## CHAPTER 10

# Haloalkanes and Haloarenes

## Introduction, Nomenclature and Preparation of Haloalkanes and Haloarenes

Haloalkanes are hydrogen atoms in aliphatic hydrocarbons replaced by halogens, whereas Haloarenes are hydrogen atoms replaced in benzene ring by halogens. In haloalkanes, halogen gets connected with the carbon through $\left(CO_2 + H_2O\right)$ hybridisation, while in Haloarenes, it is connected with $CO_2$ hybridisation.

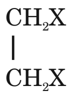
### Classification

- **On the Basis of Number of Halogen Atoms**

  It depends on the number of halogen atoms attached to the structure. It may be mono, di, tri or tetra etc. For example,

$C_2H_5X$

Monohaloalkane

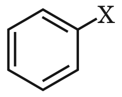


$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$$

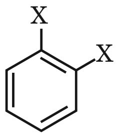
Dihaloalkane

$$\begin{array}{c} CHX \\ \| \\ C \\ \| \\ CHX \end{array}$$

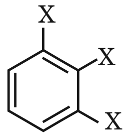
Trihaloalkane



Monohaloarene



Dihaloarene



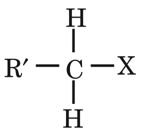
Trihaloarene

- **Compounds Containing** $\text{ppm}\left(\text{mass to mass}\right) = \dfrac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6$ **C-X Bond (X= F, Cl , Br, I)**

  - **Alkyl halides or haloalkanes (R-X):** The series is represented as

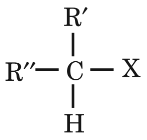
    $$\text{ppm}\left(\text{volume to volume}\right) = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6.$$

    It has further 3 categories, i.e., primary, secondary or tertiary depending on the nature of carbon to which halogen is attached.



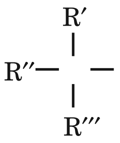
$$\begin{array}{c} H \\ | \\ R'-C-X \\ | \\ H \end{array}$$

Primary (1°)



$$\begin{array}{c} R' \\ | \\ R''-C-X \\ | \\ H \end{array}$$

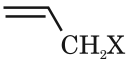
Secondary (2°)

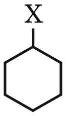


$$\begin{array}{c} R' \\ | \\ R''- \quad - \\ | \\ R''' \end{array}$$

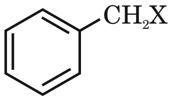
Tertiary (3°)

- **Allylic halides:** The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond.

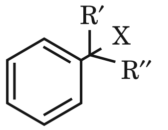




- **Benzylic halides:** The halogen atom is attached to the carbon atom right next to an aromatic ring.



(1°)

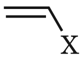


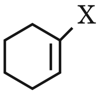
R′ = $CH_3$, R″ = H(2°)

R′ = R″ = CH3(3°)

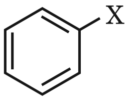
- **Compounds Containing** $\text{ppm}\left(\text{mass to volume}\right) = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$ **C-X Bond**

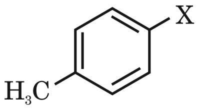
  - **Vinylic halides:** The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond (C=C).





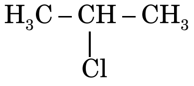
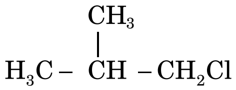
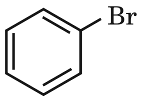
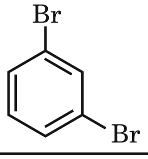
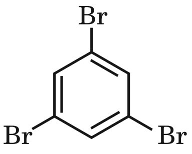
  - **Aryl halides:** The halogen atom is attached to the carbon atom right next to an aromatic ring.





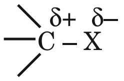
## Nomenclature

Alkyl halides are named as halo-substituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides.

| Structure | IUPAC Names | Common Names |
|---|---|---|
| $CH_3CH_2CH_2Br$ | 1-Brompropane | n-Propyl bromide |
|  $H_3C-\underset{\underset{Cl}{\vert}}{CH}-CH_3$ | 2-Chloropropane | Isopropyl chloride |
|  $H_3C-\overset{\overset{CH_3}{\vert}}{CH}-CH_2Cl$ | 1-Chloro-2-methylpropane | Isobutyl chloride |
|  | Bromobenzene | Bromobenzene |
|  | 1,3-Dibromobenzene | m-Dibromobenzene |
|  | 1,3,5-Tribromobenzene | sym-Tribromobenzene |
| $H_3C-CHCl_2$ | 1,1-Dicholoroethane | Ethylidene Chloride |

## Nature of C-X Bond

They form a polarised bond as the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



## Methods of preparation

- **From Alcohols**

  Alkyl halides are most commonly prepared from alcohols as the hydroxyl group of an alcohol can be easily replaced by any halogen atom.

$$R\text{–}OH + HX \xrightarrow{ZnCl_2} R\text{–}X + H_2O$$

$$R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$$

$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

$$R\text{–}OH \xrightarrow[X_2 = Br_2, I_2]{red\ P/X_2} R\text{–}X$$

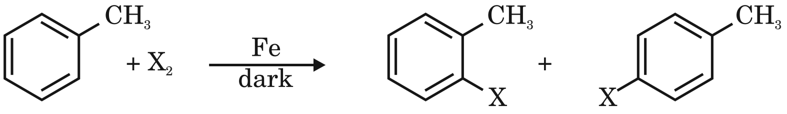
$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$$

## From Hydrocarbons

- **By free radical halogenation:** Under certain conditions we can obtain mixture of isomeric mono and polyhaloalakanes.

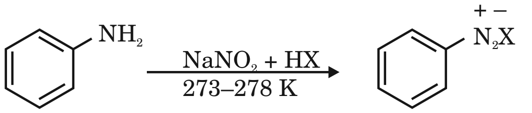
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

- **By electrophilic substitution:** This requires the presence of Lewis acid catalyst like iron or iron(III) chloride. Chloride and bromide compounds can be prepared from this method but not fluoro compounds due to the high reactivity of fluorine.

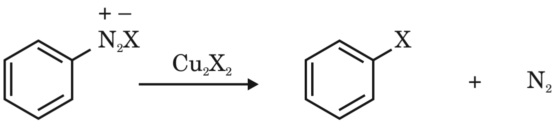


o-Halotoluene p-Halotouene

- **Sandmeyer's reaction:** This requires suspension of primary aromatic amine in cold aqueous mineral acid in the presence of sodium nitrate. A diazonium salt is formed which on reaction with cuprous chloride or bromide will replace diazonium group by Cl or Br.



Benzene diazonium halide



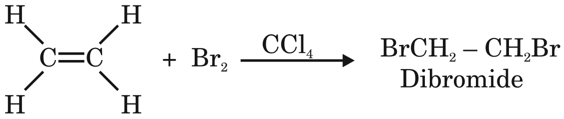
Aryl halide
X = Cl, Br

- **From alkenes**
  - (*i*) **Addition of hydrogen halides:** This requires a reaction of alkyl halide with hydrogen chloride, bromide or iodide.

$$CH_3CH = CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(*ii*) **Addition of halogens:** The following reaction takes place in presence of

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} = \frac{W_B \times 1000}{M_B \times V(\text{ml})}.$$



- **Halogen Exchange**

  The reaction in which the alkyl iodides are prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone is known as **Finkelstein Reaction.**

  $$R–X \quad + \quad NaI \longrightarrow R–I \quad + \quad NaX$$

  $X = Cl, Br$

  The reaction in which alkyl fluorides are prepared by the reaction of alkyl chlorides/ bromides with metallic fluoride is known as **Swarts Reaction**.

  $$H_3C–Br + AgF \longrightarrow H_3C–F \; + \; AgBr$$

# Properties of Haloalkanes and Haloarenes Including Polyhalogen Compounds

## Physical Properties

- **Melting and boiling points**

  Because of the polarity of halogen compounds, the intermolecular forces of attraction are stronger due to which the boiling and melting points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons. The decreasing order of boiling points of some alkyl hydrides is: RI>RBr>RCl>RF. The boiling points of some isomers are high due to the symmetry.

- **Density**

  The density of alkyl hydrides increases with the number of carbon atoms and halogen atoms and their atomic masses.

- **Solubility**

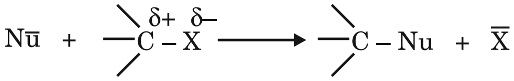
  The solubility of haloalkanes in water is quiet low because of strong hydrogen and carbon bond which is not easy to overcome or break. However, haloalkanes are soluble in solvent molecules because of the new intermolecular interactions between haloalkanes and solvent molecules which do not require much energy.

## Chemical Reactions

- **Reactions of Haloalkanes**

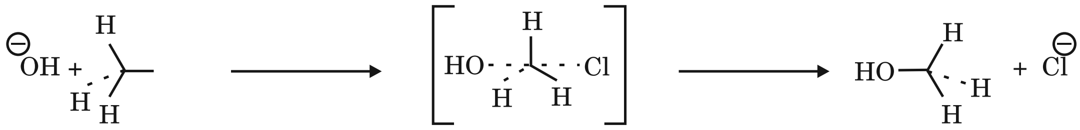
  ➢ **Nucleophilic substitution reactions**

  A nucleophile reacts with a partial positive charge on a carbon atom of the haloalkanes, which then gets substituted by the nucleophile and separates out as halide ion.

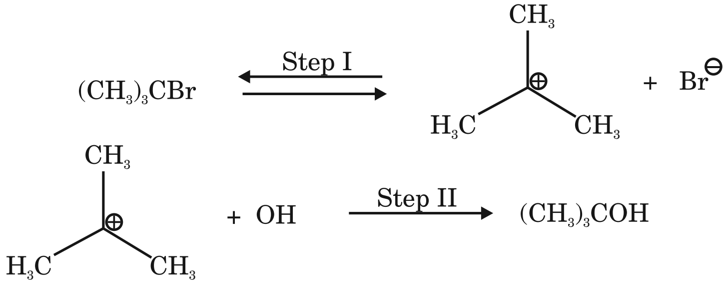
  ➢ **bimolecular nucleophilic Substitution**

  In this case of nucleophilic substitution, a new carbon-OH bond is formed while simultaneously breaking the carbon-halide bond. Since both the steps take place simultaneously, this process is called **Inversion of configuration**.



- **unimolecular nucleophilic Substitution**

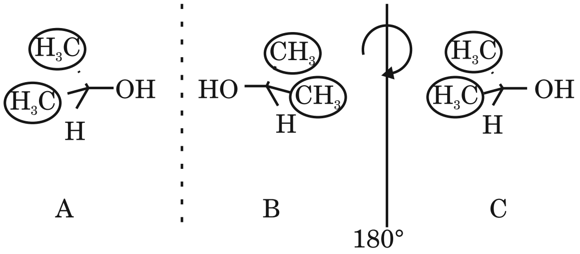
These reactions require a presence of polar protic solvents like water or alcohol and follow the first order kinetics in which the reaction rate depends on only one reactant. This happens in two steps. In first step, bromide ion is separated out and then in the next step carbocation formed is attacked upon by the nucleophile.



- **Stereochemical aspects of nucleophilic substitution reactions**

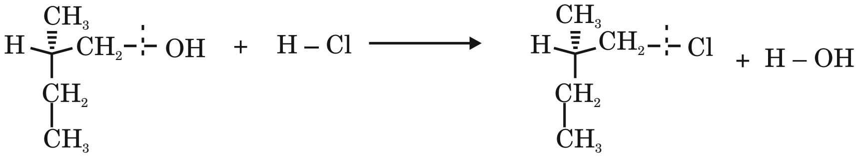
(*i*) **Plane polarised light and optical activity:** Those compounds which rotate the plane polarised light when passed through their solutions are called optically active compounds. If the light is rotated to the right by the compound, then it is called dextrorotatory and is represented by placing a positive sign before the degree of rotation. If the light is rotated to the left by the compound, then it is called laevorotatory and is represented by placing a positive sign before the degree of rotation. These isomers are called optical isomers and the phenomenon is called optical isomerism.

(*ii*)**Molecular asymmetry, chirality and enantiomers:** A carbon atom is called asymmetric carbon or stereocentre if the spatial arrangement of four groups around the central carbon is tetrahedral. The molecule so formed is referred to as asymmetric molecule. The super imposable objects when placed in front of the mirror are said to be achiral and the property is called as chirality. Those objects which are non-super imposable are known as chiral. For ex, propanol.



Enantiomers are stereoisomers which are related to each other as non-super imposable mirror images. When the rotation due to one isomer is cancelled by the rotation of other isomer in a mixture containing two equal enantiomers is known as racemic mixture and this process is known as racemisation.

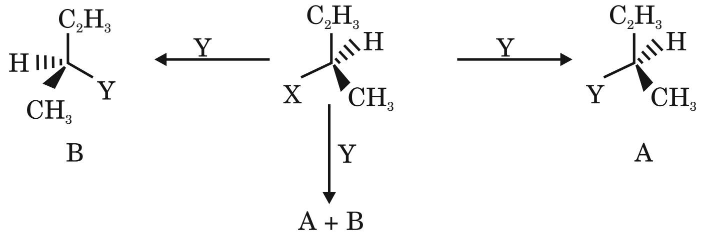
(*iii*) **Retention:** The preservation of integrity of the spatial arrangement of bonds during transformation or a chemical reaction is known as retention.



(–) –2-Methyl butan-1-ol

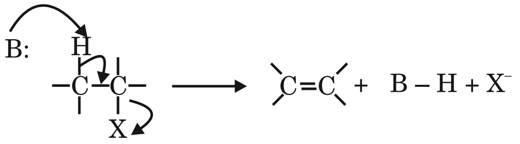
(+)-1-chloro-2-methyl butane

(*iv*) Inversion, retention and racemisation: If in a chemical reaction, compound A is produced, the process is called retention of configuration. If compound B is produced, then it is called inversion of configuration. If a mixture is produced, then the process is called racemisation.



- **Elimination reactions**

  This reaction requires the presence of alcoholic potassium hydroxide when a haloalkane with β-hydrogen is heated with it and the process is known as β-elimination.



B = Base ; X = Leaving group

- **Reaction with metals**

  The compounds obtained when chlorides or bromides react with certain metals are known as organo-metallic compounds. Grignard reagents of the form, RMgX, are obtained in such reactions.

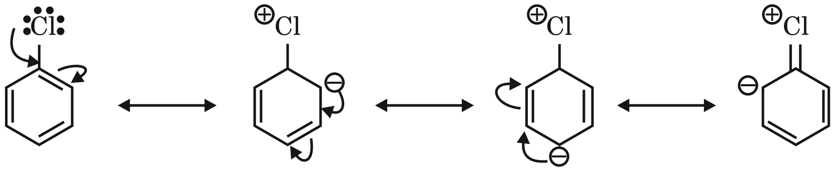
  $$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

  **Wurtz reaction:** The reactions in which alkyl halides reacts with sodium in dry ether to produce hydrocarbons with double the number of carbon atoms present in the halide.

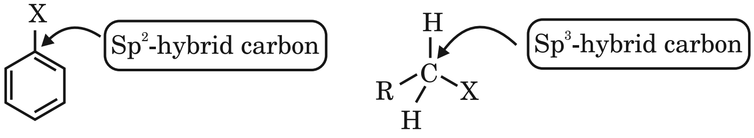
  $$2RX + Na \longrightarrow RR + NaX$$

- **Reaction of Haloarenes**
  - **Nucleophilic substitution**

(*i*) **Resonance effect:** The electron pairs on halogen atom are in conjugation with $\pi$- electrons of the ring. The following resonating structures can be formed.

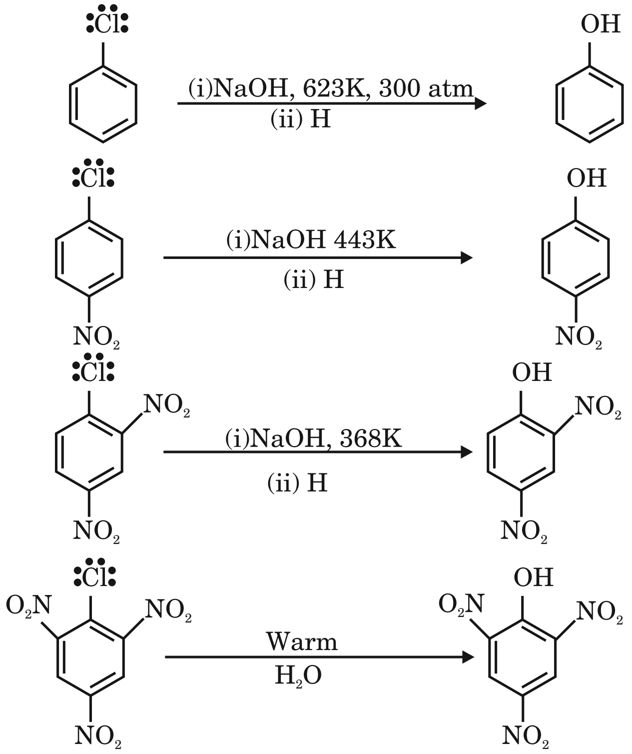


(*ii*) **Difference in hybridisation of carbon atom in C-X bond:** In haloalkanes, halogen gets connected with the carbon through $sp^3$ hybridisation, while in Haloarenes, it is connected with $sp^2$ hybridisation.



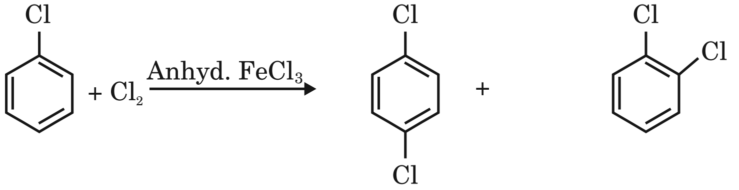
(*iii*) **Instability of phenyl cation:** In Haloarenes, the phenyl cation formed is not stabilized by resonance due to self-ionisation.

(*iv*) **Replacement by hydroxyl group:** Phenol is formed by heating chlorobenzene in aqueous sodium hydroxide solution.



- **Electrophilic substitution reactions**

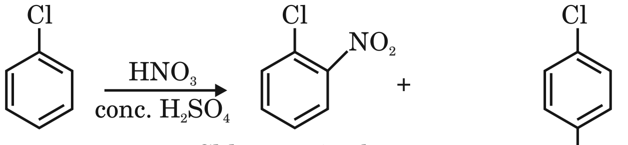
(*i*) **Halogenation:**



1, 4-Dichlorobenzene
(Major)

1, 2-Dichlorobenzene
(Minor)

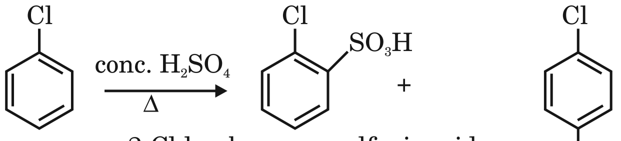
(*ii*) **Nitration:**



1-Chloro-2-nitrobenzene
(Minor)

1-Chloro-4-nitrobenzene
(Major)

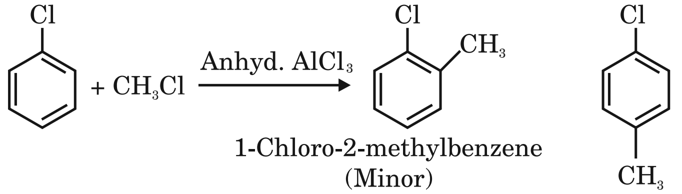
(*iii*) **Sulphonation:**



2-Chlorobenzene sulfonic acid
(Minor)

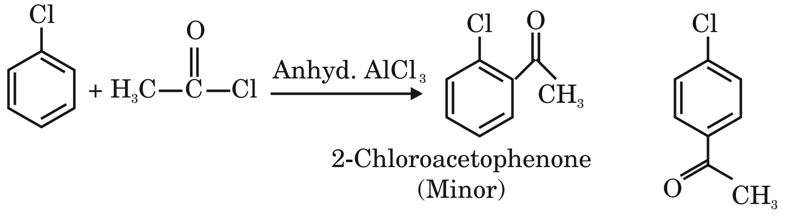
4-Chlorobenzene sulfonic acid
(Major)

(*iv*) **Friedel-Crafts reaction:**



1-Chloro-2-methylbenzene
(Minor)

1-Chloro-4-methylbenzene
(Major)



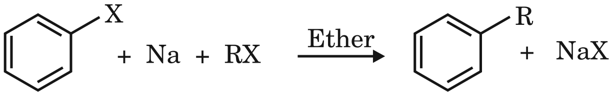
2-Chloroacetophenone
(Minor)

4-Chloroacetophenone
(Major)

- **Reaction with metals**

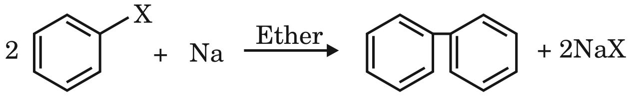
(*i*) **Wurtz-Fittig reaction**

Alkylarene is obtained on reaction of a mixture of alkyl halide and aryl halide with sodium in dry ether.



(*ii*) **Fittig reaction**

Analogous compounds are also formed in which two aryl groups are joined together.



- **Polyhalogen Compounds**

- **Dichloromethane (Methylene chloride):** It is prepared industrially by the direct chlorination of methane.

$$CH_4 + 2Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + 2HCl$$

Fractional distillation is used to separate the mixture so obtained. It is used as a solvent, as a paint remover, as a propellant in aerosols and also as a metal cleaning and finishing solvent.

- **Trichloromethane (Chloroform):** It is manufactured by chlorination of methane followed by separation by fraction.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\nu} CHCl_3 + 3HCl$$

It is extensively used as solvent for waxes, resins, rubber, fats etc. Earlier, chloroform was used as anesthetic but at present this practice has been dropped as it is slowly oxidized by air in the presence of light to form highly poisonous phosgene gas. Therefore, it is stored in closed dark coloured bottles completely filled so that air is kept out.

- **Triiodomethane (Iodoform):** It is prepared by heating ethanol or acetone with sodium hydroxide or $Na_2CO_3$ and $I_2$ in water. It is insoluble in water and thus forms yellow precipitate of $CHI_3$.

$$CH\ CH_2OH + 6NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

It is used as an antiseptic for dressing wounds.

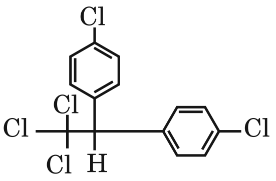
- **Tetrachloromethane (Carbon tetrachloride):** It is prepared by chlorination of methane and by action of chlorine on $CS_2$ in the presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + \underset{\text{(Sulphur dichloride)}}{SCl_2}$$

$$CH_4 + 4Cl_2 \xrightarrow{h\upsilon} CCl_4 + 4HCl$$

It is used in fire extinguisher. Also, it is used as solvent for fats, resins etc.

- **Freons:** The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- **p, p'-Dichlorodiphenyltrichloroethane(DDT):** It is non-biodegradable and extremely stable. It is used as an insecticide. It is manufactured by the condensation of chlorobenzene with chloral in the presence of sulphuric acid. It was earlier used to control malaria and typhoid but due to its highly toxic nature, it was banned in India and USA.



DDT

## EXERCISE

1. Which of the following halide is 2°
   - (*a*) Isopropyl chloride
   - (*b*) Isobutyl chloride
   - (*c*) n-propyl chloride
   - (*d*) n-butyl chloride
2. Haloforms are trihalogen derivatives of
   - (*a*) Ethane
   - (*b*) Methane
   - (*c*) Propane
   - (*d*) Benzene
3. Which of the following is a primary halide
   - (*a*) Isopropyl iodide
   - (*b*) Secondary butyl iodide
   - (*c*) Tertiary butyl bromide
   - (*d*) Neo hexyl chloride
4. What is the main product of the reaction between 2-methyl propene with HBr
   - (*a*) 1-bromo butane
   - (*b*) 1-bromo-2 methyl propane
   - (*c*) 2-bromo butane
   - (*d*) 2-bromo-2 methyl propane
5. Silver acetate + $Br_2 \xrightarrow{CS_2}$. The main product of this reaction is
   - (*a*) $CH_3 - Br$
   - (*b*) $CH_3COI$
   - (*c*) $CH_3COOH$
   - (*d*) None of these
6. $C_3H_8 + Cl_2 \xrightarrow{Light} C_3H_7Cl + HCl$ is an example of which of the following types of reactions
   - (*a*) Substitution
   - (*b*) Elimination
   - (*c*) Addition
   - (*d*) Rearrangement
7. Benzene reacts with chloride to form benzene hexachloride in presence of
   - (*a*) Nickel
   - (*b*) $AlCl_3$
   - (*c*) Bright sunlight
   - (*d*) Zinc

**8.** Which of the following is obtained when chloral is boiled with NaOH.

(*a*) $CH_3Cl$ (*b*) $CHCl_3$
(*c*) $CCl_4$ (*d*) None of these

**9.** Chlorine reacts with ethanol to give

(*a*) Ethyl chloride (*b*) Chloroform
(*c*) Acetaldehyde (*d*) Chloral

**10.** Which compound gives yellow ppt. with iodine and alkali

(*a*) 2-hydroxy propane (*b*) Acetophenone
(*c*) Methyl acetone (*d*) Acetamide

**11.** Ethanol is converted into ethyl chloride by reacting with

(*a*) $Cl_2$ (*b*) $SOCl_2$
(*c*) HCl (*d*) NaCl

**12.** The starting substance for the preparation of $CH_3I$ is

(*a*) $CH_3OH$ (*b*) $C_2H_5OH$
(*c*) $CH_3CHO$ (*d*) $(CH_3)_2CO$

**13.** Reaction of ethyl chloride with sodium leads to

(*a*) Ethane (*b*) Propane
(*c*) n-butane (*d*) n-pentane

**14.** $2CHCl_3 + O_2 \xrightarrow{X} 2COCl_2 + 2HCl$

In the above reaction, X stands for

(*a*) An oxidant (*b*) A reductant
(*c*) Light and Air (*d*) None of these

**15.** Phosgene is the common name for

(*a*) $CO_2$ and $PH_3$
(*b*) Phosphoryl chloride
(*c*) Carbonyl Chloride
(*d*) Carbon tetrachloride

**16.** When chloroform is treated with amine and KOH, we get

(*a*) Rose odour smell
(*b*) Sour almond like smell
(*c*) Offensive odour
(*d*) Sour oil of winter green like smell

**17.** Which of the following compound will make precipitate most readily with $AgNO_3$

(*a*) $CCl_3CHO$ (*b*) $CHCl_3$
(*c*) $C_6H_5CH_2Cl$ (*d*) $CHI_3$

**18.** Grignard reagent is prepared by the reaction between

(*a*) Zinc and alkyl halide
(*b*) Magnesium and alkyl halide
(*c*) Magnesium and alkane
(*d*) Magnesium and aromatic hydrocarbon

**19.** War gas is formed from

(*a*) $PH_3$ (*b*) $C_2H_2$
(*c*) Zinc phosphate (*d*) Chloropicrin

**20.** What happens when $CCl_4$ is treated with $AgNO_3$

(*a*) $NO_2$ will be evolved
(*b*) A white ppt. of AgCl will be formed
(*c*) $CCl_4$ will dissolve in $AgNO_3$
(*d*) Nothing will happen

**21.** If we use pyrene ($CCl_4$) in the Riemer-Tiemann reaction in place of chloroform, the product formed is

(*a*) Salicylaldehyde (*b*) phenolphthalein
(*c*) Salicylic acid (*d*) Cyclohexanol

**22.** Ethylidene chloride on treatment with aqueous KOH gives

(*a*) Ethylene glycol (*b*) Acetaldehyde
(*c*) Formaldehyde (*d*) None

**23.** Ethylene difluoride on hydrolysis gives

(*a*) Glycol (*b*) Fluoroethanol
(*c*) Oifluoroethanol (*d*) Freon

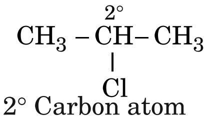
**24.** Benzyl Chloride when oxidised by $Pb(NO_3)_2$ gives

(*a*) Benzoic acid
(*b*) Benzaldehyde
(*c*) Benzene
(*d*) None

# Answer Keys

**1.** (*a*) **2.** (*b*) **3.** (*d*) **4.** (*d*) **5.** (*a*) **6.** (*a*) **7.** (*c*) **8.** (*b*) **9.** (*d*) **10.** (*b*)
**11.** (*b*) **12.** (*a*) **13.** (*c*) **14.** (*c*) **15.** (*c*) **16.** (*d*) **17.** (*d*) **18.** (*b*) **19.** (*d*) **20.** (*d*)
**21.** (*c*) **22.** (*b*) **23.** (*a*) **24.** (*b*)

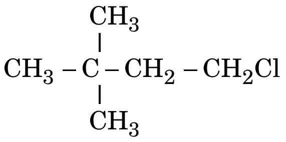
# Solutions

**1.** Isopropyl chloride  $CH_3-\overset{2^\circ}{CH}(Cl)-CH_3$ chlorine atom is attached to 2° Carbon atom

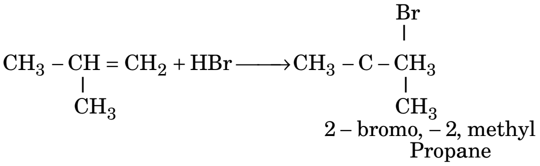
**2.** $CH_4 \xrightarrow[+3X]{-3H} CHX_3$

Where X = Cl, Br, I

**3.** Neohexyl chloride is a primary halide as in it Cl-atom is attached to a primary carbon.



$CH_3-C(CH_3)_2-CH_2-CH_2Cl$

**4.** 

$CH_3-CH(CH_3)=CH_2 + HBr \longrightarrow CH_3-C(Br)(CH_3)-CH_3$

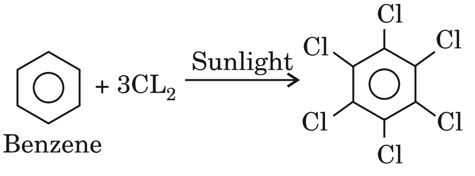
2 – bromo, – 2, methyl Propane

2-bromo,–2, methyl propane

**5.** $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_3Br + AgBr + CO_2$

**6.** $C_3H_8 + Cl_2 \xrightarrow{Light} C_3H_7Cl + HCl$

This is an example of substitution reaction. Hydrogen atom of alkane is replaced by halogen atom.

**7.** 

Benzene

BHC

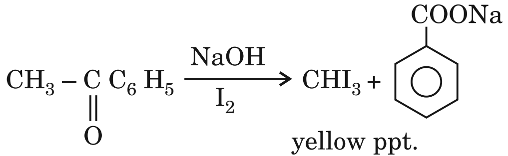
**8.** $CCL_3CHO + NaOH \xrightarrow{Boil} CHCl_3 + HCOONa$

Chlorol Chloroform

**9.** $CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$

$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$

Chloral

**10.** 

A Cetophenone

yellow ppt.

**11.** $C_2H_5OH + SOCl_2 \xrightarrow{Pyridine} C_2H_5Cl + SO_2 + HCl$

**12.** $CH_3OH + HI \xrightarrow{ZnCl_2} CH_3I + H_2O$

**13.** $C_2H_5Cl + 2Na + ClC_2H_5 \xrightarrow[Ether]{Dry} C_2H_5-C_2H_5 + 2NaCl$

**14.** $2CHCl_3O_2 \xrightarrow[air]{Light} 2COCl_2 + 2HCl$

Phosgene

**15.** $COCl_2$ Carbonyl Chloride is Commonly Called as Phosgene

**16.** $C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5-N=C + 3KCl + 3H_2O$

(Ethylisocyanide)

**17.** $CHI_3$ gives a yellow ppt. of AgI

**18.** $RX + Mg \xrightarrow[ether]{Dry} R-Mg-X$

Grignard's reagent

(Where X = Cl, Br, I)

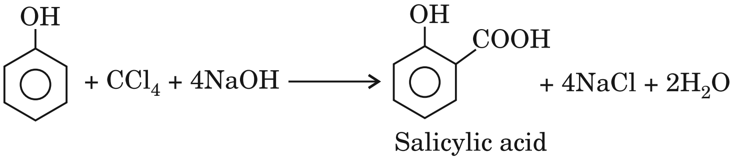
**19.** $CHCl_3 + HO-NO_2 \longrightarrow CCl_3NO_2 + H_2O$

Chloropicrin (war gas)

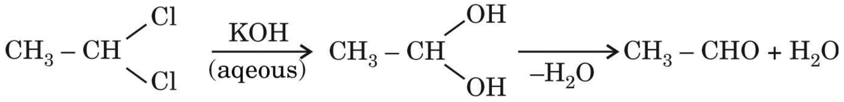
**20.** $CCl_4 + AgNO_3 \longrightarrow$ No reaction

$CCl_4$ is a covalent compound. Therefore does not provide $Cl^-$ ions.

**21.**

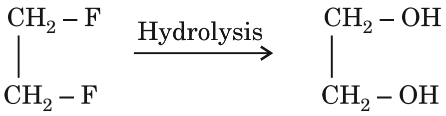


**22.**



$$\mathrm{CH_3-CH}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} \xrightarrow[\text{(aqeous)}]{\mathrm{KOH}} \mathrm{CH_3-CH}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} \xrightarrow[-\mathrm{H_2O}]{} \mathrm{CH_3-CHO + H_2O}$$

**23.**



$$\begin{matrix}\mathrm{CH_2-F}\\ |\\ \mathrm{CH_2-F}\end{matrix} \xrightarrow{\text{Hydrolysis}} \begin{matrix}\mathrm{CH_2-OH}\\ |\\ \mathrm{CH_2-OH}\end{matrix}$$

**24.**