



# HALOALKANES AND HALOARENES

# INTRODUCTION

- The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.
- Haloalkanes contain halogen atom(s) attached to the  $sp^3$  hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to  $sp^2$  hybridised carbon atom(s) of an aryl group.

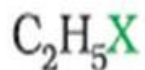
# USES

- Many halogen containing organic compounds are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds.
- Chlorine containing antibiotic, *chloramphenicol*, produced by soil microorganisms is very effective for the treatment of typhoid fever.
- Our body produces iodine containing hormone, *thyroxine*, the deficiency of which causes a disease called *goiter*.
- Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria;
- halothane is used as an anaesthetic during surgery.
- Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

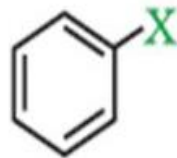
# CLASSIFICATION

## On the Basis of Number of Halogen Atoms

- Haloalkanes and haloarenes may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.)



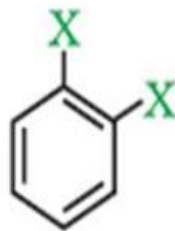
Monohaloalkane



Monohaloarene



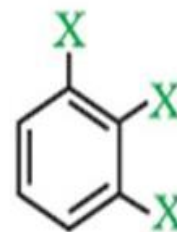
Dihaloalkane



Dihaloarene

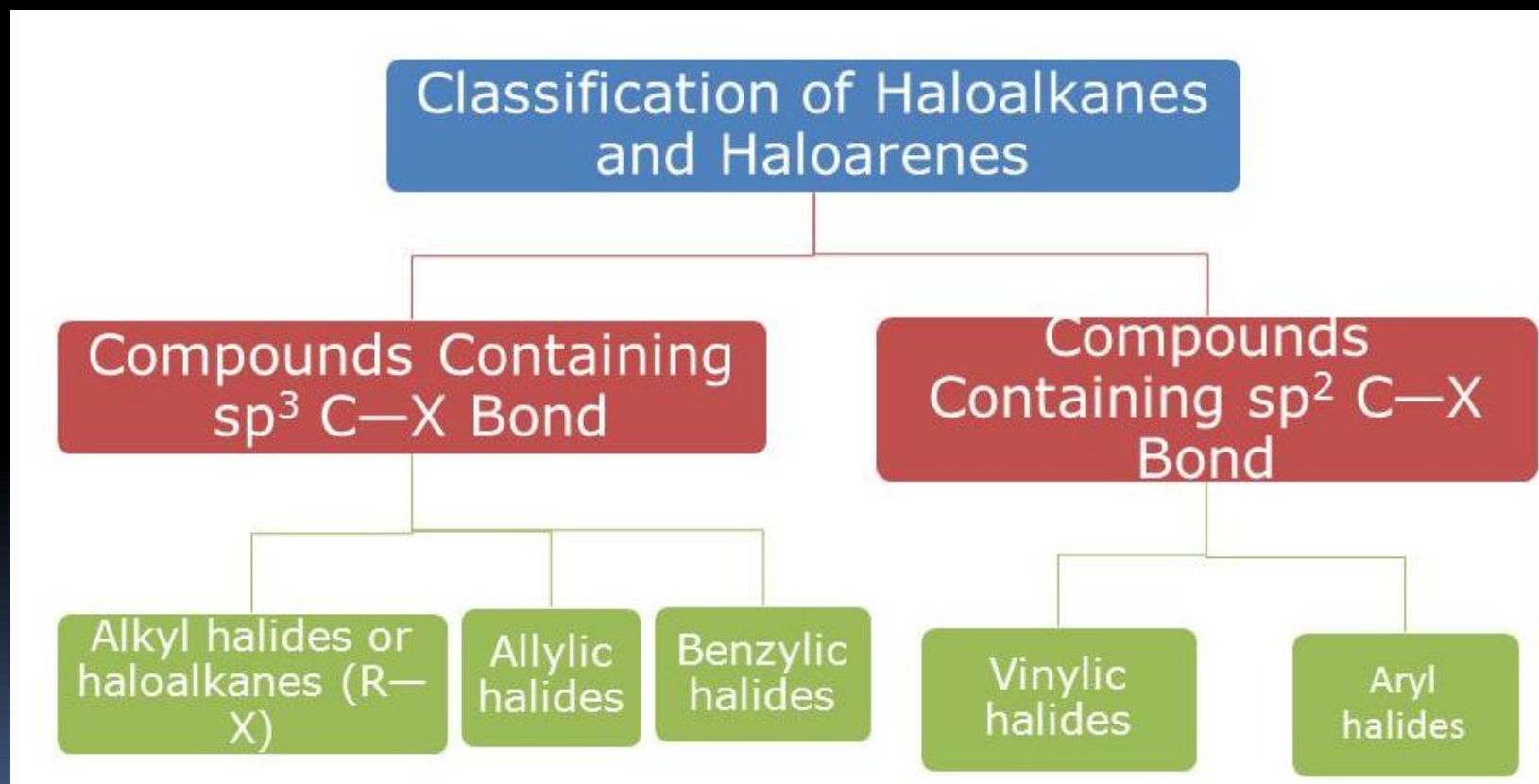


Trihaloalkane



Trihaloarene

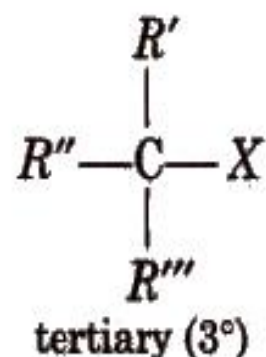
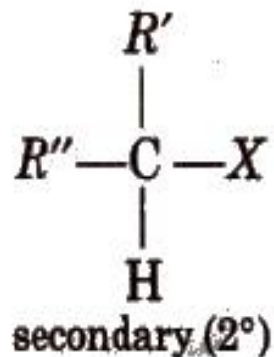
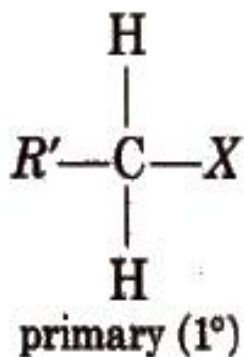
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded.



# COMPOUNDS CONTAINING $Sp^3C-X$ BOND

## (a) Alkyl halides or haloalkanes ( $R-X$ )

- In alkyl halides, the halogen atom is bonded to an alkyl group (R).
- They form a homologous series represented by  $C_nH_{2n+1}X$ .
- They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



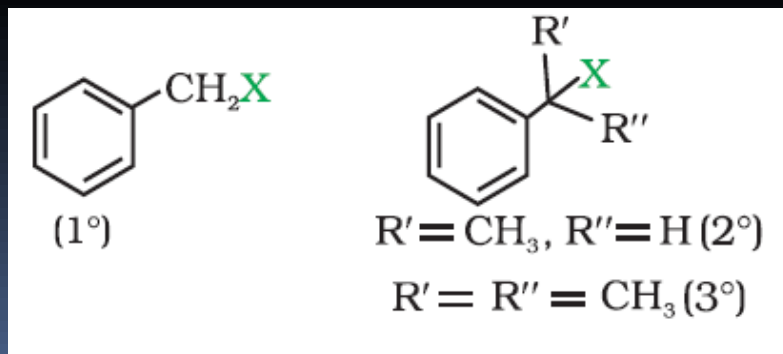
## (b) Allylic halides

These are the compounds in which the halogen atom is bonded to an  $sp^3$  hybridised carbon atom next to carbon-carbon double bond (C=C)



## (c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an  $sp^3$ -hybridised carbon atom next to an aromatic ring.

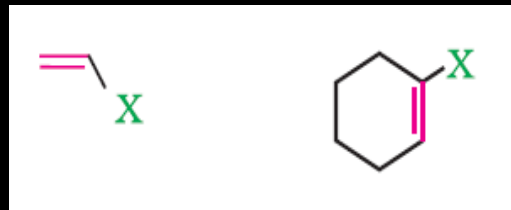


# Compounds Containing $sp^2$ C–X Bond

## Bond

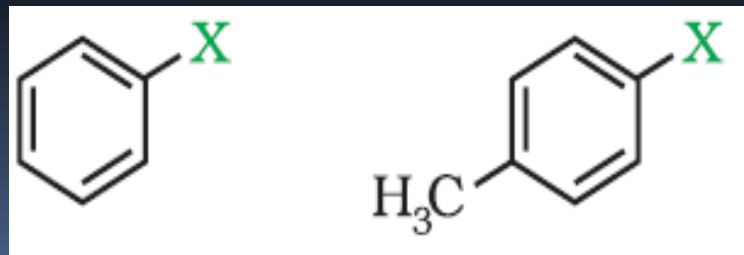
### (a) *Vinylic halides*

- the halogen atom is bonded to an  $sp^2$ -hybridised carbon atom of a carbon-carbon double bond (C = C).



### (b) *Aryl halides*

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





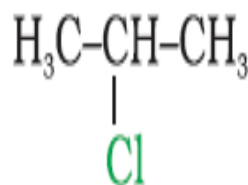
# Nomenclature

- Alkyl halides
- Common names are derived by naming the alkyl group followed by the halide.
- In the IUPAC system of nomenclature are named as halosubstituted hydrocarbons



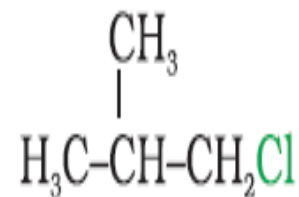
Common name: n-Propyl bromide

IUPAC name: 1-Bromopropane



Isopropyl chloride

2-Chloropropane



Isobutyl chloride

1-Chloro-2-methylpropane

The dihalo-compounds having same type of halogen atoms are further classified as geminal halides (halogen atoms are present on the same carbon atom) and vicinal halides (halogen atoms are present on the adjacent carbon atoms).

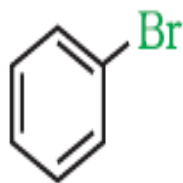
In common name system, *gem*-dihalides are named as alkylidene halides and *vic*-dihalides are named as alkylene dihalides.

In IUPAC system, they are named as dihaloalkanes.

	$\text{H}_3\text{C}-\text{CHCl}_2$	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$
Common name:	Ethylidene chloride ( <i>gem</i> -dihalide)	Ethylene dichloride ( <i>vic</i> -dihalide)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

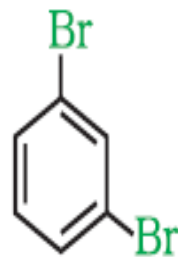
## Aryl halides

- Haloarenes are the common as well as IUPAC names .
- For dihalogen derivatives, the prefixes *o-*, *m-*, *p-* are used in common system. In IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.



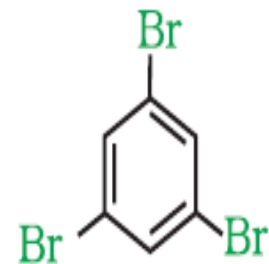
Common name: Bromobenzene

IUPAC name: Bromobenzene



*m*-Dibromobenzene

1,3-Dibromobenzene

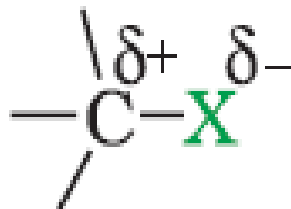


*sym*-Tribromobenzene

1,3,5-Tribromobenzene

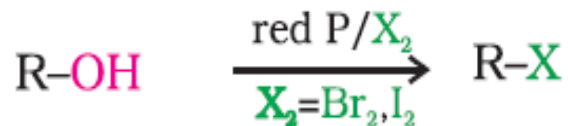
# Nature of C-X Bond

- Since halogen atoms are more electronegative than carbon, the carbon halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.
- Since the size of halogen atom increases as we go down the group in the periodic table. Consequently the carbon-halogen bond length also increases from C—F to C—I.



# Methods of Preparation

- From Alcohols

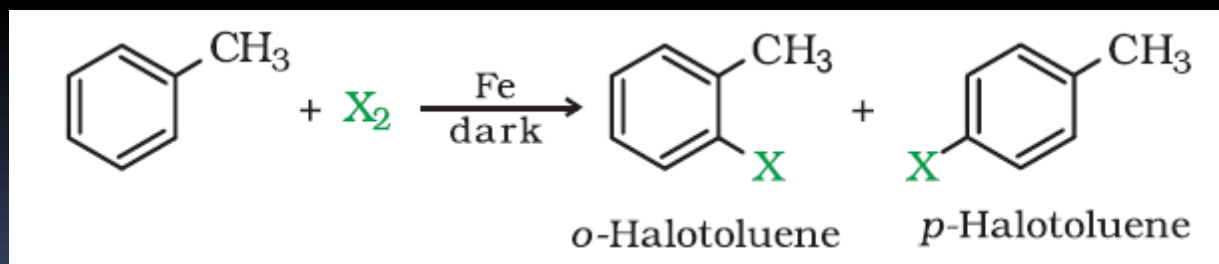


# From Hydrocarbons

(a) *By free radical halogenation*



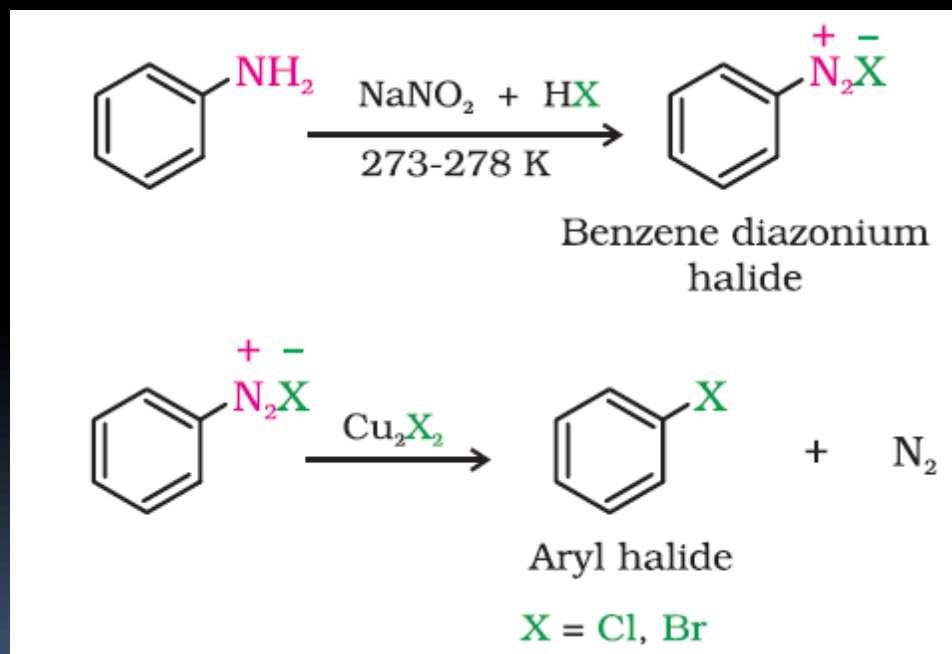
(b) *By electrophilic substitution*



## (c) Sandmeyer's reaction

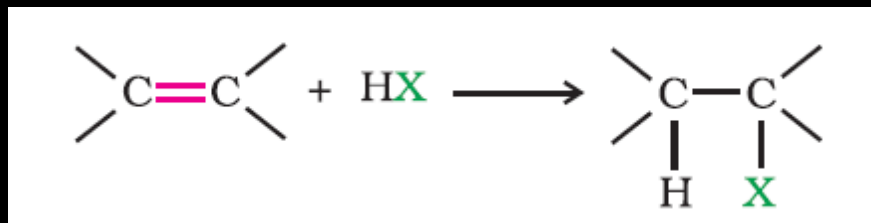
When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed.

Mixing diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by  $-Cl$  or  $-Br$ .

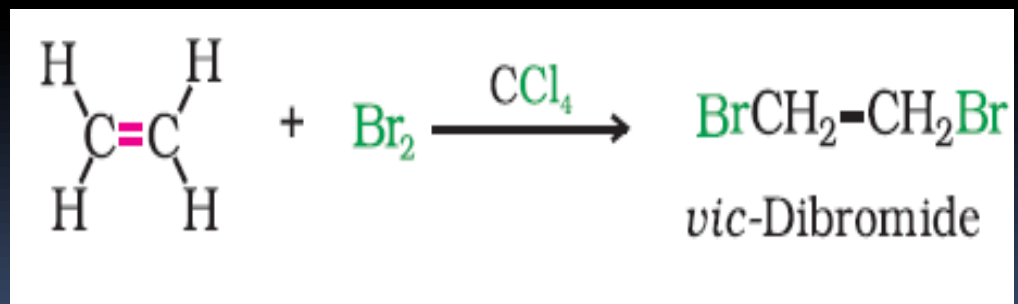


**(d) From alkenes**

**(i) Addition of hydrogen halides:**



**(ii) Addition of halogens:**





## Halogen Exchange

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



- The synthesis of alkyl fluorides is best accomplished by heating an 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>. The reaction is termed as Swarts reaction



# Physical Properties

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light.

## Melting and boiling points

- Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids.
- The boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons.
- The attractions get stronger as the molecules get bigger in size and have more electrons.
- Order of boiling points:  $RI > RBr > RCl > RF$ .
- The boiling points of isomeric haloalkanes decrease with increase in branching .
- Boiling points of isomeric dihalobenzenes are very nearly the same.
- The *para*-isomers are high melting as compared to their *ortho* and *meta*-isomers.

## Density

- Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms

## Solubility

- *The haloalkanes are only very slightly soluble in water.* In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

# Chemical Reactions

## Reactions of Haloalkanes

### (i) Nucleophilic substitution reactions

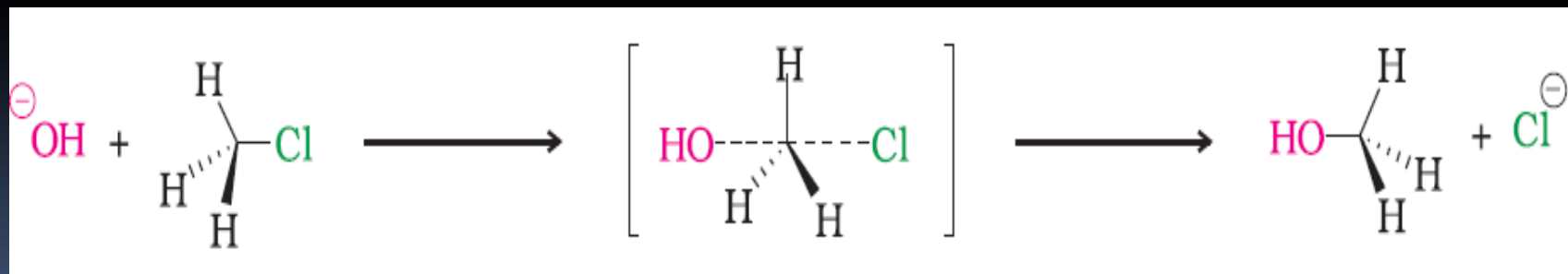
- A nucleophile reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion.



- Groups like cyanides and nitrites possess two nucleophilic centres and are called *ambident nucleophiles*. Cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways, linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides.
- Similarly nitrite ion also represents an ambident nucleophile. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

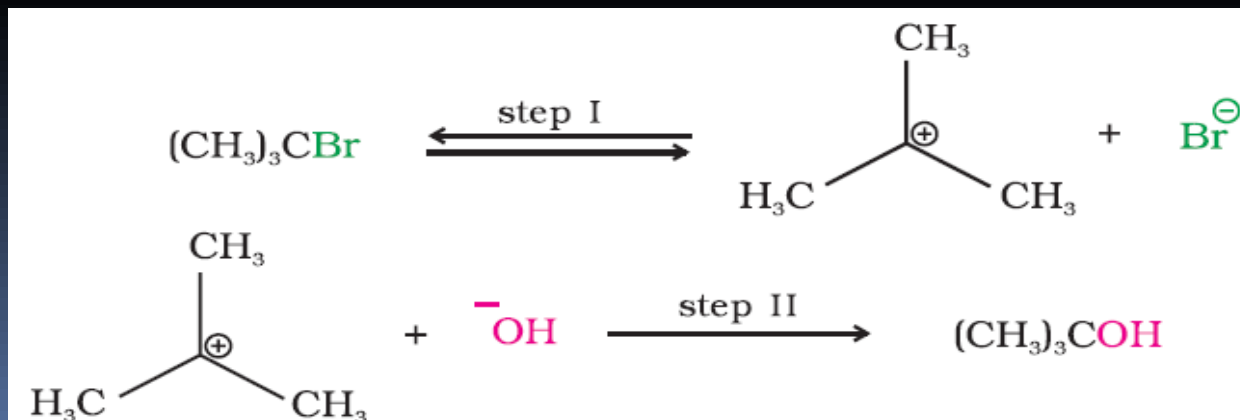
# Mechanism:

- **(a) Substitution nucleophilic bimolecular (SN<sub>2</sub>)**
- Follows a second order kinetics, the rate depends upon the concentration of both the reactants.
- The incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break while forming a new carbon-OH bond.
- These two processes take place simultaneously in a single step and no intermediate is formed.
- Inversion of configuration happens during the reaction
- order of reactivity followed is:  
Primary halide > Secondary halide > Tertiary halide.



## (b) Substitution nucleophilic unimolecular (SN1)

- SN1 reactions are generally carried out in polar protic solvents.
- Follows the first order kinetics, the rate of reaction depends upon the concentration of only one reactant.
- Step I: the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion.
- step II: The carbocation thus formed is then attacked by nucleophile .
- Rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.
- Order of reactivity: R-I > R-Br > R-Cl >> R-F.



## (c) Stereochemical aspects of nucleophilic substitution reactions

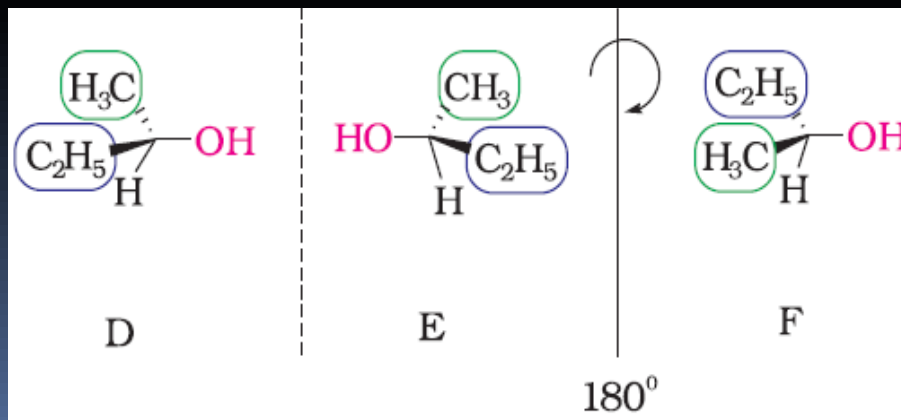
**Plane polarised light:** Light having oscillations in one plane. It is produced by passing ordinary light through Nicol prism

**Optical activity:** optically active compounds rotate the plane polarised light when it is passed through their solutions.

- If the compound rotates the plane polarised light to the clockwise direction, it is called *dextrorotatory* or the d-form and is indicated by placing a positive (+) sign before the degree of rotation.
- If the light is rotated towards anticlockwise direction) the compound is said to be laevorotatory or the l-form and a negative (–) sign is placed before the degree of rotation.
- Such (+) and (–) isomers of a compound are called **optical isomers** or **enantiomers** and the phenomenon is termed as optical isomerism or enantiomerism.

## (ii) Molecular asymmetry, chirality and enantiomers:

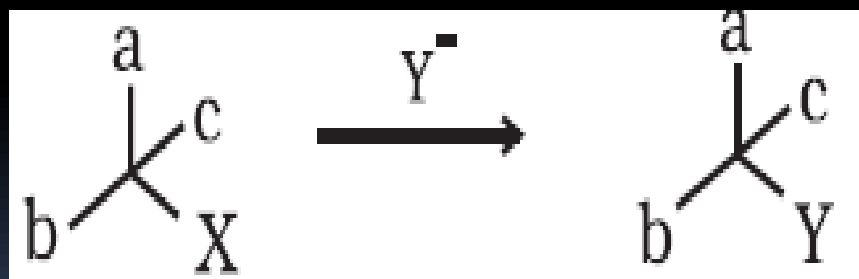
- Crystals of certain compounds exist in the form of mirror images. Aqueous solutions of both types of crystals showed optical rotation, equal in magnitude (for solution of equal concentration) but opposite in direction.
- Arrangement of four groups around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, such a carbon is called asymmetric carbon or stereocentre or chiral
- The asymmetry of the molecule is responsible for the optical activity.
- The stereoisomers related to each other as non-superimposable mirror images are called enantiomers





### (iii) Retention:

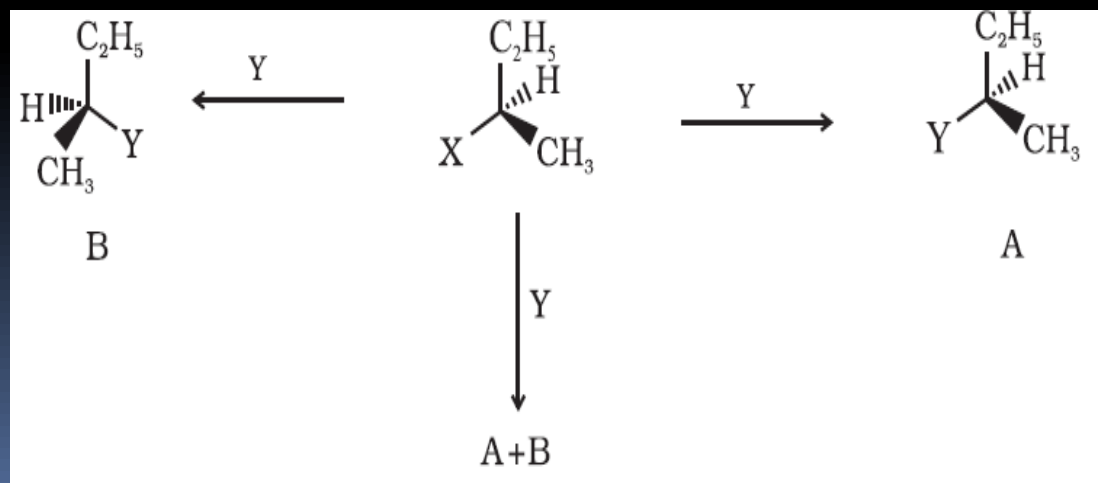
- Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.
- If during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration around the stereocentre as that of reactant. Such a reaction is said to proceed with retention of the configuration.



## (iv) *Inversion, retention and racemisation:*

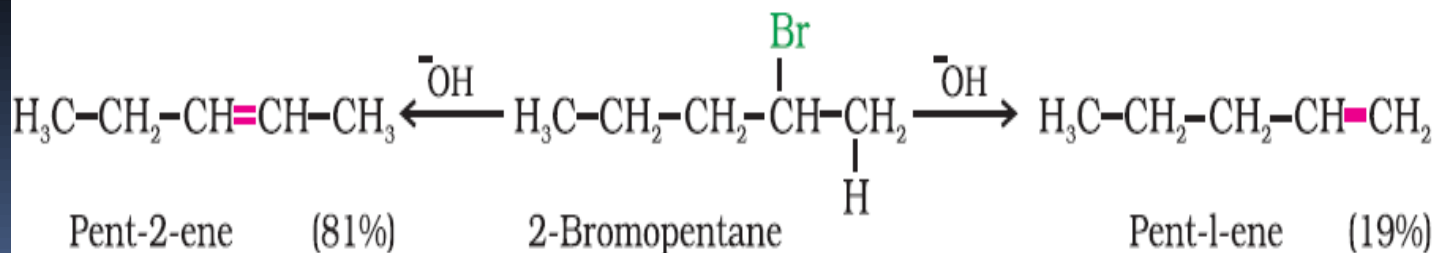
for a reaction at an asymmetric carbon atom.

- If (A) is the only compound obtained, the process is called retention of configuration.
- If (B) is the only compound obtained, the process is called inversion of configuration.
- If a 50:50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive.



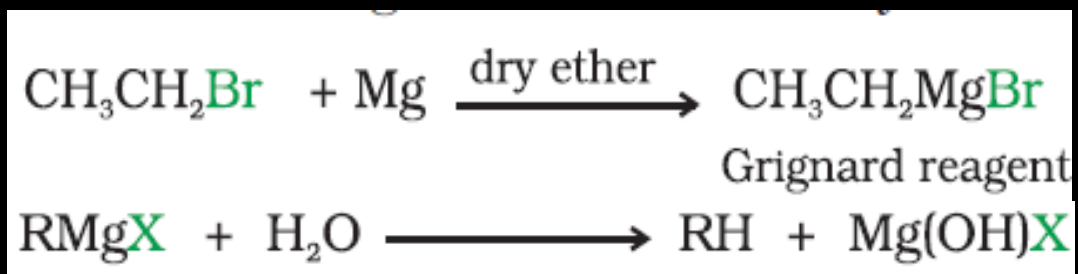
# Elimination reactions

- When a haloalkane with  $\beta$ -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from  $\beta$ -carbon and a halogen atom from the  $\alpha$ -carbon atom.
- It is called  $\beta$ -elimination or dehydrohalogenation
- If there is possibility of formation of more than one alkene due to the availability of more than one  $\beta$ -hydrogen atoms, usually one alkene is formed as the major product.
- The formation of products is governed by Zaitsev rule  
*“in dehydrohalogenation reactions, the major product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms”*



# Reaction with metals

- An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide,  $\text{RMgX}$ , referred as Grignard Reagents. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.
- One of the methods for converting halides to hydrocarbons.



## *Wurtz reaction*

- Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.



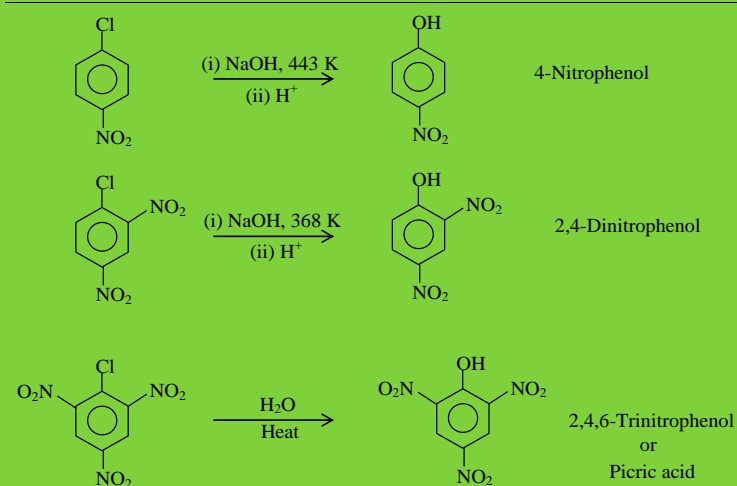
# Reactions of Haloarenes

## *Nucleophilic substitution*

- Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:
  - (i) Resonance effect: In haloarenes, the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring. C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult and therefore, they are less reactive towards nucleophilic substitution reaction.
  - (ii) Difference in hybridisation of carbon atom in C—X bond: in case of haloarene, the carbon atom attached to halogen is  $sp^2$ -hybridised.
    - With a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than  $sp^3$ -hybridised carbon in haloalkane therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.
  - (iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore,  $SN_1$  mechanism is ruled out.
  - (iv) Because of the repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

# Replacement by hydroxyl group

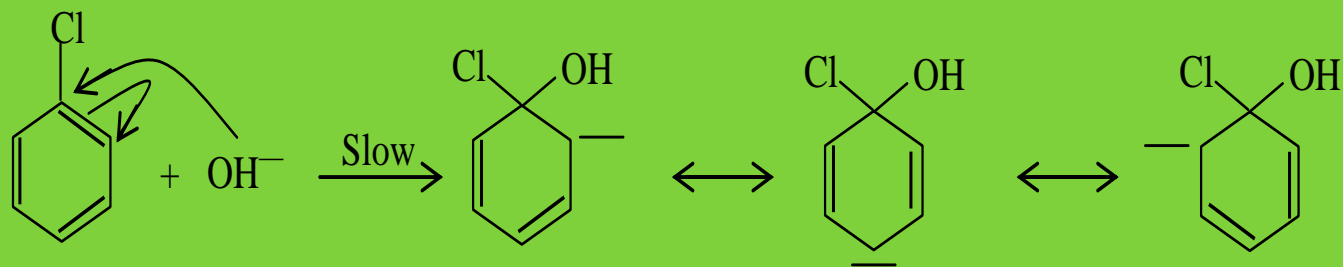
- Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atmospheres.
- The presence of an electron withdrawing group (-NO<sub>2</sub>) at *ortho*- and *para*-positions increases the reactivity of haloarenes.



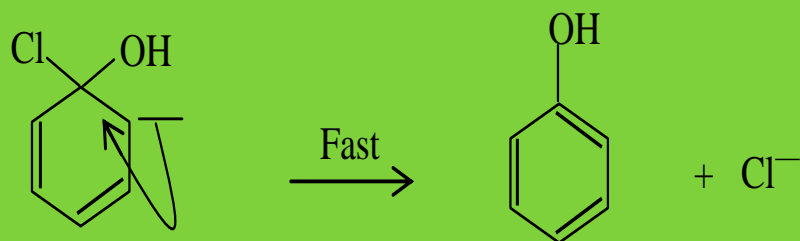
## Mechanism of aryl substitution reaction: $S_N$ aryl

The reaction occurs in two steps;

Step 1: Nucleophile attacks aryl halide to form carbanion or arenium ion intermediate which is resonance stabilised.

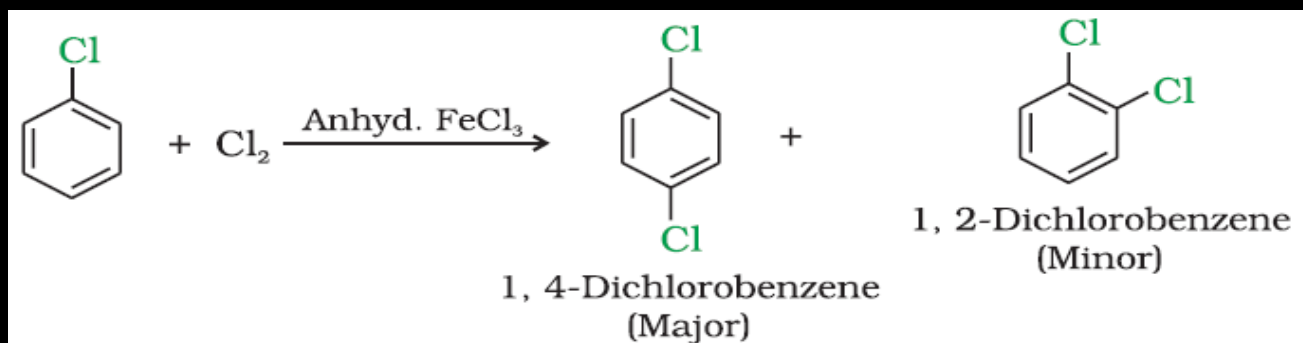


Step 2: Loss of halide ion to give the product.

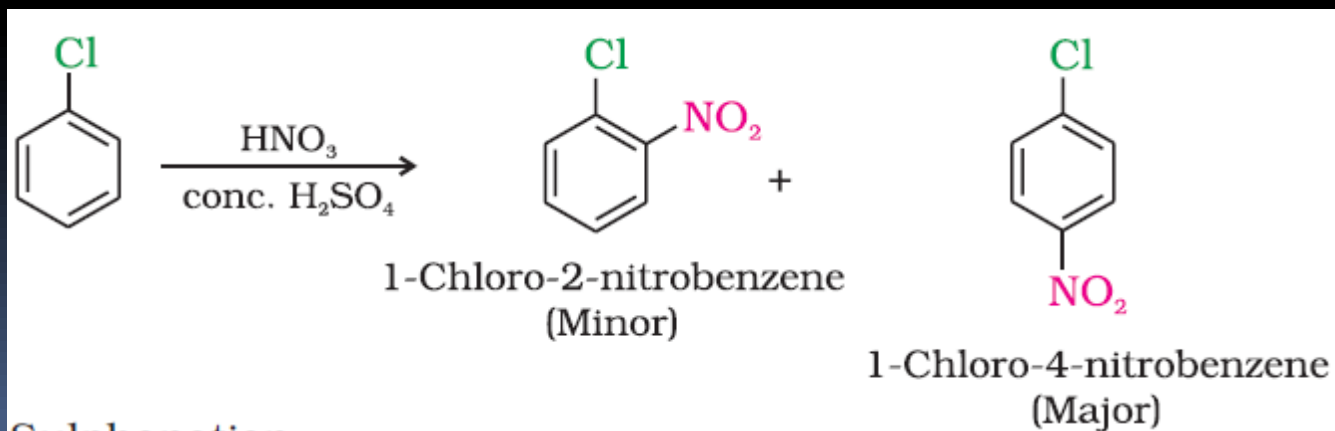


# Electrophilic substitution reactions

- Halogen is deactivating but *o*, *p* directing; Electrophilic substitution occurs at *ortho*- and *para* positions.
- Halogenation

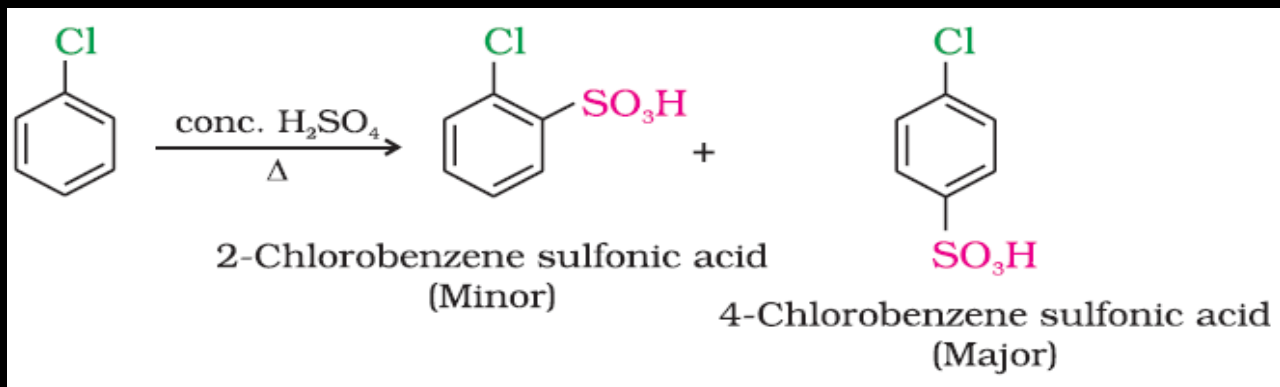


- Nitration

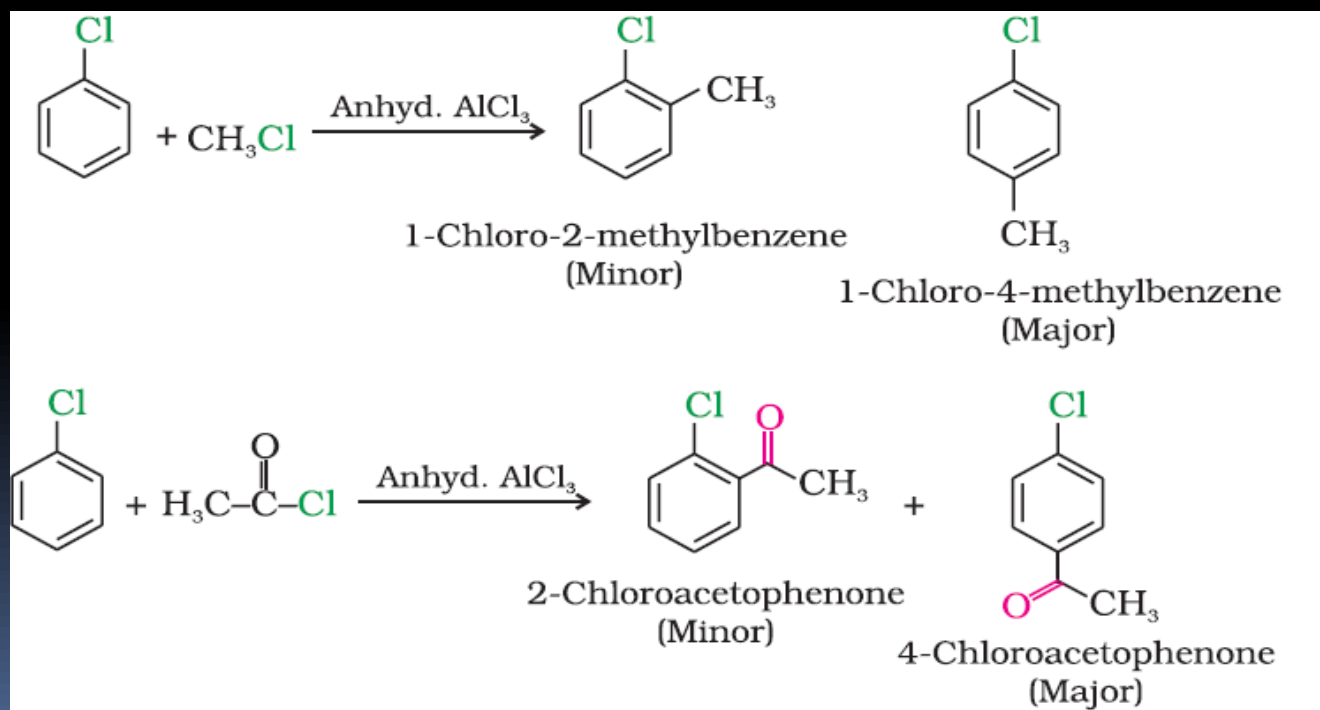




# Sulphonation



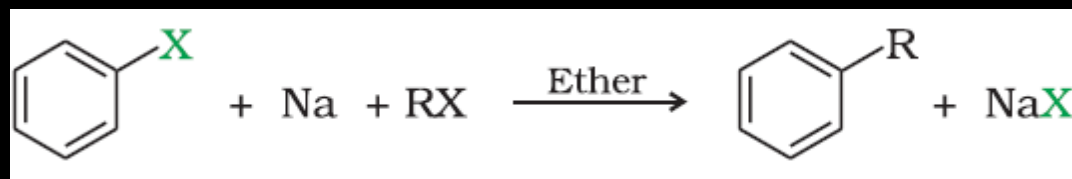
# Friedel-Crafts reaction



# Reaction with metals

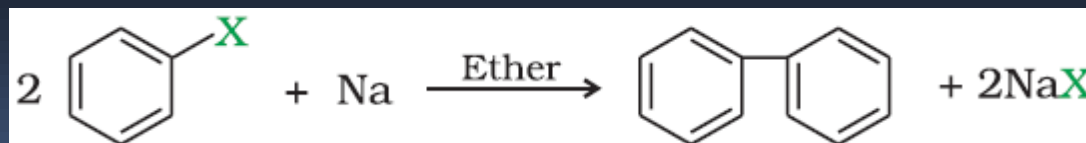
## Wurtz-Fittig reaction A

mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



## Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



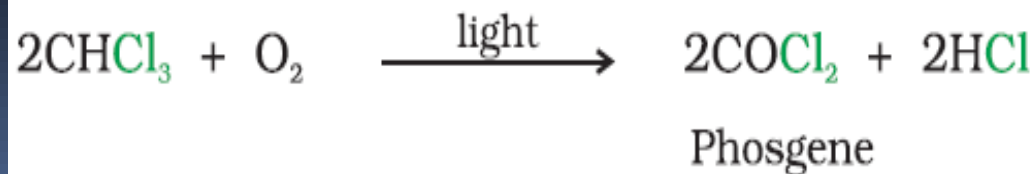
# Polyhalogen Compounds

## Dichloromethane (Methylene chloride)

- Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs.
- It is also used as a metal cleaning and finishing solvent.
- Methylene chloride harms the human central nervous system.
- Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision.
- Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

## Trichloromethane (Chloroform)

- Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22.
- Inhaling chloroform vapours depresses the central nervous system.
- Breathing about 900 parts of chloroform per million parts of air for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.



## Triiodomethane (Iodoform)

- It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

## 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. Freon 12 ( $\text{CCl}_2\text{F}_2$ ) is one of the most common freons in industrial use.
- It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
- Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.

## 4 Tetrachloromethane (Carbon tetrachloride)

- It is for use in the manufacture of refrigerants and propellants for aerosol cans.
- It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use.
- Exposure to carbon tetrachloride can cause liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to  $\text{CCl}_4$  can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact.
- It depletes the ozone layer. Depletion of the ozone layer increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

# Dichlorodiphenyltrichloroethane (DDT)

- DDT was the first chlorinated organic insecticides.
- The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus.
- Problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues.
- If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

# Test

- On treatment with aq. KOH followed by dil. HNO<sub>3</sub> and AgNO<sub>3</sub> alkyl, allyl and benzyl halides give a curdy white precipitate which is soluble in excess of NH<sub>4</sub>OH where as phenyl and vinyl halides do not give.





*THANK  
YOU*