

# Haloalkanes and Haloarenes

## [TOPIC 1] Introduction, Nomenclature and Preparation

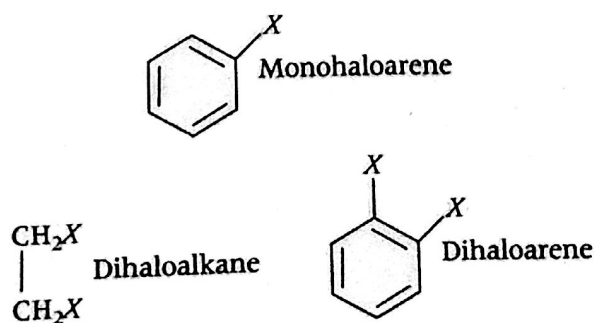
Haloalkanes and haloarenes are obtained by the replacement of a hydrogen atom of an alkane and arene respectively by a halogen atom (F, Cl, Br, I). Haloalkanes contain halogen atoms attached to the  $sp^3$ -hybridised carbon atom of an alkyl group, whereas haloarenes contain halogen atoms attached to  $sp^2$ -hybridised carbon atoms of an aryl group. Haloalkanes have general formula,  $C_nH_{2n+1}X$ .

### 1.1 Classification of Haloalkanes and Haloarenes

#### On the Basis of Number of Halogen Atoms

Haloalkanes and haloarenes can be classified as mono, di or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in the structure.

e.g.  $C_2H_5X$ -Monohaloalkane

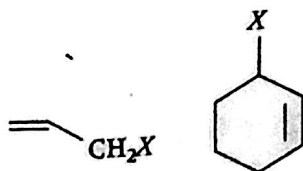


Mono halocompounds can be classified according to the hybridisation of the carbon atom to which the halogen is bonded.

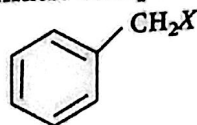
## On the Basis of Nature of Carbon of C-X Bond

### Compounds containing $sp^3$ C-X Bond

- (a) **Alkyl Halides** In alkyl halides, the halogen atom is bonded to an alkyl group. They can be further classified as primary, secondary or tertiary.
- (b) **Allylic Halides** These are the compounds in which the halogen atom is bonded to an allylic carbon.



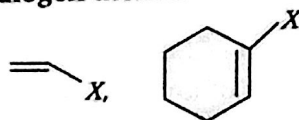
- (c) **Benzylic Halides** These are the compounds in which the halogen atom is bonded to a  $sp^3$  hybridised carbon atom next to an aromatic compound.



### Compounds Containing $sp^2$ C-X Bond

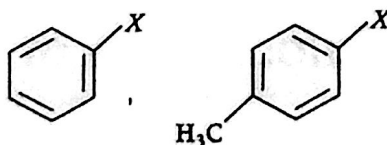
#### (a) Vinylic Halides

These are the compounds in which the halogen atom is bonded to vinylic carbon.



#### (b) Aryl Halides

These are the compounds in which the halogen atom is bonded to  $sp^2$  hybridised carbon atom of an aromatic ring



## Nomenclature

The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halo substituted hydrocarbon in the IUPAC system of nomenclature.

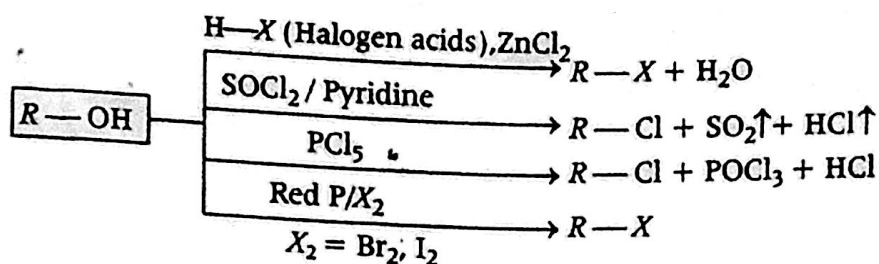
Structure	Common Name	IUPAC Name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	<i>sec</i> -butyl chloride	2-chlorobutane
$\text{CH}_2 = \text{CHCl}$	Vinyl chloride	Chloroethene
	<i>o</i> -chlorotoluene	1-chloro-2-methyl benzene
	Benzyl chloride	Chlorophenyl methane

## 1.2 Nature of C-X Bond

C-X bond of haloarenes is less polar and shorter than C-X bond of haloalkanes. The reason for this occurrence is that haloarenes are more electron rich, due to the presence of double bonds.

## 1.3 Preparation of Haloalkanes

### From Alcohols



In the preparation of alkyl halides from alcohols, the best method is the reaction of alcohols with SOCl<sub>2</sub> as it yields gaseous products leaving behind pure haloalkanes.

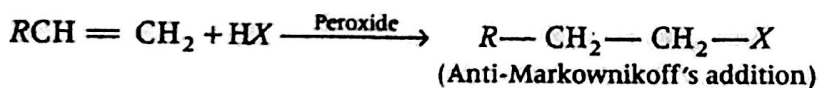
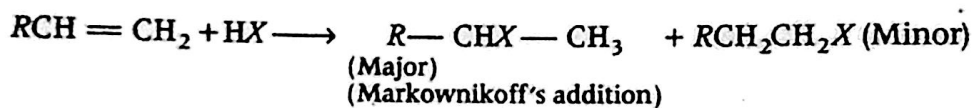
### From Alkanes

By free radical halogenation

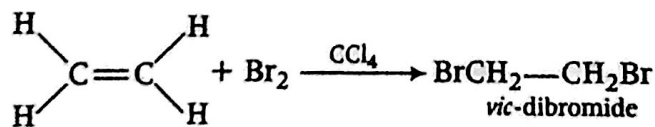


### From Alkenes

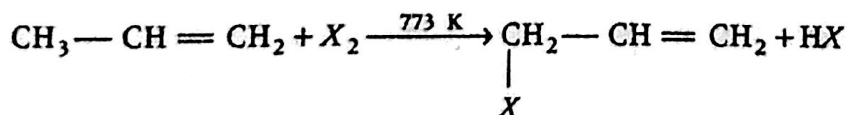
Addition of halogen acids



Addition of halogens

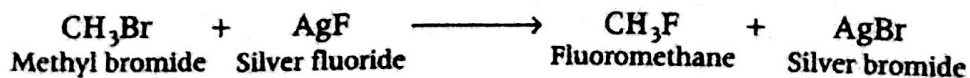


Allylic halogenation



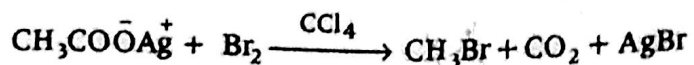
### Swarts Reaction

Fluoroalkanes are prepared by treating alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg<sub>2</sub>F<sub>2</sub>, CoF<sub>2</sub> or SbF<sub>3</sub>. This reaction is known as Swarts reaction.



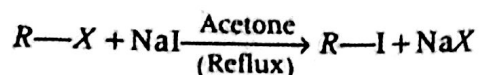
## Borodine-Hunsdiecker reaction

Generally, bromoalkanes are prepared by the reaction known as Borodine-Hunsdiecker reaction.



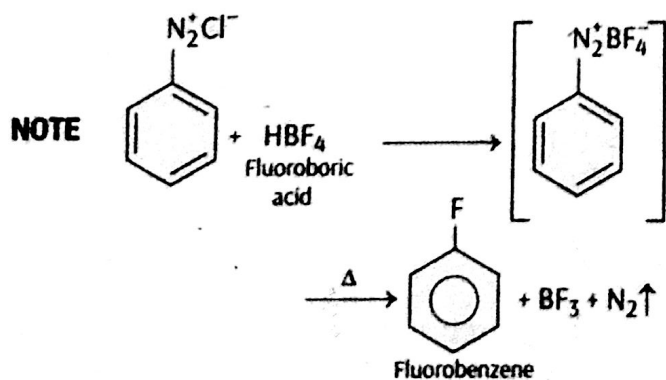
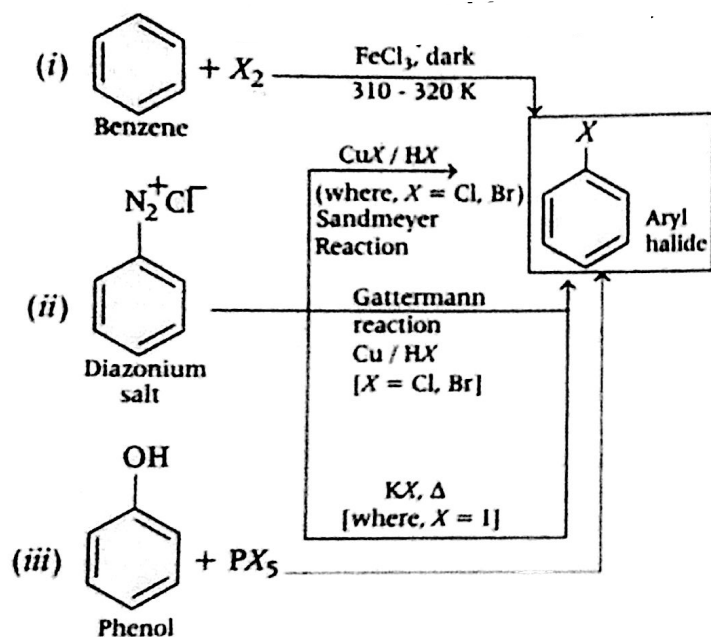
## Finkelstein reaction

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as **Finkelstein reaction**.



where,  $X = \text{Cl, Br}$

## 1.4 Preparation of Haloarenes



This reaction is called **Balz-Schiemann reaction** and is used to prepare fluoroarenes.

## [TOPIC 2] Properties of Haloalkanes and Haloarenes Including Polyhalogen Compounds

### 2.1 Physical Properties

- (i) For a given halogen atom, the boiling point of alkyl halides increases with increase in the size of alkyl group.
- (ii) For the same alkyl group, the boiling point decreases in the order  
 $RI > RBr > RCl > RF$
- (iii) Amongst, isomeric dichlorobenzene, *p*-isomer has highest melting point due to symmetry. For isomeric alkyl halides, boiling point decreases with branching.
- (iv) Alkyl halides are slightly soluble in water because they do not form H-bonds with water.
- (v) The stability of haloalkanes decreases as the strength of C—X bond decreases, ( $RF > RBr > RCl > RI$ ) due to increase in size of halogen atom down the group. Alternatively, bond dissociation enthalpy for C—X bond decreases down the group.
- (vi) C—X bond in aryl halides is shorter (due to partial double bond character acquired by C—X bond due to resonance), stronger and less polar than in alkyl halides.

### 2.2 Chemical Properties

#### Nucleophilic substitution reactions

Nucleophilic substitution reactions are of two types

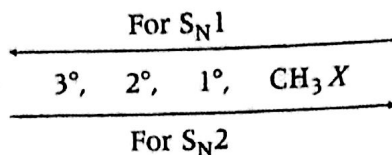
#### $S_N1$ reactions

Rate  $\propto [RX]$ , occurs in two steps: step 1- involving formation of carbocation intermediates, and in step 2, the carbocation thus formed is attached by the nucleophile. Step 1 is slowest and hence, is a rate determining step favoured by polar solvents. During  $S_N1$  reactions, optically active alkyl halides give racemic products.  $S_N1$  is shown by  $3^\circ$  alkyl halides.

#### $S_N2$ reactions

Rate  $\propto [RX][O^-H]$  occurs in one step through a transition state, favoured by solvents of low polarity and occurs from back side resulting in inversion of products.  $S_N2$  is shown by  $1^\circ$  alkyl halides.

Order of reactivity in  $S_N1$  and  $S_N2$  mechanisms are as follows

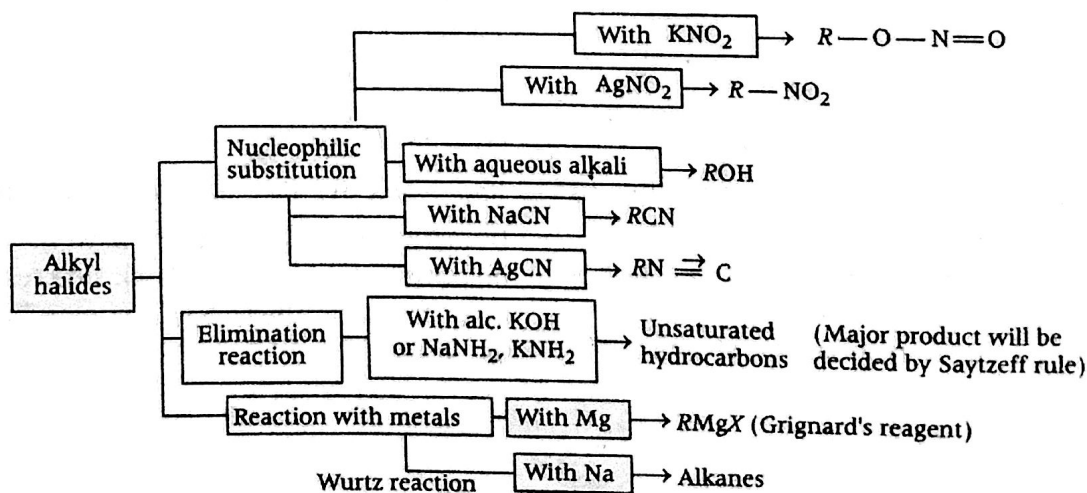


- For a given alkyl group, reactivity of alkyl halides in  $S_N1$  and  $S_N2$  reactions is  $RI > RBr > RCl > RF$  and order of leaving group tendency is  $I^- > Br^- > Cl^- > F^-$ .
- In case of optically active alkyl halides,  $S_N2$  mechanism results in the inversion of configuration while,  $S_N1$  mechanism results in racemisation.
- Ambident nucleophiles have two nucleophilic sites through which they can attack, e.g. nitrite ion.
- Alkyl halides are more reactive than aryl halides towards nucleophilic substitution reactions. It is due to the following reasons :
  - (i) In haloalkanes, there is single bond between  $R-X$ , which needs less bond dissociation energy, hence, they are more reactive toward nucleophiles. In haloarenes, there is double bond character between  $C-X$  bond due to resonance, therefore, has more bond dissociation energy.
  - (ii) Carbon attached to halogen is  $sp^3$ -hybridised in haloalkane and  $sp^2$ -hybridised in haloarene.  $sp^3$ -hybridised carbon is less electronegative than  $sp^2$ -hybridised carbon due to less  $s$ -character. Thus,  $C-X$  bond length is shorter in haloarenes than in haloalkanes.
  - (iii) It is difficult for electron rich nucleophiles to approach electron rich benzene ring in haloarenes. There is no such thing in haloalkane.
- The phenyl cation formed as a result of self ionisation in haloarenes is not stabilised by resonance. Thus, it doesn't undergo  $S_N1$  mechanism.

## Elimination reactions

Haloalkanes having  $\beta$ -hydrogen atom undergoes  $\beta$ -elimination when heated with alcoholic solution of KOH. Hydrogen atom from  $\beta$ -position and halogen atom from  $\alpha$ -position is eliminated to give unsaturated product.

## Flow Chart for Some Chemical Properties of Alkyl Halides



## 2.3 Basic Points About Optical Isomerism

- (i) The carbon atom which is attached to four different monovalent atoms is called **asymmetric or chiral carbon atom**.
- (ii) **Enantiomers** are the mirror images of each other and are non-superimposable.
- (iii) Substances which rotate the plane polarised light towards right are called **dextrorotatory (+)** and those which rotate the plane polarised light towards left are called **laevorotatory (-)**.
- (iv) If the product formed in a reaction has same stereochemistry as that of reactant, this process is called **retention of configuration**.
- (v) If the product formed in a reaction has a stereochemistry opposite to that of reactant, it leads to **inversion of configuration**. Many of the alkyl or aryl halide compounds can show optical isomerism.
- (vi) If in a reaction, 50% inversion and 50% retention occurs, the process is called **racemisation** and the product is called **racemic mixture**. A racemic mixture is optically inactive as it is a mixture containing two enantiomers in equal proportion and have zero optical rotation.

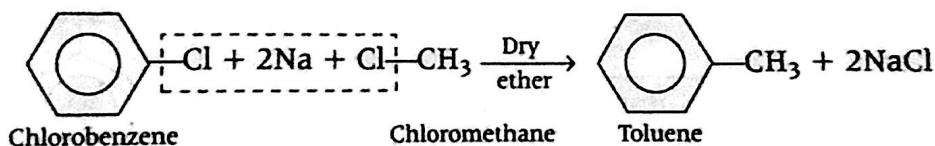
## Electrophilic Substitution Reactions (In Aryl halides)

Halogen atom is *o*-, *p*-directing in electrophilic substitution reactions since, electron density increases at *o* and *p*-positions due to +R-effect.

### Reaction with Metals

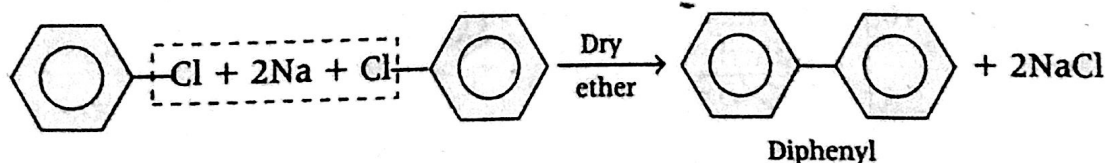
#### (a) Wurtz-Fittig Reaction

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**.

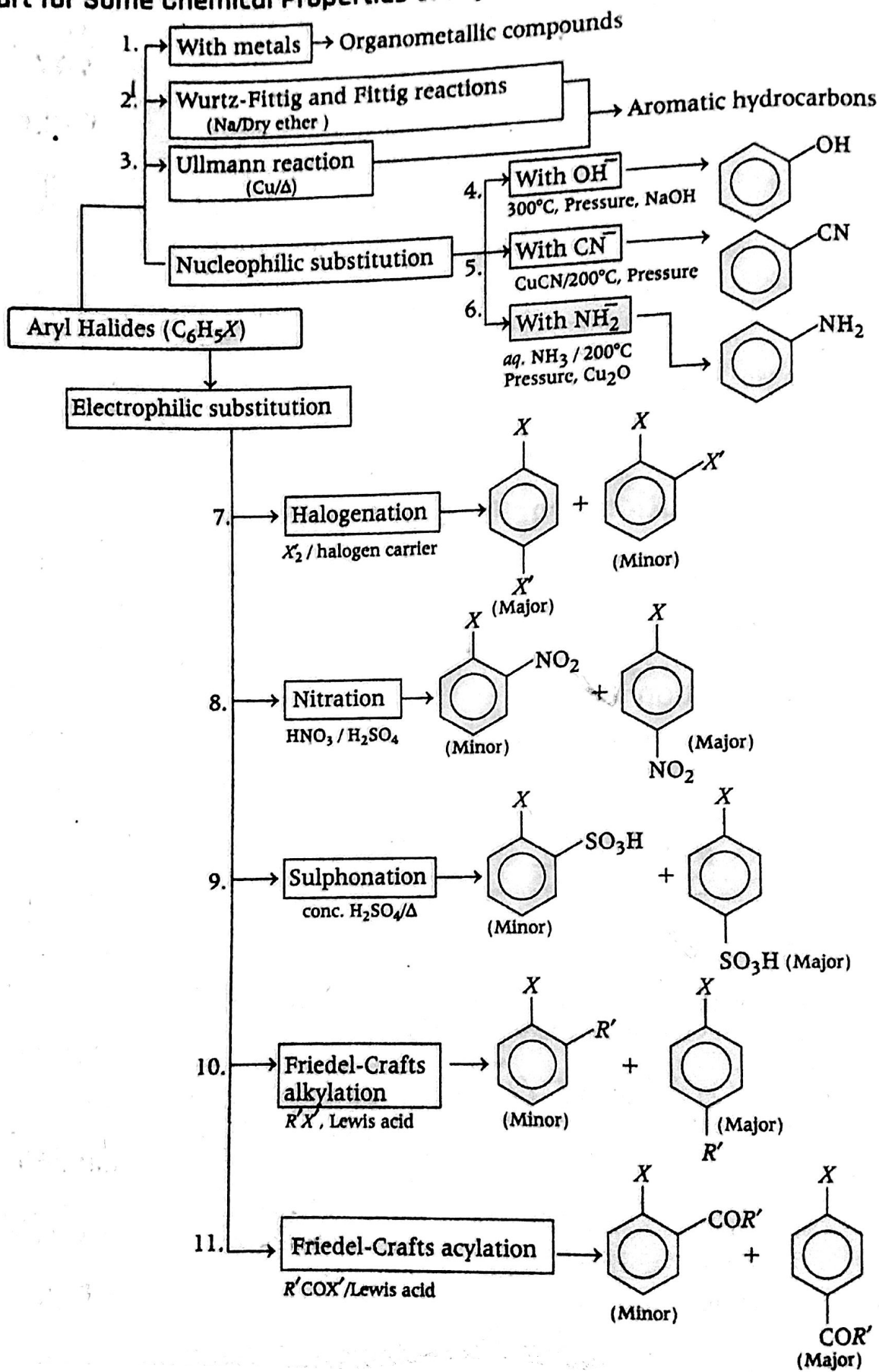


#### (b) Fittig Reaction

When aryl halides react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called Fittig reaction.



# Flow Chart for Some Chemical Properties of Aryl Halides





## 2.4 Polyhalogen Compounds

- (i) Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) is used as propellant in aerosols, as paint remover. Exposure to higher levels causes nausea, dizziness.
- (ii) The trihalogen derivatives of methane are called **haloforms**.  
e.g.  $\text{CHCl}_3$  (Chloroform),  $\text{CHI}_3$  (Iodoform, used as an antiseptic)
- (iii) Chloroform is stored in dark coloured bottles as in presence of light, it gets converted into highly poisonous substance, phosgene ( $\text{COCl}_2$ ).
- (iv) DDT is 1, 1, 1-trichloro-2, 2-bis (4-chlorophenyl) ethane and is used as a powerful insecticide.
- (v)  $\text{CCl}_4$  is used as a fire extinguisher under the name pyrene.
- (vi) Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) is used as a refrigerant.