CHAPTER / 14

# Haloalkanes and Haloarenes

## Topics Covered

*Haloalkanes*
- Classification
- Nomenclature
- Methods of Preparation
- Properties of Haloalkanes

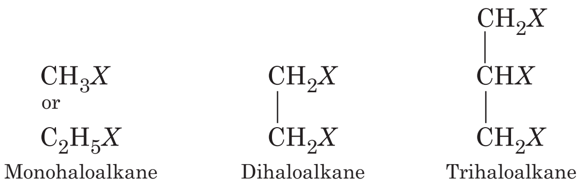
*Haloarenes*
- Classification
- Nomenclature
- Methods of Preparation
- Physical Properties
- Chemical Properties
- Polyhalogen Compounds

## TOPIC ~01 Haloalkanes

Haloalkanes are also known as **alkyl halides**. They contain halogen atom attached to $sp^3$-hybridised carbon atom(s) of an alkyl group.

### Classification

Depending on the number of halogen atoms in their structures, haloalkanes may be mono, di, tri or polyhalogen (tetra, penta, etc.) compounds.



$$\begin{array}{c} CH_3X \\ \text{or} \\ C_2H_5X \end{array} \qquad \begin{array}{c} CH_2X \\ | \\ CH_2X \end{array} \qquad \begin{array}{c} CH_2X \\ | \\ CHX \\ | \\ CH_2X \end{array}$$

Monohaloalkane Dihaloalkane Trihaloalkane

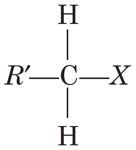
(where, $X = F, Cl, Br, I$)

### Monohalogen Derivatives of Alkanes

When one hydrogen atom of alkane is replaced by halogen atom (F, Cl, Br, I) then monohalogen derivatives of alkanes are formed. The general formula of their homologous series is $C_nH_{2n+1}X$.

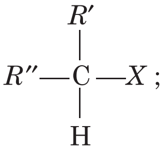
They are further classified as primary (1°), secondary (2°) or tertiary (3°) depending upon the nature of carbon atom to which the halogen is attached.

e.g.



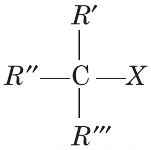
$$R'-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-X$$

Primary (1°)



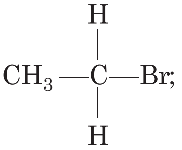
$$R''-\overset{\displaystyle R'}{\underset{\displaystyle H}{C}}-X$$

Secondary (2°)



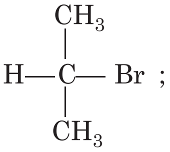
$$R''-\overset{\displaystyle R'}{\underset{\displaystyle R'''}{C}}-X$$

Tertiary (3°)



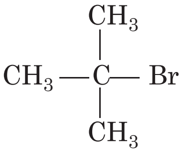
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Br$$

Bromoethane
(Primary or 1°)



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

2-bromopropane
(Secondary or 2°)



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

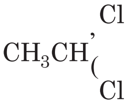
2-bromo-2-methylpropane
(Tertiary or 3°)

## Disubstituted Haloalkanes

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo compounds having same type of halogen atoms are further classified as:

(i) ***Geminal* halides** In these halides, halogen atoms are present on the same carbon atom.

e.g.

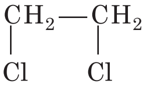


$$CH_3CH\begin{matrix}Cl\\Cl\end{matrix}$$

*Gem*-dihalide ethylene dichloride 1, 1-dichloroethane

(ii) ***Vicinal* halides** In these halides, halogen atoms are present on the adjacent carbon atoms.

e.g.



$$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH_2}$$

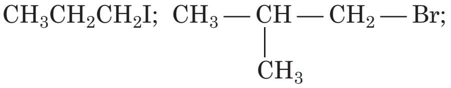
*Vic*-dihalide(ethylene dichloride 1, 2-dichloroethane)

## Nomenclature

The **common names** of alkyl halides are derived by naming the alkyl group followed by the name of halide (chloride, bromide, etc). Here, the prefixes *n*-, *iso*-, *sec*-, *tert*-, etc. are used.

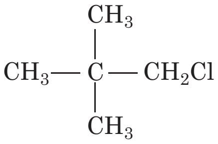
In **IUPAC system**, alkyl halides are named as halosubstituted hydrocarbons, i.e. haloalkanes. The names are written by prefixing the word 'halo' to the name of alkane corresponding to the longest continuous carbon chain having the halogen atom.

e.g.



$$CH_3CH_2CH_2I;\quad CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-Br;$$

| | | |
|---|---|---|
| **Common name** | *n*-propyliodide | *Iso*-butylbromide |
| **IUPAC name** | (1-iodopropane) | (1-bromo-2-methylpropane) |



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2Cl$$

*Neo*-pentylchloride
(1-chloro-2, 2-dimethylpropane)

**Common and IUPAC Name of Some Alkyl Halides**

| Structural formula | Common name | IUPAC name |
|---|---|---|
| $CH_3CH_2CH_2F$ | *n*-propyl fluoride | 1-fluoropropane |
| $(CH_3)_3CCH_2-Br$ | *neo*-pentyl bromide | 1-bromo-2,2-dimethyl propane |
| $CH_3CH_2CH(Cl)CH_3$ | *sec*-butyl chloride | 2-chlorobutane |
| $(CH_3)_3C-Br$ | *tert*-butyl bromide | 2-bromo-2-methyl propane |
| $CH_2=CH-CH_2Br$ | Allyl bromide | 3-bromopropene |
| $CH_2=CHCl$ | Vinyl chloride | Chloroethene |
| $CHCl_3$ | Chloroform | Trichloromethane |
| $CCl_4$ | Carbon tetrachloride | Tetrachloromethane |

# Methods of Preparation

Haloalkanes can be prepared from a wide range of organic compounds through various methods.

Some important methods of preparation are as follows:

## 1. From Hydrocarbons

Alkyl halides can be prepared from alkanes through substitution and from alkenes through addition of halogen acids (like HCl, HBr) or through allylic substitution.

(i) **From alkanes** Alkanes react with halogens ($Cl_2$ and $Br_2$) in the presence of sunlight (UV-light) or at high temperature (400°C) or in the presence of catalyst such as $FeCl_3$, $FeBr_3$, $CuCl_2$, etc. to form haloalkanes.

$$\underset{\text{Alkane}}{R-H} + X_2 \xrightarrow{h\nu} RX + HX$$

The reaction proceeds through free-radical mechanism.

(ii) **From alkenes** Alkyl halide can be prepared by addition of hydrogen halide ($HX$) to alkene. The order of reactivity of hydrogen halide is

$$HI > HBr > HCl > HF$$

## 2. From Alcohols

In this method, the hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride.

(i) **By the action of halogen acids**

Alkyl halides are prepared by the treatment of alcohols with halogen acids as follows:

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Halogen acid}}{HX} \xrightarrow{ZnCl_2} \underset{\text{Haloalkane}}{RX} + \underset{\text{Water}}{H_2O}$$

The rate of reaction depends on the nature of alcohol as well as the halogen acid.

(ii) **By the action of phosphorus halides**

Alkyl halides are obtained by the action of $PCl_5$ or $PCl_3$ on alcohols.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + PCl_5 \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + \underset{\text{Phosphoryl chloride}}{POCl_3} + HCl$$

$$3\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + PCl_3 \longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl} + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

(iii) **By the action of thionyl chloride**

Chloroalkanes are prepared by refluxing alcohols with $SOCl_2$ in the presence of pyridine.

This method is preferred as both the by products of this reaction ($SO_2$ and HCl) are escapable gases. Hence, the reaction gives pure alkyl halide.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

## 3. From Monocarboxylic Acid (Hunsdiecker Reaction)

Generally, bromoalkanes are prepared by refluxing silver salts of acids with bromine in $CCl_4$. This reaction is known as **Borodine-Hunsdiecker reaction**.

$$\underset{\text{Silver acetate}}{CH_3CO\overset{-}{O}\overset{+}{Ag}} + Br_2 \xrightarrow{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + CO_2 + AgBr$$

# Properties of Haloalkanes

## Physical Properties

(i) **Physical state** Lower haloalkanes like methyl chloride, methyl bromide, ethyl chloride, etc. are gases at room temperature. Higher members are liquids (upto $C_{18}$) or solids (beyond $C_{18}$). Many volatile halogen compounds have sweet smell.

(ii) **Colour** Alkyl halides are colourless when they are pure. However, bromides and iodides develop colour when exposed to light. Alkyl iodides decompose even on exposure to light and therefore, they turn brown on standing due to the liberation of iodine.

$$2RI \longrightarrow R—R + I_2$$

(iii) **Boiling point** Boiling points of alkyl halides are higher than the corresponding hydrocarbons. Boiling point rises with the increase in molecular mass and decreases with branching of alkyl group.

(iv) **Density** Fluoro and chloroalkanes are lighter than water while bromo, iodo and polychloro derivatives are heavier than water. Density increases with increase in the number of C-atoms, halogen atoms and atomic mass of halogen atom.

(v) **Solubility** Alkyl halides are slightly polar, so their solubility is low in water. They are soluble in organic solvents.

(vi) **Stability** The stability also decreases as the strength of C—$X$ bond decreases.

$$RF > RBr > RCl > RI$$

Therefore, their order of reactivity would be:

$$RI > RCl > RBr > RF$$

## Chemical Properties

Haloalkanes are highly reactive compounds due to the presence of a polar C—$X$ bond. The shared pair of electrons in C—$X$ bond lies closer to the halogen atom due to higher electronegativity of halogen atom.

Some of the important reactions given by haloalkanes due to the polar nature of C — $X$ bond are as follows :

### 1. Reduction

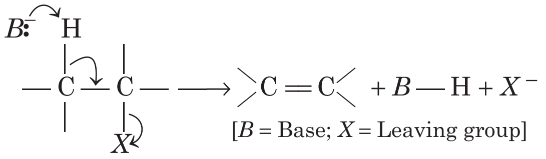
Alkyl halides react with reducing agents to form their corresponding alkanes. Various reducing agents are Zn-Cu couple and ethanol, Sn/HCl, $LiAlH_4$, hydrogen in the presence of Pd, sodium in ethanol, sodium amalgam and water, Zn/HCl etc.

$$R—X + 2H \longrightarrow R—H + HX$$

### 2. Elimination Reactions : Dehydrohalogenation (Formation of Alkenes)

In elimination reactions, alkyl halides form alkenes with the removal of a molecule of hydrogen halide. In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms.

In these reactions, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result, an alkene is formed as a product. Due to the involvement of elimination of β-hydrogen atom, the process is often called **β-elimination**.



[$B$ = Base; $X$ = Leaving group]

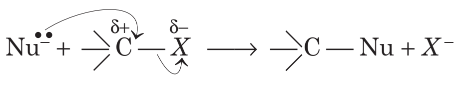
Order of elimination reactions is:

Tertiary halides > Secondary halides > Primary halides

### 3. Nucleophilic Substitution Reactions

Electron rich reagents are called nucleophilic reagents and the substitution reactions by these reagents are called nucleophilic substitution reactions.

These are abbreviated as $S_N$:



### 4. Reactions with Metals

Organometallic compounds are formed when alkyl halides react with metals. The reaction of various metals with alkyl halides are given as follows :

(i) **Action with magnesium** (Formation of Grignard reagents) Alkyl halides react with magnesium in dry ether solution to form Grignard reagent (alkyl magnesium halide).

$$R\text{—}X + \text{Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{(Alkyl magnesium}\\ \text{halide)}}}{R\text{—Mg—}X}$$

(ii) **Action with sodium** (Wurtz reaction) Alkyl halides react with sodium in the presence of dry ether to form higher alkanes containing double the number of carbon atoms present in the halide. This reaction is also known as **Wurtz reaction**.

$$2RX + 2\text{Na} \xrightarrow{\text{Dry ether}} 2R + 2\text{Na}X$$

(iii) **Reaction with lead sodium alloy** Tetra ethyl lead (TEL) is formed when alkyl halide is treated with lead sodium alloy.

The product obtained is used as an antiknocking compound in petrol but as lead is an air pollutant, TEL is not used.

### 5. Alkylation of Aromatic Hydrocarbons

Alkyl halide react with benzene in the presence of anhydrous aluminium chloride to form alkyl benzenes. This reaction is known as **Friedel-Craft's reaction**.

$$R - X + C_6H_6 \xrightarrow{\text{Anhy.FeCl}_3} C_6H_5 - R + HX$$

# PRACTICE QUESTIONS

## Exams', Textbook's Other Imp. Questions

## 1 MARK *Questions*

### Important Questions

**Q.1** Ethyl iodide reacts with sodium ethoxide to produce **[Textbook]**

(a) butane (b) acetic acid
(c) diethyl ether (d) ethane

***Ans*** (*c*) $C_2H_5I + C_2H_5ONa \longrightarrow C_2H_5OC_2H_5 + NaI$

$\therefore$ Diethyl ether is formed when ethyl iodide reacts with sodium ethoxide.

**Q.2** When alkyl halide is treated with alc. KOH the compound formed is **[Textbook]**

(a) alkane (b) alkene (c) alcohol (d) ether

***Ans*** (*b*) Alkenes are formed when alkyl halide is treated with alc. KOH.

$$CH_3 - CH_2Cl \xrightarrow{\text{Alc.KOH}} CH_2 = CH_2 + HCl$$

**Q.3** Which of the following is known as freon ? **[Textbook]**

(a) $CCl_2F_2$ (b) $CHCl_3$ (c) $CH_2F_2$ (d) $CF_4$

***Ans*** (*a*) $CCl_2F_2$ is known as freon.

**Q.4** Which of the following is optically active? **[Textbook]**

(a) $CH_3CHCl_2$ (b) $CH_3CH_2CHClCH_3$
(c) $CH_3CH_2Cl$ (d) $CH_2ClCH_2Cl$

***Ans*** (*b*) $CH_3CH_2CHClCH_3$ is optically active as the chiral carbon atom is attached to four different groups.

**Q.5** Which of the following reaction provides an example of nucleophilic substitution of an alkyl halide ($RX$) ? **[Textbook]**

(a) $RX + \text{Mg} \longrightarrow R\text{Mg}X$
(b) $RX + 2\text{H} \longrightarrow R\text{H} + \text{H}X$
(c) $RX + \text{KOH} \longrightarrow R\text{OH} + \text{K}X$
(d) $2RX + \text{Na} \longrightarrow R\text{—}R + 2\text{Na}X$

***Ans*** (*c*) The reaction $RX + \text{KOH} \longrightarrow R\text{OH} + \text{K}X$ provides an example of nucleophilic substitution of an alkyl halide.

**Q.6** The reagent required to convert $CH_3I$ to $CH_4$ is **[Textbook]**

(a) Zn — Cu couple and ethanol
(b) magnesium in ether
(c) sodium methoxide
(d) sodium in ether

***Ans*** (*a*) $CH_3I$ is converted to $CH_4$ using Zn — Cu couple and ethanol.

**Q.7** For a given alcohol, the order of reactivity with halogen acid is **[Textbook]**

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

***Ans*** (*a*) The order of reactivity of alcohols with halogen acid is HI > HCl > HBr.

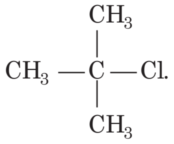
**Q.8** IUPAC name of the compound having formula $(CH_3)_3CCl$ is **[Textbook]**

(a) *t*-butyl chloride]

(b) isobutyl chloride

(c) 2-methyl-2-chloropropane (d) *n*-butyl chloride

***Ans*** (*c*) The given compound is,



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

The IUPAC name of the given compound is 2-methyl-2-chloropropane.

**Q.9** When ethylene dibromide reacts with alc. KOH we get, **[Textbook]**

(a) $C_2H_4$ (b) $C_2H_2$ (c) $C_3H_6$ (d) $C_2H_6$

***Ans*** (*b*) Ethylene dibromide reacts with alc. KOH to give $C_2H_2$.

$$BrCH_2-CH_2Br \xrightarrow[-2HBr]{Alc.KOH} CH \equiv CH$$

**Q.10** Which of the following compound is used as refrigerant? **[Textbook]**

(a) Chloroform

(b) Carbon tetrachloride

(c) Dichlorodifluoromethane

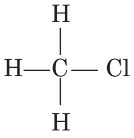
(d) Carbontetrafluoride

***Ans*** (*c*) $CF_2Cl_2$ (dichlorodifluoromethane) is used as a refrigerant.

**Q.11** How many bonds are present in methyl chloride molecule?

**Hint :** 4 sigma, 3 sigma and one $\pi$, 2 sigma and 2 pi, 1 sigma and 2 $\pi$ **[Textbook]**

***Ans*** The structure of methyl chloride is,



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-Cl$$

There are 4 sigma bonds.

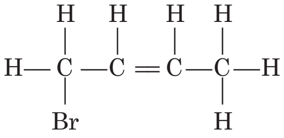
**Q.12** What happens when chloroform is boiled with aqueous solution of caustic potash ? **[Textbook]**

***Ans*** When $CHCl_3$ is boiled with aqueous solution of caustic potash then it gives HCOOK.

$$CHCl_3 + aq.KOH \longrightarrow HCO\overset{-}{O}\overset{+}{K} + 3KCl + 2H_2O$$

**Q.13** Write the structure of 1- bromo-4-chlorobut-2-ene

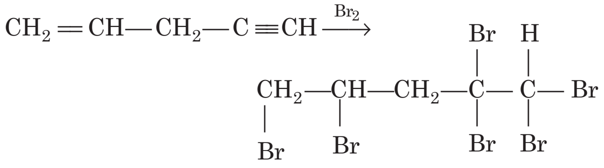
***Ans***



$$H-\underset{\displaystyle Br}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-H$$

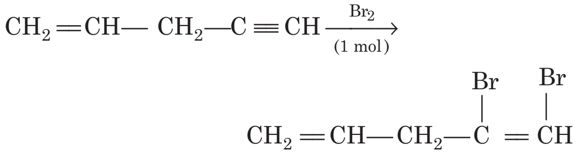
**Q.14** What happens, when $Br_2$ attacks on $CH_2=CH-CH_2-C\equiv CH$? **[Textbook]**

***Ans***



$$CH_2=CH-CH_2-C\equiv CH \xrightarrow{Br_2} \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle Br}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-Br$$

This product is formed when $Br_2$ is used in excess. But if only one mole of $Br_2$ is used, the following product will be formed.



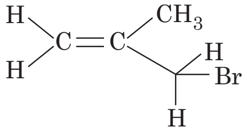
$$CH_2=CH-CH_2-C\equiv CH \xrightarrow[(1\ mol)]{Br_2} CH_2=CH-CH_2-\overset{\displaystyle Br}{\overset{|}{C}}=\overset{\displaystyle Br}{\overset{|}{CH}}$$

**Q.15** Complete the following chemical equation:

$$CH_3CH_2CH=CH_2 + HBr \xrightarrow{Peroxide}$$

***Ans*** $CH_3CH_2CH=CH_2 + HBr \xrightarrow{Peroxide} \underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2Br}$

**Q.16** Write the IUPAC name of the following compound.



**[Textbook]**

***Ans*** The IUPAC name of the compound is 3-bromo-2- methylprop-1-ene.

## 2 MARK *Questions*

### Important Questions

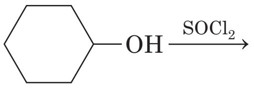
**Q.17** What are freons? What are their harmful effects on the environment? **[Textbook]**

***Ans*** **Freons** are chlorofluorocarbons (CFCs) and related compounds. They are non-reactive, non-inflammable, non-toxic organic molecules. These are widely used in airconditioners, refrigerators. These can induce skin cancer and cause ozone depletion in polar regions.

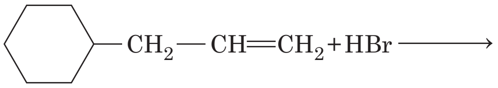
Depletion of ozone layer of environment is its harmful effect. **(2)**

**Q.18** Draw the structure of major monohaloproduct in each of the following reactions :

(i)

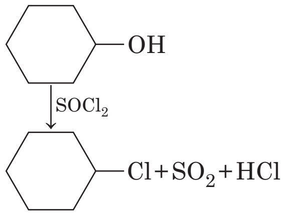


(ii)



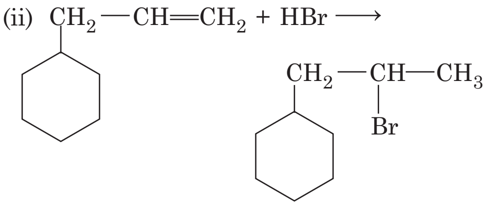
***Ans***

(i)



**(1)**

(ii)



**(1)**

**Q.19** What happens, when methyl iodide is treated with metallic zinc? **[Textbook]**

***Ans*** When methyl iodide is treated with metallic zinc then reaction takes place as follows:

$$CH_3I + Zn \longrightarrow CH_4 + ZnI$$ **(2)**

**Q.20** Write with equation, what happens when ethyl iodide is boiled with aqueous alkali? **[Textbook]**

***Ans*** $C_2H_5I + aq.\ NaOH \longrightarrow \underset{\text{Alcohol}}{C_2H_5OH} + NaI$

Nucleophilic substitution reaction occurs. **(2)**

**Q.21** How will you prepare ethylamine from ethyl iodide? **[Textbook]**

***Ans*** Preparation of ethylamine from ethyl iodide.

$$\underset{\text{Ethyl iodide}}{C_2H_5 - I} + AgNO_2 \longrightarrow C_2H_5NO_2 \xrightarrow[4H]{[R]} \underset{\text{Ethylamine}}{C_2H_5NH_2}$$ **(2)**

**Q.22** Give equation for the reaction of ethyl iodide with aqueous and alcoholic potassium hydroxide. **[Textbook]**

***Ans*** Reaction of ethyl iodide with *aq.* potassium hydroxide (nucleophilic substitution reaction).

$$C_2H_5I + aq.\ KOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KI$$ **(1)**

Reaction of ethyl iodide with alc. KOH (elimination reaction).

$$C_2H_6 + alc.\ KOH \longrightarrow \underset{\text{Ethene}}{CH_2 = CH_2}$$ **(1)**

**Q.23** What happens, when ethyl iodide is heated with sodium in dry ethereal solution? Give equation. **[Textbook]**

***Ans*** $2C_2H_5—I + Na \xrightarrow[\text{ether}]{\text{Dry}} C_2H_5—C_2H_5 + 2NaI$

When ethyl iodide reacts with Na in dry ethereal solution, butane is formed. **(2)**

**Q.24** Write balanced equation for the reaction of methyl iodide with AgOH, $C_2H_5\overset{-}{O}\overset{+}{N}a$, $CH_3CO\overset{-}{O}\overset{+}{A}g$ and $AgNO_2$. **[Textbook]**

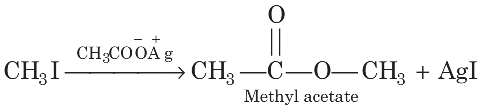
***Ans*** Reaction of $CH_3I$ with AgOH.

$$CH_3I + AgOH \longrightarrow CH_3OH + AgI$$

Reaction of $CH_3I$ with $C_2H_5\overset{-}{O}\overset{+}{N}a$

$$CH_3I \xrightarrow{C_2H_5\overset{-}{O}\overset{+}{N}a} CH_3OC_2H_5 + NaI$$ **(1)**

Reaction of $CH_3I$ with $CH_3CO\overset{-}{O}\overset{+}{A}g$



$$CH_3I \xrightarrow{CH_3CO\overset{-}{O}\overset{+}{A}g} \underset{\text{Methyl acetate}}{CH_3—\overset{\overset{\large O}{||}}{C}—O—CH_3} + AgI$$

Reaction of $CH_3I$ with $AgNO_2$

$$CH_3I \xrightarrow{AgNO_2} \underset{\text{Nitroalkane}}{CH_3NO_2} + AgI$$ **(1)**

# 3 MARK *Questions*

## Important Questions

**Q.25** Complete the following chemical reactions

(i) $CH_3I + AgCN \longrightarrow$ **[Textbook]**

(ii) $CH_3I + NH_3 \longrightarrow$

(iii) $CH_3I + KOH(aq.) \longrightarrow$

***Ans*** (i) $CH_3I + AgCN \longrightarrow \underset{\text{Alkyl isocyanate}}{CH_3—NC} + AgI$ **(1)**

(ii) $CH_3I + NH_3 \longrightarrow \underset{1°\text{ amine}}{CH_3—NH_2} + HI$ **(1)**

(iii) $CH_3I + aq.\ KOH \longrightarrow CH_3OH + KI$ **(1)**

**Q.26** Explain, why **[Textbook]**

(i) although alkyl halides are slightly polar, they are insoluble in water?

(ii) alkyl halides have higher boiling points than the corresponding hydrocarbons?

***Ans*** (i) Alkyl halides are polar as they contain electronegative halide groups. Even though they are polar, they are unable to form hydrogen bonds with water. Therefore, alkyl halides are insoluble in water. **(2)**

(ii) Refer to text on page 208. **(1)**

**Q.27** Explain, why **[Textbook]**

(i) For a given alkyl group, the order of boiling point is $RI > RBr > RCl > RF$ ?

(ii) For a given alkyl group, the order of reactivity is $RI > RBr > RCl > RF$?

***Ans*** (i) Refer to text on page 208. **(1½)**

(ii) Refer to text on page 208. **(1½)**

**Q.28** Explain, why **[Textbook]**

(i) alkyl halide of lower alkanes when treated with metallic sodium give higher alkanes?

(ii) hydrogen atom of chloroform is definitely acidic but that of methane is not?

(iii) an alkyl halide can be utilised for the synthesis of a desired aliphatic compound?

***Ans*** (i) Refer to text on page 209 (Wurtz reaction). **(1)**

(ii) Hydrogen atom of chloroform is definitely acidic but that of methane is not. It is due to the presence of three electronegative chlorine atoms on carbon, the latter acquires a partial positive charge due to $-I$ effect of chlorine. It tends to attract electrons of the C — H bond towards itself. **(1)**

(iii) Refer to text on page 209 (Wurtz reaction). **(1)**

**Q.29** Identify *A*, *B* and *C* in the following reaction sequence. **[Textbook]**

(i) $A \xrightarrow{\mathrm{PCl_5}} B \xrightarrow{\mathrm{Alc.KOH}} C \xrightarrow{\mathrm{H_2/Ni}} \mathrm{CH_3CH_2CH_3}$

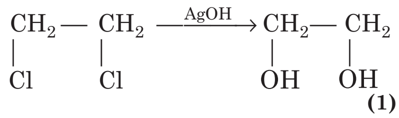
(ii) $A \xrightarrow{\mathrm{KCN}} B \xrightarrow{\mathrm{4H}} \mathrm{CH_3CH_2CH_2NH_2}$

(iii) $A \xrightarrow{\mathrm{Alc.KOH}} B \xrightarrow{\mathrm{Cl_2}} C \xrightarrow{\mathrm{AgOH}} \mathrm{CH_2OH - CH_2OH}$

***Ans*** (i) $\underset{(A)}{\mathrm{CH_3CH_2CH_2OH}} \xrightarrow{\mathrm{PCl_5}} \underset{(B)}{\mathrm{CH_2CH_2CH_2Cl}} \xrightarrow{\mathrm{Alc.KOH}} \underset{(C)}{\mathrm{CH_3-CH{=}CH_2}} \xrightarrow{\mathrm{H_2/Ni}} \underset{(D)}{\mathrm{CH_3CH_2CH_3}}$ **(1)**

(ii) $\underset{(A)}{\mathrm{CH_3CH_2Cl}} \xrightarrow{\mathrm{KCN}} \underset{(B)}{\mathrm{CH_3CH_2CN}} \xrightarrow{\mathrm{Reduction}} \mathrm{CH_3CH_2CH_2NH_2}$ **(1)**

(iii) $\underset{(A)}{\mathrm{CH_3CH_2Cl}} \xrightarrow{\mathrm{Alc.\ KOH}} \underset{(B)}{\mathrm{CH_2 = CH_2}} \xrightarrow{\mathrm{2Cl_2}}$



$$\underset{\mathrm{Cl}}{\mathrm{CH_2}} - \underset{\mathrm{Cl}}{\mathrm{CH_2}} \xrightarrow{\mathrm{AgOH}} \underset{\mathrm{OH}}{\mathrm{CH_2}} - \underset{\mathrm{OH}}{\mathrm{CH_2}}$$

**(1)**

## 7 MARK *Questions*

### Important Questions

**Q.30** Describe the general method (only one) of preparation of an alkyl halide. How does it react with ammonia, metallic sodium and dilute caustic potash? **[Textbook]**

***Ans*** Refer to text on page 207.

$R{-}X \xrightarrow{\mathrm{NH_3}} R{-}\mathrm{NH_2}, \quad R{-}X \xrightarrow[\text{Dry ether}]{\mathrm{Na}} 2R + \mathrm{Na}{-}X$

$R{-}X \xrightarrow{\text{Dil.KOH}} R{-}\mathrm{OH} + \mathrm{K}X$ **(7)**

**Q.31** (i) How will you obtain the ethyl bromide from ethylene? How does ethyl bromide reacts with sodium, *aq*. KOH and silver nitrite?

(ii) Explain the preparation of alkyl halides from alkenes. **[Textbook]**

***Ans.*** (i) Ethyl bromide from ethylene

$\mathrm{CH_2 = CH_2 \xrightarrow{HBr} CH_3 - CH_2Br}$

(a) Reaction of ethyl bromide with Na

$\mathrm{2C_2H_5Br + 2Na \xrightarrow[ether]{Dry} C_2H_5 - C_2H_5 + 2NaBr}$

(b) Reaction of ethyl bromide with *aq*. KOH.

$\mathrm{C_2H_5Br} + aq.\mathrm{KOH} \longrightarrow \mathrm{C_2H_5OH + KBr}$

(c) Reaction of ethyl bromide with silver nitrite.

$\mathrm{C_2H_5Br + AgNO_2 \longrightarrow CH_3NO_2 + AgBr}$ **(4)**

(ii) Refer to text on pages 207 and 208. **(3)**

## TOPIC TEST 1

**1.** Reactivity of halogens towards alkanes is in the order

(a) $F_2 > Br_2 > Cl_2 > I_2$ (b) $F_2 > Cl_2 > I_2 > Br_2$
(c) $Cl_2 > I_2 > Br_2 > F_2$ (d) $F_2 > Cl_2 > Br_2 > I_2$

**2.** Which of the following is a primary halide?

(a) *Neo*-hexyl chloride
(b) *Tert*-butyl bromide
(c) *Sec*-butyl iodide
(d) Isopropyl iodide

**3.** When isopropyl iodide in ethereal solution is warmed with sodium, the product formed is

(a) *n*-hexane
(b) *neo*-hexane
(c) 2, 3-dimethylbutane
(d) All of these [***Ans.*** *1.* (d) *2.* (a) *3.* (c)]

**4.** Why is the solubility of haloalkanes in water very low?

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

(i) $\mathrm{(CH_3)_3CBr + alc.KOH \xrightarrow[Heat]{Ethanol}}$

(ii) $\mathrm{CH_3 - CH(Br)CH_2CH_3 + NaOH \xrightarrow{Water}}$

**6.** Why is $H_2SO_4$ not used during the reaction of alcohols with KI?

**7.** Predict the major product formed when HCl is added to isobutylene. Give its mechanism also.

**8.** Answer the following:

(i) Why do haloalkanes easily dissolve in organic solvents?
(ii) What is racemisation? Give examples.

**9.** How will you obtain ethyl bromide from ethylene? How does ethyl bromide react with sodium, aq.KOH and silver nitrate?

# TOPIC ~02 Haloarenes

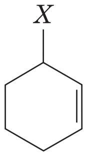
Haloarenes are also known as aryl halides.They contain halogen atom attached to $sp^2$-hybridised carbon atom (s) of an aryl group.

## Classification

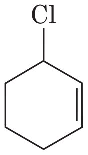
Depending on the nature of C — $X$ bond, haloarenes are classified as follows :

### (i) Allylic Halides

In these halides, the halogen is bonded to an $sp^3$-hybridised carbon atom next to a carbon-carbon double bond that is, an allylic carbon.



3-halocyclohex-1-ene

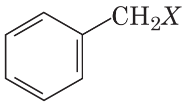


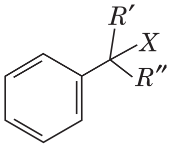
3-chlorocyclohex-1-ene

### (ii) Benzylic Halides

In these halides, the halogen atom is bonded to an $sp^3$-hybridised carbon atom next to an aromatic ring, i.e. to a benzylic carbon.

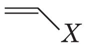
e.g.





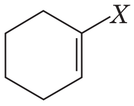
### (iii) Vinylic Halides

In these halides, the halogen atom is bonded to an $sp^2$-hybridised carbon of one of the carbon atoms of a double bond, i.e. vinylic carbon.



Haloethene
(Vinyl halide )

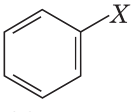
,



1-halocyclohex-1-ene

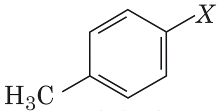
### (iv) Aryl Halides

In these halides, the halogen atom is bonded to the $sp^2$-hybridised carbon atom of an aromatic ring.



Halobenzene

,

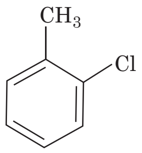
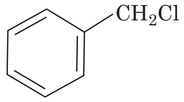
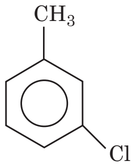
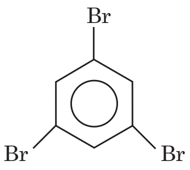


*p*-halotoluene

## Nomenclature

Halogen containing compounds are named by prefixing 'halo' before the name of the aromatic hydrocarbon. Haloarenes have common as well as IUPAC names.
For dihalogen derivatives, the prefixes *o, m, p* are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used. In case the parent aromatic hydrocarbon carries a side chain or substituent, then the numbering of the carbon atom of the ring begins with the substituent. In case the parent hydrocarbon is benzene then numbering begins with halogen atom.

**Common and IUPAC Name of Some Aryl Halides**

| Structure | Common name | IUPAC name |
|---|---|---|
|  | *o*-chlorotoluene | 1-chloro-2-methyl benzene<br>*or*<br>2-chlorotoluene |
|  | Benzyl chloride | Chlorophenylmethane |
|  | *m*-chlorotoluene | 1-chloro-3 methyl benzene |
|  | – | 1,3,5-tribromo benzene |

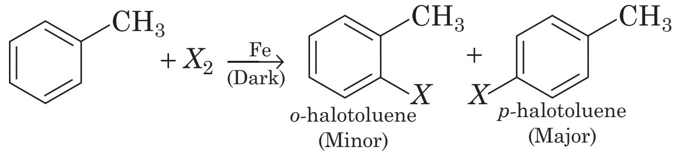
## Methods of Preparation

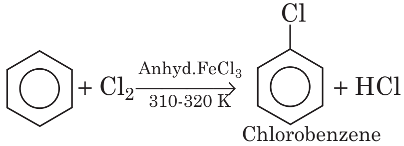
Haloarenes can be prepared by the following methods :

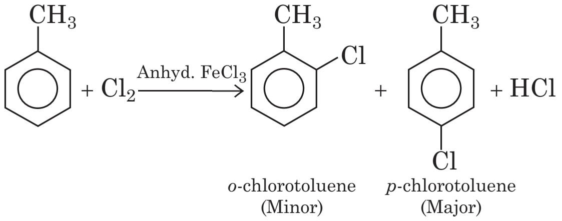
### 1. From Aromatic Hydrocarbons by Direct Halogenation

### (i) Nuclear Halogenation

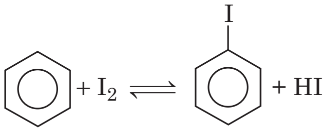
Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine, respectively in dark, at ordinary temperature in the presence of a Lewis acid catalyst such as iron or ferric or aluminium halides ($FeCl_3$, $FeBr_3$, $AlCl_3$).







- The *o* and *p*-isomers can be easily separated due to large difference in their melting points.
- Reaction of iodine with aromatic hydrocarbons is reversible as the formed HI during the reaction is a good reducing agent that reduces the aryl halide again to aromatic hydrocarbon and iodine.



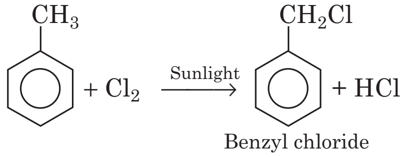
- The formation of iodobenzene from aromatic hydrocarbon can be achieved in the presence of oxidising agents such as $HNO_3$, $HIO_3$, etc. These agents oxidise the formed HI to iodine and hence the reaction proceeds in forward direction.

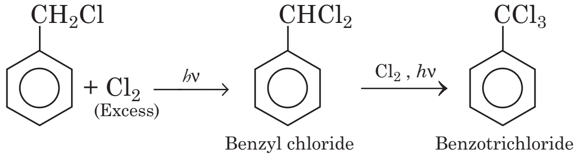
$$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

- The reaction of hydrocarbon with fluorine is violent and uncontrollable, hence fluoroarene cannot be prepared by direct fluorination of aromatic hydrocarbon.

### (ii) Side Chain Halogenation

The preparation of side chain substituted aryl halide can be done by direct halogenation of suitable arene. When toulene reacts with chlorine in presence of sunlight, benzyl chloride is obtained and if excess of chlorine is passed then the formed benzyl chloride gets converted into benzotrichloride.

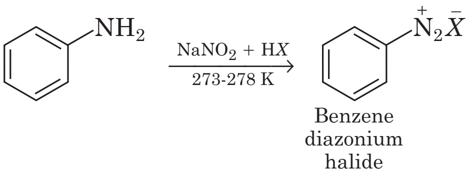




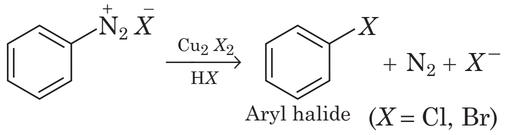
## 2. From Diazonium Salts

### (i) By Sandmeyer's reaction

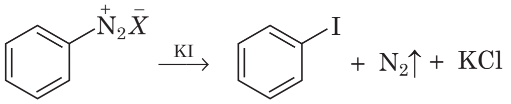
The diazonium salt is prepared by treating aniline dissolved in cold aqueous mineral acid with an aqueous solution of sodium nitrite at low temperature (0-5°C).



Bromo and chloroarenes can be prepared by treating a freshly prepared diazonium salt solution with cuprous bromide or cuprous chloride dissolved in HBr or HCl respectively. This reaction is known as **Sandmeyer reaction**.

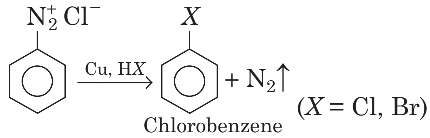


Replacement of the diazonium group by iodine is done by shaking and warming the diazonium salt with potassium iodide.



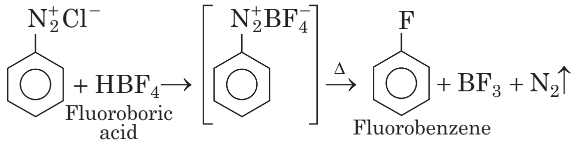
### (ii) By Gattermann Reaction

In this reaction, benzene diazonium chloride is reacted with Cu in the presence of halogen acid.



### (iii) By Balz-Schiemann Reaction

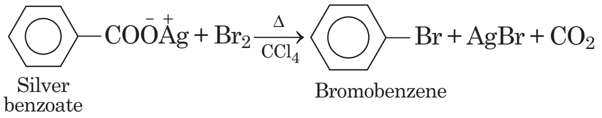
If the diazonium group is replaced using fluoroboric acid, the reaction is called **Balz-Schiemann reaction**.



## 3. From Silver Salt of Aromatics

### (Borodine-Hunsdiecker Reaction)

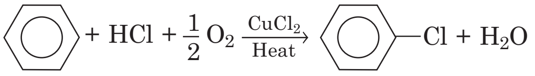
Refluxing of silver salts of aromatic acids with $Br_2$ in $CCl_4$ yields aryl bromides.



## 4. Commercial Preparation of Chlorobenzene (Raschig Process)

This is a commercial method of manufacturing chlorobenzene.

In this process, benzene vapours, air and HCl are passed over heated cupric chloride.



# Physical Properties

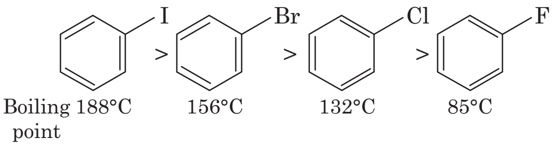
Some important physical properties are as follows:

### (i) Physical State

Haloarenes are colourless oily liquids or low melting solids, insoluble in water but soluble in organic solvents like ethanol.

### (ii) Boiling Point

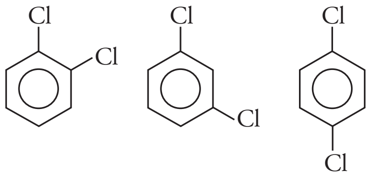
For the same aryl group, the boiling point increases as the size of the halogen atom increases. Similarly, for the halogen atom, boiling point increases as the size of aryl group increases.



### (iii) Melting Point

When aryl group is same, melting point increases as the size of the halogen atom increases. When halogen atom is same melting point increases as the size of aryl group increases.

In case of dihalobenzene, melting point of the *p*-isomer is always higher than that of *o* and *m*-isomers because *p*-isomer is more symmetrical.



| | *o*-dichloro benzene | *m*-dichloro benzene | *p*-dichloro benzene |
|---|---|---|---|
| Boiling point (°C) | 179 | 172 | 175 |
| Melting point (°C) | – 17 | – 26 | – 53 |

### (iv) Stability

Stability of haloarenes having the same aryl group decreases in the order arylfluorides > aryl chlorides > arylbromides > aryl iodides

This is because the strength of C—$X$ bond decreases in the order.

$$\text{C—F} > \text{C—Cl} > \text{C—Br} > \text{C—I}$$

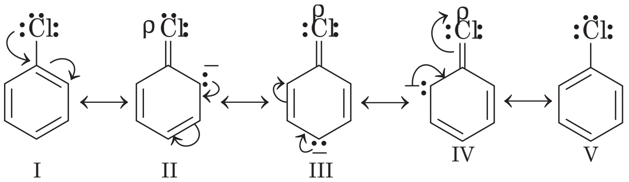
# Chemical Properties

Some important chemical reactions of haloarenes are :

## 1. Nucleophilic Substitution of Aromatic Halogens

Nucleophilic substitution reactions in aryl halides occur only under drastic conditions as haloarenes are chemically less reactive towards nucleophilic substitution reactions (than haloalkanes). This is due to the following reasons:

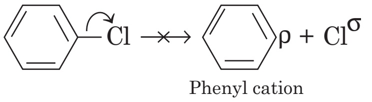
(i) **Resonance effect** In haloarenes, the lone pair of electrons on halogen atom are in conjugation with π-electrons on the ring and hence these are delocalised on the benzene ring as shown below:



As a result of resonance, C—Cl bond acquires a partial double bond character. Thus, the bond cleavage in haloarene is difficult than haloalkane and thus they are less reactive towards nucleophilic substitution reactions.

(ii) **Difference in hybridisation of carbon atom in C—*X* bond** In haloalkanes, the carbon atoms attached to halogen is $sp^3$-hybridised, while in haloarenes, it is $sp^2$-hybridised. The $sp^2$-hybridised C-atom with greater *s*-character is more electronegative. As a result, the C — $X$ bond in haloarenes is shorter that in haloalkanes. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction as it is difficult to break a shorter bond than a longer bond.

(iii) **Instability of phenyl cation** In haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance, as the *p*-orbital of phenyl ring is perpendicular to the $sp^2$ hybridised carbon having positive charge, hence $S_N1$ -mechanism does not occur.



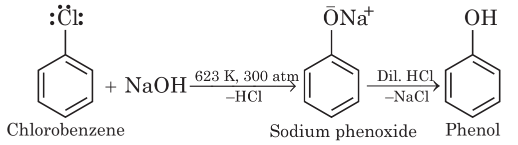
Phenyl cation

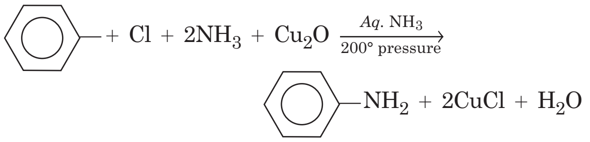
(iv) **Polarity of C—*X* bond** The C—$X$ bond of haloarenes is less polar than that in haloalkanes because of more electronegative nature of $sp^2$-hybridised C-atom of C—$X$ bond.

Due to this, the C — $X$ bond cannot be cleaved easily and therefore aryl halides undergo nucleophilic substitution reactions with great difficulty.

(v) **Electronic repulsions** Arenes are electron-rich and when strong nucleophiles approach aryl halides, repulsion takes place making $S_N$ reactions impossible.

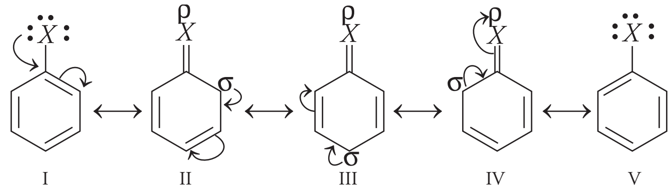
Some reactions involving nucleophilic substitution are given below :





## 2. Electrophilic Substitution Reactions

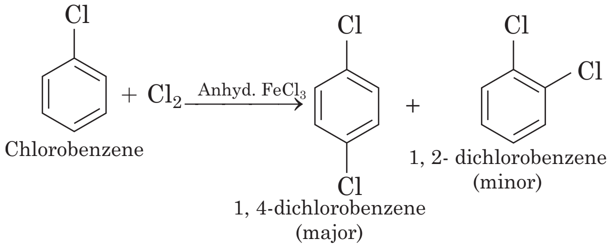
Haloarenes undergo electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel Craft's reactions. The resonance structures of halobenzene are shown below.



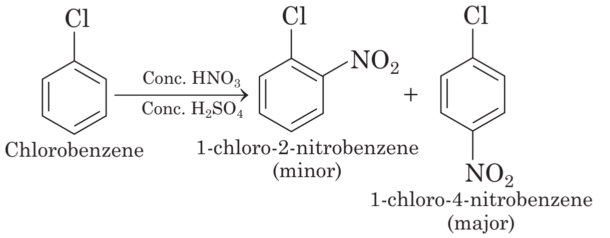
Electrophilic substitution reactions in haloarenes take place at a slower rate as the halogen group is electron withdrawing and decreases the electron density on benzene ring. It can be seen from the above resonance structures that due to resonance, electron density increases at *ortho* and *para* positions than at *meta*-position. Hence, electrophitic substitution reactions occur at *ortho* and *para* positions.

The common electrophilic substitution reactions of haloarenes are depicted below:

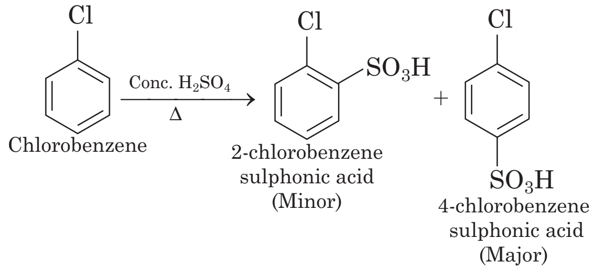
### (i) Halogenation



### (ii) Nitration



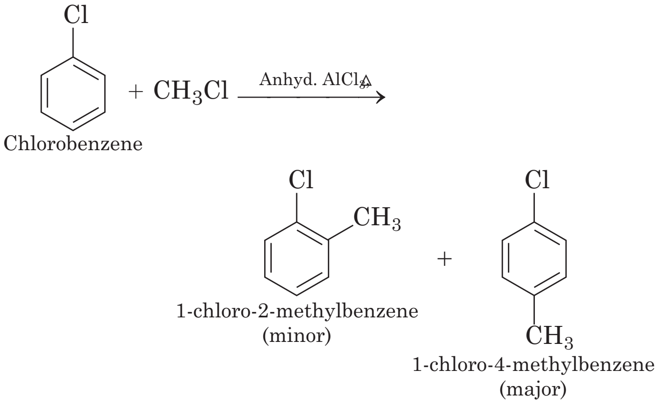
### (iii) Sulphonation



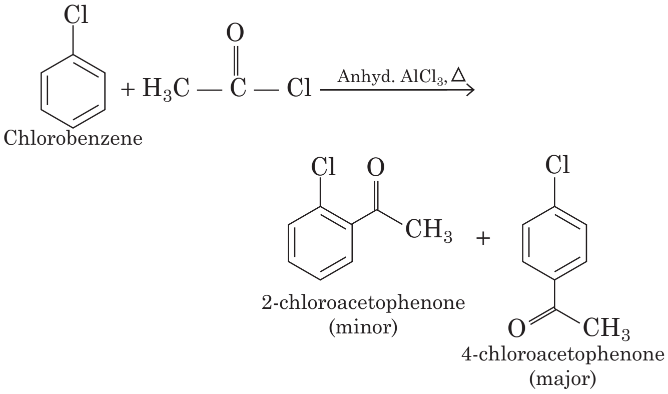
### (iv) Friedel-Craft's Reaction

There are two main types of Friedel-Craft's reactions:

(a) **Alkylation**



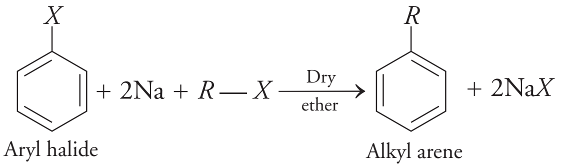
(b) **Acylation**

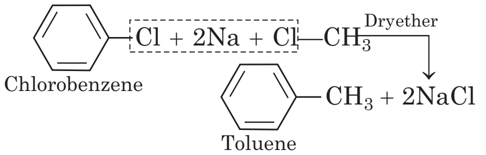


Acetic anhydride, i.e. $(CH_3CO)_2O$ can also be used instead of $CH_3COCl$ in Friedel-Craft's arcylation reaction.

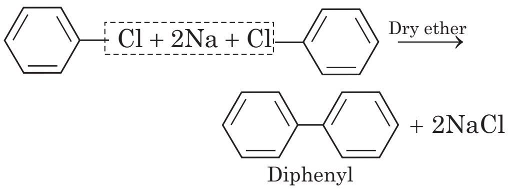
## 3. Miscellaneous Reactions

(i) **Wurtz-Fittig reaction** When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkyl arene is formed. This reaction is called Wurtz-Fittig reaction.

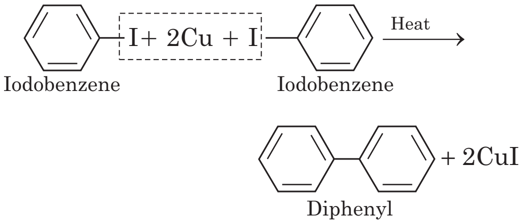




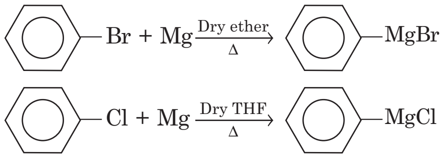
(ii) **Fittig reaction** In this reaction, haloarenes react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed.



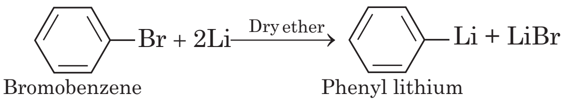
(iii) **Reaction with copper powder** (Ullmann biaryl synthesis) In this reaction, iodobenzene is heated with copper powder in a sealed tube and diphenyl is formed.



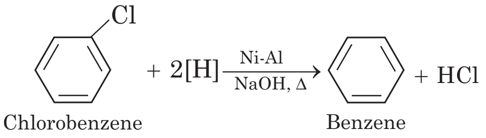
(iv) **Reaction with Mg** Bromo and iodo arenes can be prepared from Grignard reagents when their ethereal solution is treated with magnesium. Chloroarenes form Grignard reagents only if the reaction is carried out in dry tetrahydrofuran (THF) as a solvent.



(v) **Reaction with lithium** Haloarenes like bromo and iodoarenes reacts with Li metal in presence of dry ether to form corresponding organometallic compounds.



(vi) **Reduction** On reduction of haloarenes with Ni-Al alloy in the presence of alkali, aromatic hydrocarbons are formed.



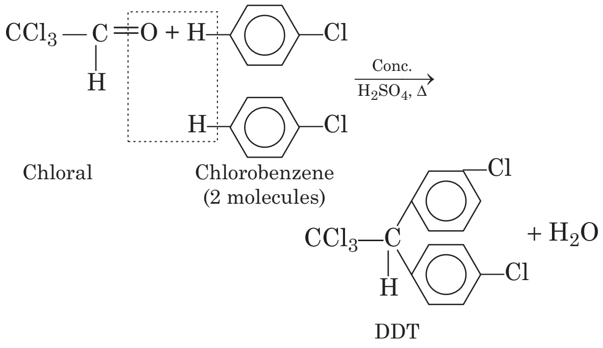
# Polyhalogen Compounds

## 1. DDT (*p*, *p′* dichloro diphenyltrichloroethane)

It is an non biodegradable compound which creates an imbalance in the water ecosystem by acting as a water pollutant. If it is consumed by animals, it gets stored in the fat tissues and its amount increases over the time.

### Preparation

DDT is prepared by treating chloral with chloro benzene in the presence of conc $H_2SO_4$.



### Uses

It is used as a powerful insecticide.

## 2. Chloroform ($CHCl_3$)

Chloroform is a heavy liquid that causes temporary unconsciousness.

### Preparation

It is prepared by the reaction of methane with $Cl_2$ in the presence of light.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu/675K} CH_3Cl \xrightarrow[-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[+HCl]{+Cl_2} \underset{\text{Chloroform}}{CHCl_3}$$

It can also be prepared by the partial reduction of carbon tetrachloride.

$$CCl_4 + 2H \xrightarrow{Fe + Steam} CHCl_3 + HCl$$

### Chemical Properties

(i) Chloroform on exposure to air and sunlight forms carbonyl chloride or phosgene, which is a highly poisonous gas.

$$2CHCl_3 + O_2 \xrightarrow[air]{Sunlight} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Therefore, $CHCl_3$ should be stored in dark coloured bottles to protect it from sunlight.

(ii) Chloroform on reduction with zinc and HCl forms methylene chloride.

$$CHCl_3 + 2H \xrightarrow[HCl]{Zn} \underset{\text{(methylene chloride)}}{CH_2Cl_2} + HCl$$

Chloroform on reduction with Zn dust and water forms methane.

$$CHCl_3 + 6H \xrightarrow[H_2O]{\text{Zn dust}} CH_4 + 3HCl$$

(iii) **Carbylamine reaction** Reaction of chloroform with an aliphatic or an aromatic primary amine forms the corresponding carbylamine.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Warm}} CH_3CH_2NC + 3KCl + 3H_2O$$

## 3. Freons

Freons are the chlorofluorocarbon compounds of methane and ethane. They are non-toxic, non-corrosive and extremely stable, e.g. freon -12. It is prepared by Swart's reaction.

$$3CCl_4 + 2SbF_3 \longrightarrow 2SbCl_3 + \underset{\text{Freon-12}}{3CCl_2F_2}$$

### Uses

Freons are used as propellants for aerosols and also in hairsprays and insecticides. They are also used as refrigerants in refrigerators and air conditioning.

Freons undergo photochemical decomposition in the atmosphere and unitiates chain reactions which leads to the depletion of the ozone layer.

# PRACTICE QUESTIONS

## Exams', Textbook's Other Imp. Questions

## 1 MARK *Questions*

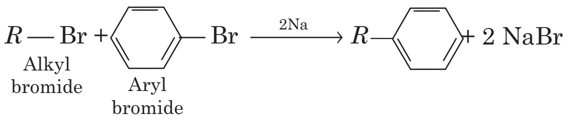
### Exams' Questions

**Q.1** Which one of the following reaction involves both aryl and alkyl halide? **[2016, Textbook]**

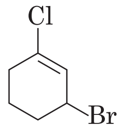
(a) Wurtz reaction
(b) Wurtz-Fittig reaction
(c) Sandmeyer reaction
(d) Friedel-Craft's reaction

***Ans*** (*b*) Wurtz-Fittig reaction involves both aryl and alkyl halide.

Example



**Q.2** The IUPAC name of the compound is:



**[2015]**

(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene

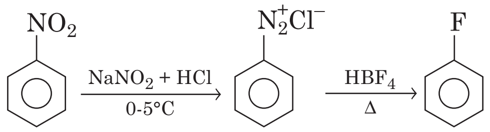
***Ans*** (*c*) The IUPAC name of the given compound is 3-bromo-1-chlorocyclohexene.

### Important Questions

**Q.3** Fluorobenzene ($C_6H_5F$) can be prepared in the laboratory

(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with $HBF_4$
(c) by direct fluorination of benzene with $F_2$ gas
(d) by reacting bromobenzene with NaF solution

***Ans*** (*b*) $C_6H_5F$ can be prepared in the laboratory from aniline by diazotisation followed by heating the diazonium salt with $HBF_4$.



**Q.4** Which of the following has highest melting point? **[Textbook]**

| | |
|---|---|
| (a) Chlorobenzene | (b) *o*-dichlorobenzene |
| (c) *m*-dichlorobenzene | (d) *p*-dichlorobenzene |

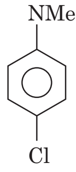
***Ans*** (*d*) *p*-dichlorobenzene has the highest melting point due to symmetry.

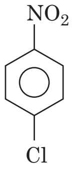
**Q.5** Chlorobenzene on treatment with sodium, dry ether gives diphenyl. The name of the reaction is **[Textbook]**

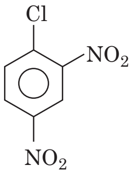
| | |
|---|---|
| (a) Fittig reaction | (b) Wurtz-Fittig reaction |
| (c) Sandmeyer reaction | (d) Gattermann reaction |

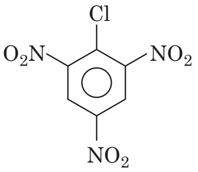
***Ans*** (*a*) The reaction of chlorobenzene with Na, dry ether to form diphenyl is Fittig reaction.

**Q.6** Order of reactivity towards nucleophilic substitution reaction of the compounds **[Textbook]**


(I)


(II)


(III)


(IV)

(a) I > II > III > IV (b) II > I > III > IV
(c) IV > III > II > I (d) III > IV > II > I

***Ans*** (*c*) The correct order is:

IV > III > II > I

Refer to text on page 215.

**Q.7** Which of the following is not an example of Wurtz-Fittig reaction? **[Textbook]**

(a) $C_6H_5CH_2Cl + CH_3Cl \xrightarrow{\text{Na/ether}}$

(b) $C_6H_5CH_2Cl + C_6H_5Cl \xrightarrow{\text{Na/ether}}$

(c) $C_6H_5Cl + CH_3Cl \xrightarrow{\text{Na/ether}}$

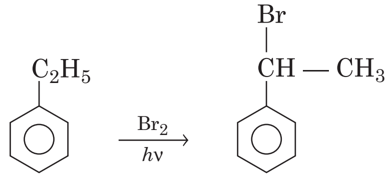
(d) None of the above

***Ans*** (*b*) The reaction (b) is not an example of Wurtz-Fitting reaction as one of the reactants is not an alkyl halide.

**Q.8** The bromination of ethylbenzene in presence of sunlight will preferentially yield, **[Textbook]**

(a) 1-bromo-1-phenylethane (b) 2-bromo-1-phenylethane
(c) *p*-bromophenylethane (d) *o*-bromophenylethane

***Ans*** (*a*)



∴ 1-bromo-1-phenylethane is the major product.

**Q.9** Formation of phenol from chlorobenzene is an example of .........aromatic substitution and occurs through ......... intermediate. **[Textbook]**

***Ans*** Nucleophilic, benzyne.

**Q.10** The reaction of *p*-nitrochlorobenzene with sodium methoxide to form *p*-nitroanisole occurs by ......... reaction. **[Textbook]**

***Ans*** Bimolecular aromatic nucleophilic substitution.

**Q.11** Preparation of chlorobenzene from benzenediazonium chloride with cuprous chloride and *aq*. HCl is known as ......... reaction. **[Textbook]**

***Ans*** Sandmeyer.

**Q.12** Chlorobenzene reacts with ......... in presence of conc. $H_2SO_4$ to form DDT. **[Textbook]**

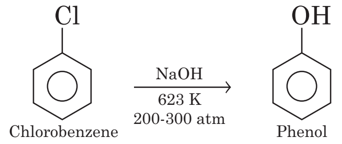
***Ans*** Chloral ($CCl_3CHO$).

**Q.13** Iodobenzene on heating with copper powder forms diphenyl. The reaction is called ...... . **[Textbook]**

***Ans*** Ullmann biaryl synthesis.

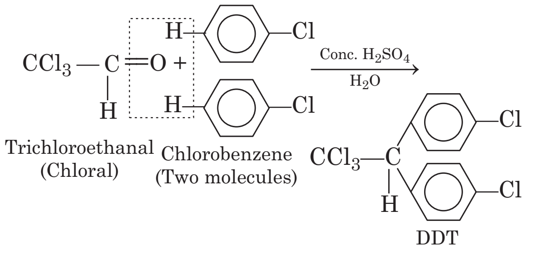
**Q.14** How will you convert chlorobenzene to phenol ?

***Ans***



**Q.15** Write the balanced equation for the preparation of DDT. **[Textbook]**

***Ans*** DDT is prepared by heating chlorobenzene with chloral in the presence of concentrated sulphuric acid.

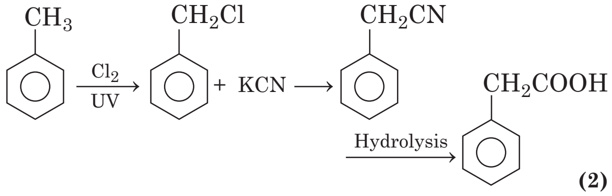


# 2 MARK *Questions*

## Important Questions

**Q.16** How will you synthesise phenylacetic acid from toluene? **[Textbook]**

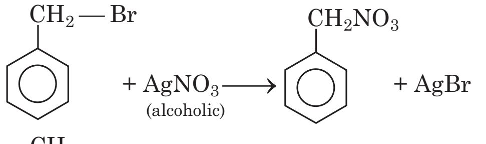
***Ans***



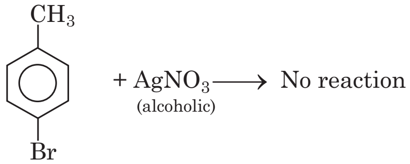
**(2)**

**Q.17** How will you distinguish between benzyl bromide and *p*-bromotoluene? **[Textbook]**

***Ans*** Benzyl bromide forms a precipitate of AgBr with alcoholic $AgNO_3$ solution, while *p*-bromotoluene does not react.



**(1)**



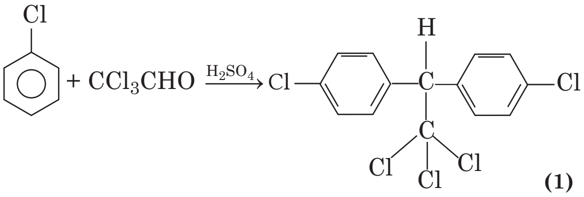
**(1)**

**Q.18** What is the product formed when **[Textbook]**

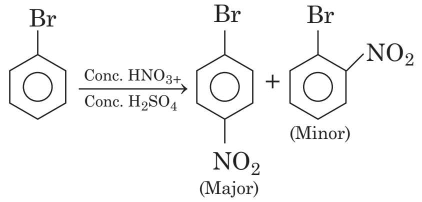
(i) chlorobenzene reacts with chloral in the presence of conc. sulphuric acid.

(ii) bromobenzene reacts with nitric acid in the presence of sulphuric acid?

***Ans***

(i) 

**(1)**

(ii) 

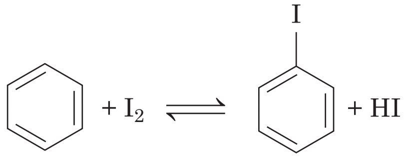
**(1)**

# 3 MARK *Questions*

## Exams' Questions

**Q.19** "Direct iodination of benzene is difficult." Explain. Suggest an alternative route for the synthesis of iodobenzene. **[2016, Textbook]**

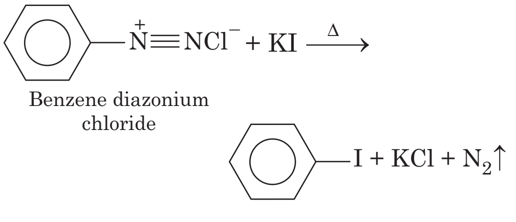
***Ans*** In case of the halogens, iodine has the least electrophilicity and electronegativity. Therefore, iodination is highly unreactive for electrophilic aromatic substitution reactions. For iodination, the reaction is endothermic with 12 kg/mol of energy absorbed. So, it cannot be done using conventional method.



Here, the reaction is reversible and the HI produced a strong reducing agent to reduce iodobenzene back to back to benzene.

All these factors does not allow direct iodination of benzene.

Alternate route to synthesise iodobenzene. It can be prepared by heating aqueous diazonium salt with potassium iodide.



**(3)**

## Important Questions

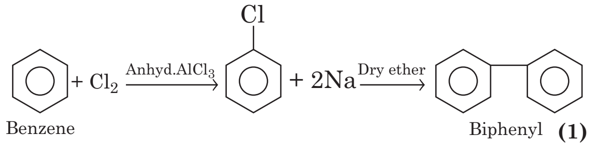
**Q.20** How can the following conversions be carried out? **[Textbook]**

(i) Benzene to biphenyl

(ii) Benzene to 4-bromonitrobenzene

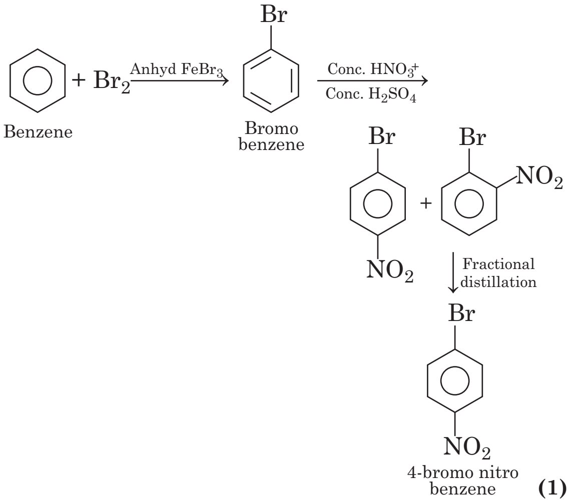
(iii) Aniline to chlorobenzene

***Ans*** (i) Benzene to biphenyl



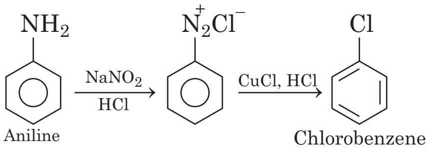
**(1)**

(ii) Benzene to 4-bromonitrobenzene



**(1)**

(iii) Aniline to chlorobenzene



**(1)**

**Q.21** Explain the following : **[Textbook]**

(i) Chlorine present in chlorobenzene is *ortho* and *para* directing.

(ii) Aryl halides are extremely less reactive towards nucleophilic substitution.

(iii) Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.

***Ans*** (i) Refer to text on page 216. **(1)**

(ii) Refer to text on page 215. **(1)**

(iii) Refer to text on page 215. **(1)**

**Q.22** Write notes on : **[Textbook]**

(i) Freons (ii) Chloroform

***Ans*** (i) Refer to text on page 218. **(1½)**

(ii) Refer to text on pages 217 and 218. **(1½)**

**Q.23** Following compounds are given to you :

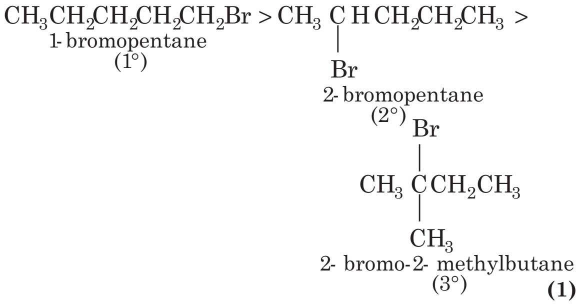
2-bromopentane, 2-bromo-2methylbutane, 1-bromopentane **[Textbook]**

(i) Write the compound which is most reactive towards $S_N2$ reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction.

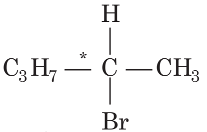
***Ans*** (i) $S_N2$ reactions involve the formation of transition state. Higher the steric hinderance, lesser the stability of transitions state and lower is their reactivity towards $S_N2$.



$$\underset{\substack{\text{1-bromopentane}\\(1^\circ)}}{CH_3CH_2CH_2CH_2CH_2Br} > \underset{\substack{\text{2-bromopentane}\\(2^\circ)}}{CH_3\underset{Br}{\underset{|}{C}}HCH_2CH_2CH_3} > \underset{\substack{\text{2-bromo-2-methylbutane}\\(3^\circ)}}{CH_3\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CH_3}$$

**(1)**

(ii) Among the given compounds, 2-bromopentane is optically active due to presence of chiral carbon (*)

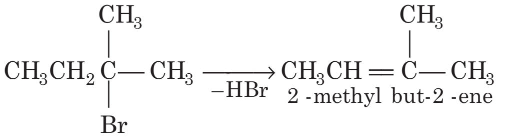


$$C_3H_7 - \overset{H}{\overset{|}{\underset{Br}{\underset{|}{\overset{*}{C}}}}} - CH_3$$

2-bromopentane

**Note** A chiral carbon have four different groups or atoms attached separately to its four valencies. **(1)**

(iii) 2-bromo-2-methylbutane is most reactive towards β-elimination reaction because in this case more substituted alkene is the major product.



$$CH_3CH_2\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3 \xrightarrow[-HBr]{} \underset{\text{2-methyl but-2-ene}}{CH_3CH=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

**(1)**

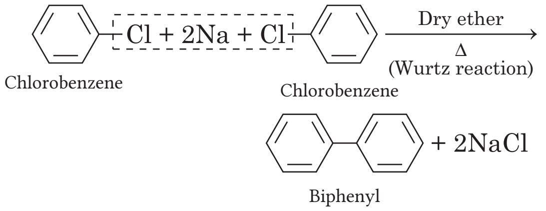
**Q.24** How do you convert the following? **[Textbook]**

(i) Chlorobenzene to biphenyl

(ii) Propene to 1-iodopropane

(iii) 2-bromobutane to but-2-ene

***Ans*** (i) **Chlorobenzene to biphenyl**



**(1)**

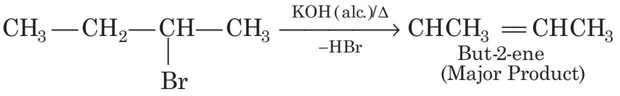
(ii) **Propene to 1-iodopropane**

$$\underset{\text{Propene}}{CH_3-CH=CH-CH_3} + HBr \xrightarrow[\substack{\text{(Anti-Markownikoff's}\\\text{addition)}}]{(C_6H_5COO)_2} \underset{\text{1-bromopropane}}{CH_3-CH_2CH_2Br}$$

$$\xrightarrow{\text{Acetone}/\Delta,\ NaI} NaBr + \underset{\text{1-iodopropane}}{CH_3-CH_2CH_2I}$$

**(1)**

(iii) 2-bromobutane to but-2-ene



$$CH_3-CH_2-\underset{Br}{\underset{|}{C}}H-CH_3 \xrightarrow[-HBr]{KOH(alc.)/\Delta} \underset{\substack{\text{But-2-ene}\\\text{(Major Product)}}}{CHCH_3=CHCH_3}$$

**(1)**

## 7 MARK *Questions*

### Important Questions

**Q.25** Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can the reactivity of aryl halides be enhanced?

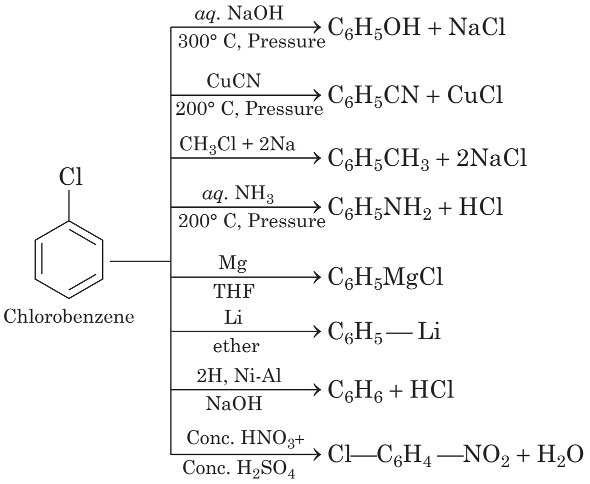
***Ans.*** Refer to text on pages 215 and 216. **(7)**

**Q.26** Discuss the resonating structures of chlorobenzene. How do you account for double bond character of C—Cl bond? Describe the industrial method of preparation of chlorobenzene. **[Textbook]**

***Ans*** Refer to text on page 215. **(7)**

**Q.27** Describe the different chemical reactions and properties of chlorobenzene. **[Textbook]**

***Ans*** Reactions given by the chlorobenzene are as follows :



**Properties** Chlorobenzene is a colourless pleasant smelling liquid having boiling point 132°C. It is insoluble in water, ethanol and ether. **(7)**

**Q.28** Write notes on : **[Textbook]**

(i) Wurtz-Fittig Reaction
(ii) Ullmann reaction
(iii) DDT

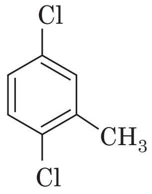
***Ans*** (i) Refer to text on page 216.
(ii) Refer to text on page 217.
(iii) Refer to text on page 217. **(7)**

## TOPIC TEST 1

**1.** The electrophile in Friedel-Crafts alkylation of arenes is

(a) $R^+$ (b) $AlCl_4^-$
(c) $RCO^+$ (d) $RO^+$ [***Ans.*** (a) ]

**2.** Write the IUPAC name of the following compound:



[***Ans.*** 1, 4-dichloro-2-methylbenzene]

**3.** Which of the following is not an example of Sandmeyer's reaction?

(a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl} C_6H_5Cl$

(b) $C_6H_5N_2^+Cl^- \xrightarrow{CuBr} C_6H_5Br$

(c) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN/KCN} C_6H_5CN$

(d) $C_6H_5N_2^+Cl^- \xrightarrow{KI/warm} C_6H_5I$ [***Ans.*** (d)]

**4.** How will you distinguish the following two compounds?

(i) $C_6H_5Cl$ and $C_6H_5CH_2Cl$
(ii) Chlorobenzene and *n*-hexyl chloride

**5.** How are polyhalogens different from other organic halogens? Explain with example.

**6.** What is Friedel-Crafts reaction? Explain with equations.

**7.** Write short notes on the following:

(i) Wurtz-Fittig reaction
(ii) Ullmann reaction
(iii) DDT

**8.** Draw and explain the resonating structures of chlorobenzene. How do you account for the double bond character of C—Cl bond? Describe the industrial method of preparation of chlorobenzene.

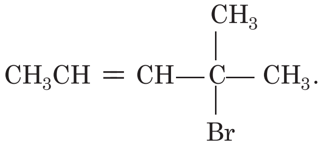
# Chapter Test

## 1 MARK *Questions*

**1** Give the balanced equation for the reaction of 1- butanol and HCl (in presence of $ZnCl_2$)

**2** The reaction of chlorine with methane is a ........... reaction which involves ........... fission of the C — H bond. [***Ans.*** Substitution, homolytic]

**3** Write the IUPAC name of



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

**4** The alkyl halide that undergoes $S_N1$ reaction more readily is

(a) ethyl bromide (b) *iso*-propyl bromide
(c) vinyl bromide (d) *t*-butyl bromide

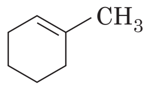
**5** The reaction of ethyl bromide and silver cyanide results in the formation of

(a) ethylene (b) ethyl cyanide
(c) ethyl isocyanide (d) ethyl alcohol

[***Ans.*** (c)]

## 2 MARK *Questions*

**6** Complete the following reactions:

(i)  + HI $\longrightarrow$

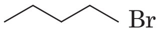
(ii) $CH_3CH_2CH=CH_2 + HBr \longrightarrow$

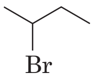
**7** Draw the structures of the following compounds:

(i) 1- *tert*-butyl -3- iodoheptane
(ii) 4- bromo - 3- methylpent -2- ene

**8** Complete the following reaction and name it
$C_3H_7NH_2 + CHCl_3 + 3KOH(alc.) \longrightarrow$

**9** (i) Which alkyl halide from the following pair is chiral and undergoes faster towards $S_N2$ reactions?

(a) 

(b) 

(ii) Our of $S_N1$ and $S_N2$, which reaction occurs with

(a) inversion of configuration?
(b) racemisation?

**10** Write chemical equations, when

(i) ethyl chloride is treated with aqueous KOH.
(ii) chlorobenzene is treated with $CH_3COCl$ in the presence of anhydrous $AlCl_3$.

## 3 MARK *Questions*

**11** Give reasons.

(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in $CH_3$—Cl.
(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(iii) $S_N1$ reactions are accompanied by racemisation in optically active alkyl halides.

**12** How can the following conversions be carried out?

(i) Aniline to bromobenzene
(ii) Chlorobenzene to 2-chloroacetophenone
(iii) Chloroethane to butane

**13** What happens, when

(i) chlorobenzene is treated with $Cl_2$ / $FeCl_3$?
(ii) ethyl chloride is treated with $AgNO_2$?
(iii) 2-bromopentane is treated with alcoholic KOH?

Write the chemical equations in support of your answer.

## 7 MARK *Questions*

**14** Rearrange the compounds of each of the following sets in order of reactivity towards $S_N2$ displacement and $S_N1$ displacement along with reason.

(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-2-methylbutane.

**15** (i) State two uses of DDT and chloroform.
(ii) Explain the $S_N1$ and $S_N2$ mechanisms.