—)_3B \xrightarrow{\text{aq. NaOH}} CH_3—CH_2—CH_2—OH$
Propan-1-ol

(ii) $CH_3—CH_2—OH \xrightarrow{PCl_5} CH_3—CH_2—Cl$
Ethanol

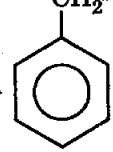
$CH_3—CH_2—Cl \xrightarrow{HC\equiv C^{\ominus}Na^{\oplus}} CH_3—CH_2—C\equiv CH$
But-1-yne

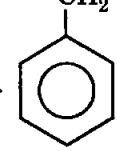
(iii) $CH_3—CH_2—CH_2—Br \xrightarrow[\Delta]{\text{alc. KOH}} CH_3—CH_2=CH_2$
1-Bromopropane

$CH_3—CH_2=CH_2 \xrightarrow{HBr} CH_3—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$
2-Bromopropane

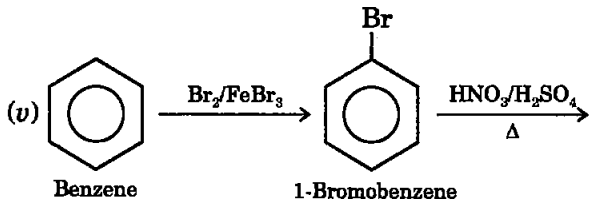
(iv) 

Toluene

$\xrightarrow{Cl_2/h\nu}$ 

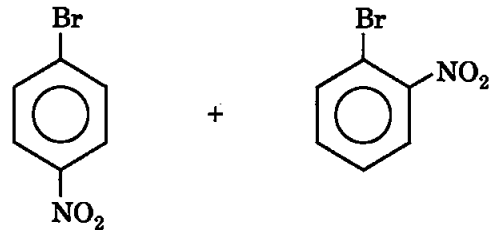
$\xrightarrow{H_2O/OH^-}$ 

Benzyl alcohol



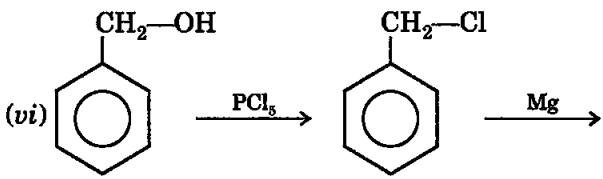
Benzene

1-Bromobenzene

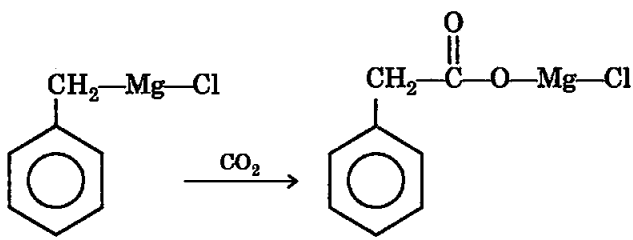


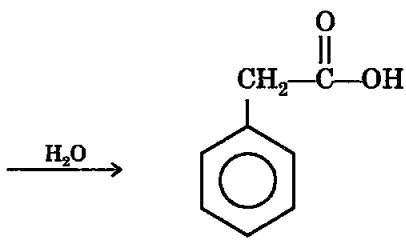
1-Bromo-4-nitrobenzene
(4-Bromonitrobenzene)

1-Bromo-2-nitrobenzene
(2-Bromonitrobenzene)



Benzyl
alcohol





2-Phenylethanoic acid

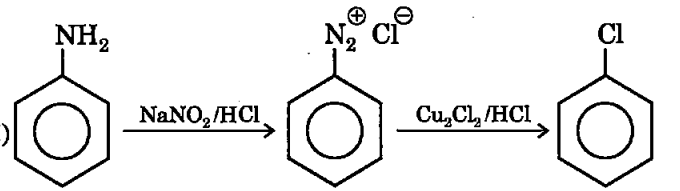
(*vii*) $CH_3 - CH_2 - OH \xrightarrow{SOCl_2} CH_3 - CH_2 - Cl$

Ethanol

$\xrightarrow{KCN} CH_3 - CH_2 - CN$

Propanenitrile

(*viii*)



Aniline Chlorobenzene

(*ix*) $CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2 - CH_3 \xrightarrow{Na/ether}$

2-Chlorobutane

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

3, 4-Dimethylhexane

(*x*) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} = CH_2 \xrightarrow{HCl} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}} - CH_3$

2-Methyl-1-propene 2-Chloro-2-methylpropane

(*xi*) $CH_3 - CH_2 - Cl \xrightarrow{Mg} CH_3 - CH_2 - Mg - Cl$

Ethyl chloride

$\xrightarrow{CO_2} CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - O - Mg - Cl$

$\xrightarrow{H_2O} CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - OH$

Propanoic acid

(*xii*) $CH_3-CH_2-CH=CH_2 \xrightarrow{HBr/peroxide}$

But-1-ene

$CH_3-CH_2-CH_2-CH_2-Br$

$\downarrow$ NaI/acetone

$CH_3-CH_2-CH_2-CH_2-I$

n-butyl iodide

(*xiii*) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow{\text{alc. KOH}} CH_3-CH=CH_2$

2-Chloropropane

$\xrightarrow{HBr/peroxide} CH_3-CH_2-CH_2-Br$

$\xrightarrow{\text{aq. NaOH}} CH_3-CH_2-CH_2-OH$

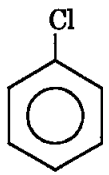
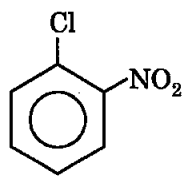
1-Propanol

(*xiv*) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{I_2/NaOH} CH_3-\overset{\overset{O}{||}}{C}-CH_3 \longrightarrow$

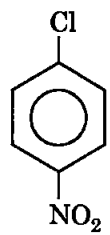
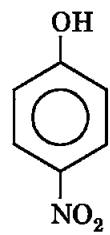
Isopropyl alcohol

$CH_3-\overset{\overset{O}{||}}{C}-CI_3 \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-O^-Na^+ + CHI_3$

Sodium acetate Iodoform

(*xv*)  $\xrightarrow{HNO_3/H_2SO_4}$ 

Chlorobenzene

 + 

NaOH soln.
Boil

p-Nitrophenol

(*xvi*) $CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc. KOH}} CH_3-CH=CH_2$

2-Bromopropane

$\xrightarrow{HBr/peroxide} CH_3-CH_2-CH_2-Br$

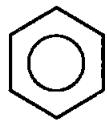
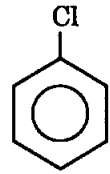
1-Bromopropane

(*xvii*) $CH_3-CH_2-Cl \xrightarrow{Na/ether}$

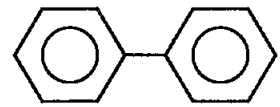
Chloroethane

$CH_3-CH_2-CH_2-CH_3$

Butane

(*xviii*)  $\xrightarrow{Cl_2/FeCl_3}$ 

Benzene Chlorobenzene

$\xrightarrow{Na/ether}$ 

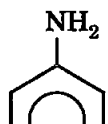
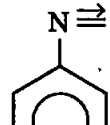
Diphenyl

(*xix*) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow{\text{alc. KOH}} CH_3-\underset{CH_3}{\overset{CH_3}{|}}{C}=CH_2$

tert-butyl bromide

$\xrightarrow[\text{peroxide}]{HBr} CH_3-\underset{CH_3}{\overset{CH_3}{|}}{CH}-CH_2-Br$

Iso-butyl bromide

(*xx*)  $\xrightarrow[\text{heat}]{CHCl_3/KOH}$ 

Aniline Phenylisocyanide

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 ionized 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 reduces the basic character of OH^- ions which therefore, fail 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. There can be two primary alkyl halides with the formula C_4H_9Br.

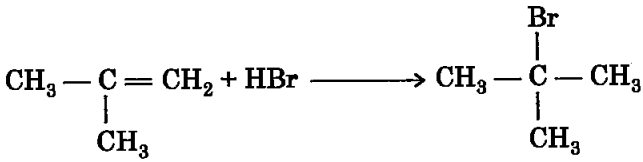
$CH_3 - CH_2 - CH_2 - CH_2 - Br$ (*n*-butyl bromide)

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_2 - Br \text{ (}iso\text{-butyl bromide)}$$

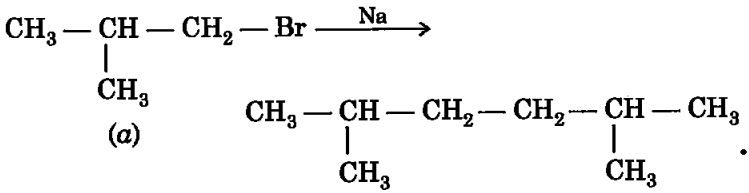
Since compound '*a*' on reaction with sodium metal gives a product which is different from the product formed by the reaction of *n*-butyl bromide with sodium metal, so '*a*' can be *iso*-butyl bromide only. It will react with alc. KOH to give 2-methylpropene '*b*'. When HBr is added to '*b*', the product formed would be 2-bromo-2-methylpropane (*c*) as the addition will follow Markovnikov's rule. The reactions involved are represented as follows:

$$\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH_3 - CH - CH_2 - Br}} \xrightarrow{\text{alc. KOH}} \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH_3 - C = CH_2}}$$

(*a*) (*b*)



(*b*) (*c*)



(*a*) (*d*)

10.22 *What happens when:*

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

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

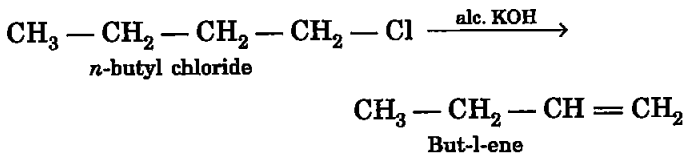
(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

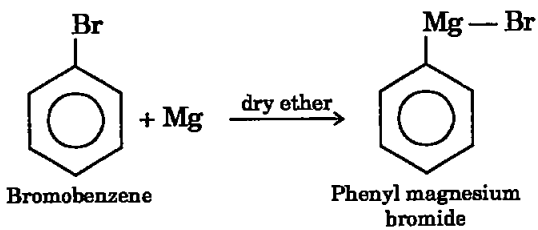
(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN?

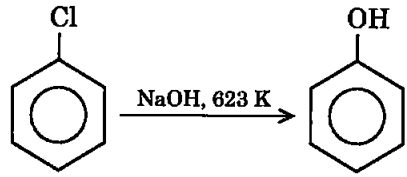
Ans. (*i*) But-l-ene is formed when *n*-butyl chloride is treated with alcoholic KOH.



(*ii*) Phenyl magnesium bromide is formed when bromobenzene is treated with magnesium.



(*iii*) Chlorobenzene on hydrolysis yields phenol.



(*iv*) Ethyl chloride on treatment with aqueous KOH yields ethanol.

$$\underset{\text{Ethyl chloride}}{CH_3 - CH_2 - Cl} \xrightarrow{\text{aq. KOH}} \underset{\text{Ethanol}}{CH_3 - CH_2 - OH}$$

(*v*) Methyl bromide on treatment with sodium in the presence of dry ether yields ethane.

$$\underset{\text{Methyl bromide}}{2CH_3 - Br} + 2Na \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaBr$$

(*vi*) The product formed is methyl cyanide when methyl chloride is treated with KCN.

$$\underset{\text{Methyl chloride}}{CH_3 - Cl} + KCN \longrightarrow \underset{\substack{\text{Methyl cyanide} \\ \text{(Ethanenitrile)}}}{CH_3 - CN} + KCl$$

❑❑❑