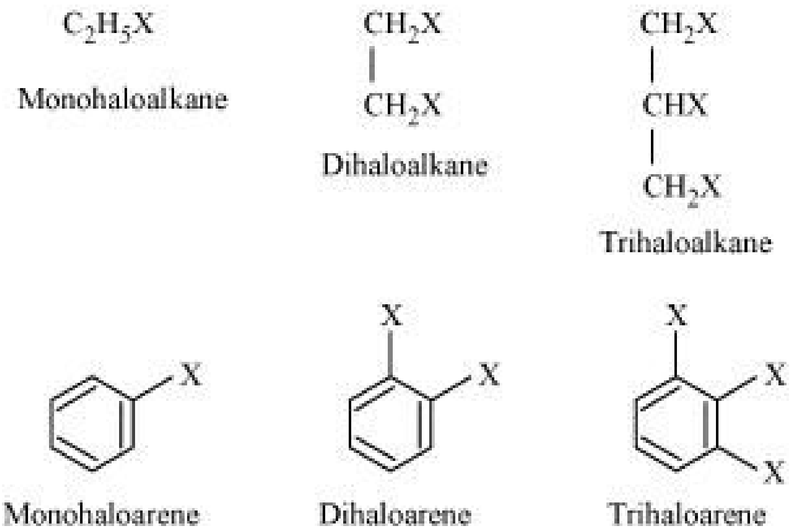
Haloalkanes and Haloarenes

Classification: Mono, di and polyhalogen (tri, tetra, etc.)



(i) Alkyl halides or haloalkanes (R−X) → They form homologous series of general formula $C_nH_{2n+1}X$. They are further classified into primary, secondary, and tertiary.

(ii) Allylic halides → Compounds containing halogen atom bonded to an allylic carbon

(iii) Benzylic halides → Compounds containing halogen atom bonded to an sp^3 hybridised carbon atom next to an aromatic ring

Methods of preparation:

- **From alcohols –**

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

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 \, (X = Cl, Br)$$

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

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

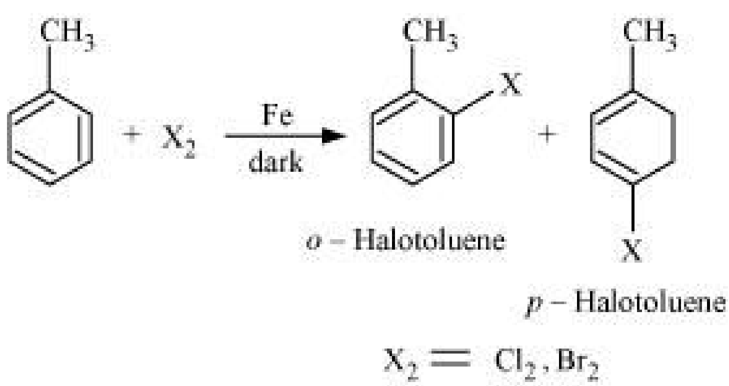
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

- **From hydrocarbons –**

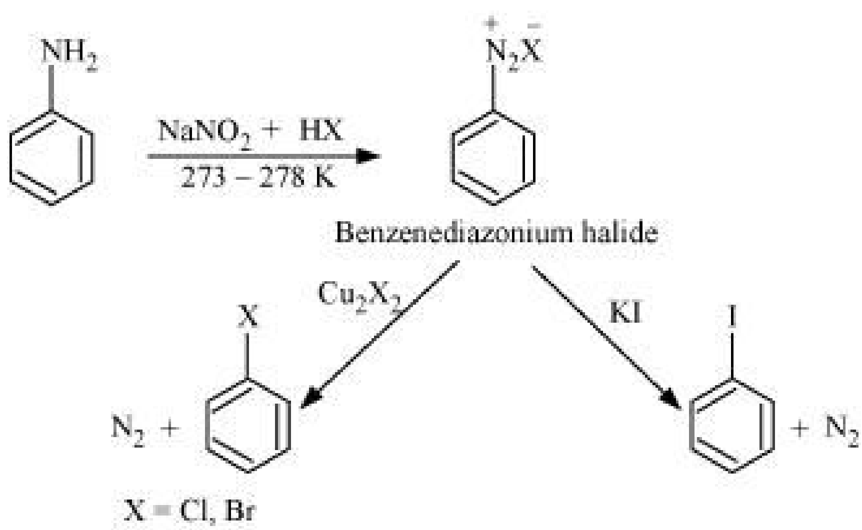
By free radical halogenations- Yields a complex mixture of isomeric mono– and polyhaloalkanes

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

- By electrophilic substitution



- **Sandmeyer's reaction –**



- **From alkenes –**

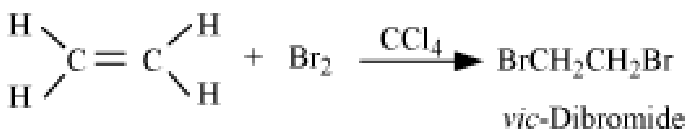
  Addition of hydrogen halides to unsaturated hydrocarbons (Markovnikov's rule)

$$CH_3CH=CH_2+H-I \longrightarrow \underset{(Minor)}{CH_3CH_2CH_2I} + \underset{(Major)}{CH_3CHICH_3}$$

- Addition of halogens

  (Method used for detecting double bond in a molecule)

  In this method, a reddish-brown colour is discharged.



- **Halogen exchange –**

  Finkelstein reaction

$$R-X+NaI \xrightarrow{\text{dry acetone}} R-I+NaX$$
$$X=Cl, Br$$

- **Swarts reaction (synthesis of alkyl fluoride) –**

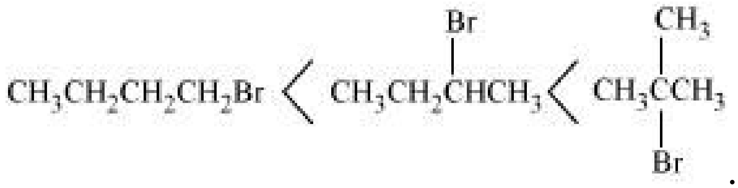
$$H_3C-X+AgF \longrightarrow H_3C-F+AgX$$
$$X=Cl, Br$$

Physical properties:

- Melting and boiling points –
- Halides have higher boiling points than hydrocarbons of comparable molecular mass because of having stronger dipole–dipole and van der Waals' forces of attraction.
- The order of increasing boiling points of the different haloalkanes is:

  RF < RCl < RBr < RI

- The boiling points of isomeric haloalkanes decrease with increase in branching. The order of branching is



Hence, order of boiling points is opposite.

- Density –

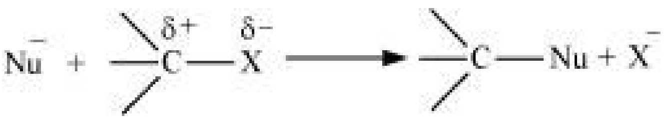
  The density of halides increases with increase in the number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

- Solubility –

  Soluble in organic solvents, but only slightly soluble in water

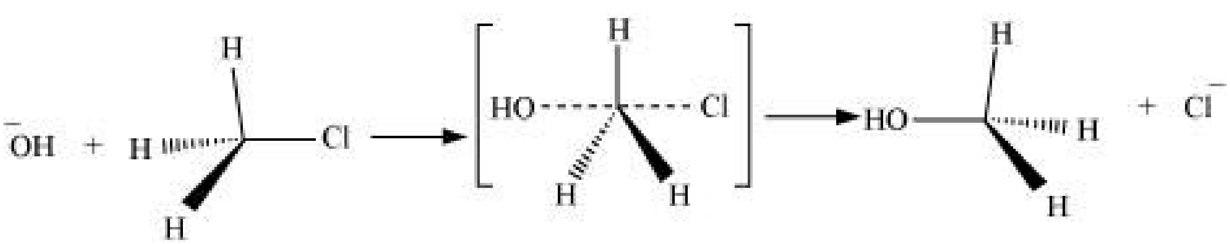
Reactions of haloalkanes –

- **Nucleophilic substitution reaction:**



Mechanism

- Substitution nucleophilic bimolecular (S_N2) (Inversion of configuration)



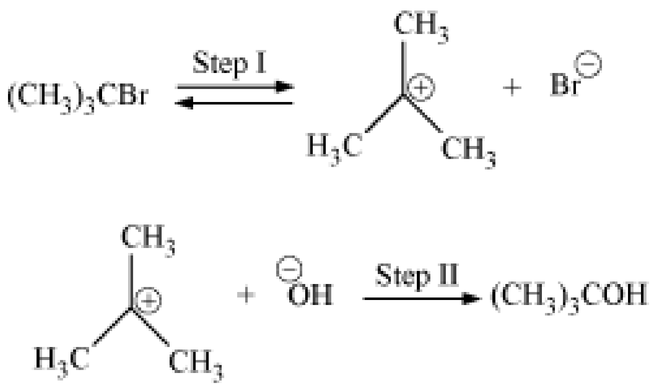
The increasing order of reactivity is

3^o halide < 2^o halide < 1^o halide < CH_3X

(Due to increase in hindrance by bulky substituent in the case of 2^o and 3^o halides)

- Substitution nucleophilic unimolecular (S_N1) (Two-step mechanism)

  Step I is the slowest; it is reversible and rate-determining step



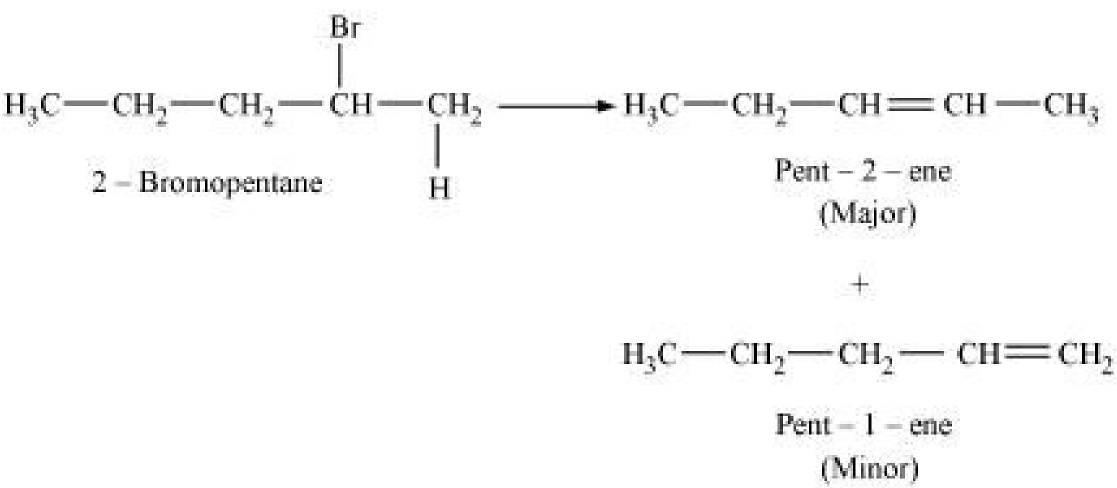
  The increasing order of reactivity

  $CH_3X < 1^o$ halide $< 2^o$ halide $< 3^o$ halide

- In both the mechanisms, for a given alkyl group, the increasing order of reactivity is

  R – F << R – Cl < R – Br < R – I

- **Elimination reactions (β – elimination):**



- **Reaction with metals:**

- Grignard reagent –

$$RX + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{RMgX}$$

- Wurtz reaction –

  (Preparation of hydrocarbons containing double the number of carbon atoms)

$$2RX + Na \xrightarrow{\text{dry ether}} R-R + NaX$$

Nucleophilic substitution reaction:

- Aryl halides are less reactive towards nucleophilic substitution due to

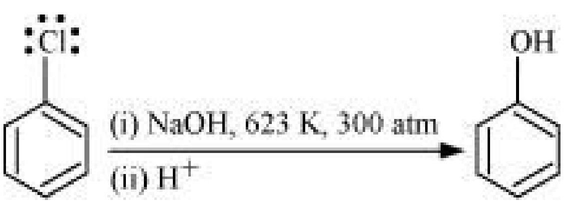
i. Resonance effect

ii. sp^2 hybridisation

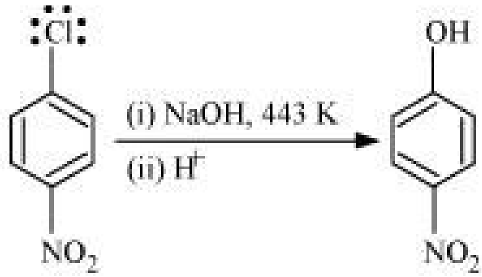
iii. Instability of phenyl cation

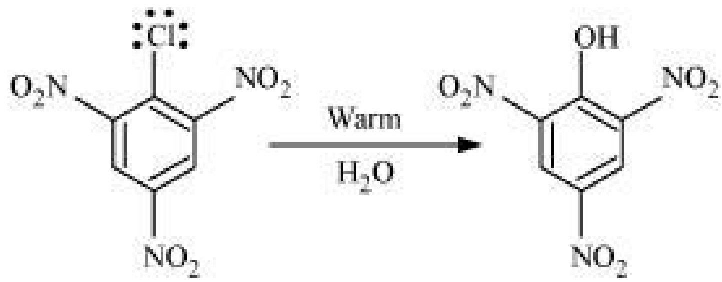
iv. Repulsion

- Replacement by alkyl group



Presence of electron-withdrawing group at *o*-and *m*-positions increases the reactivity of haloarenes.

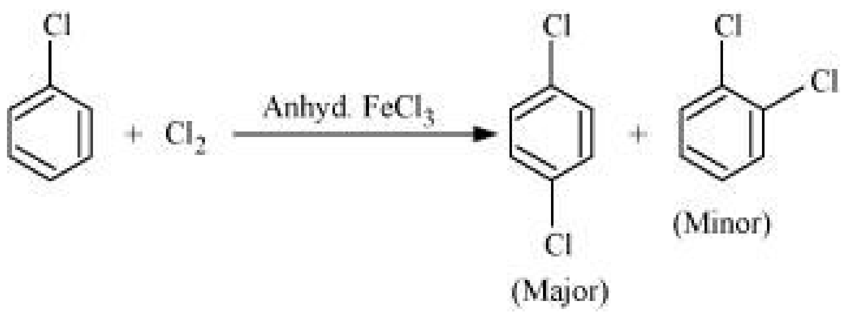




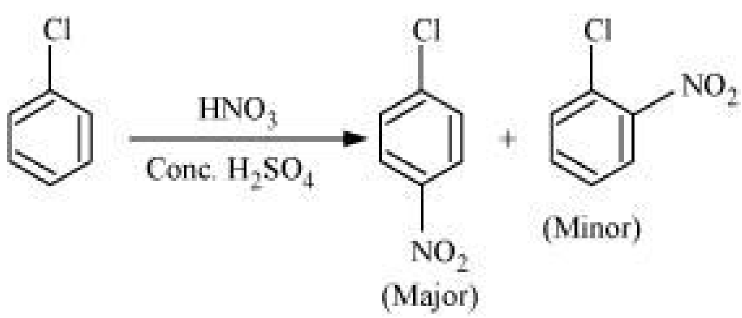
- **Electrophilic substitution reaction:**

  The electron density at ortho-and para-position is more than at meta-position

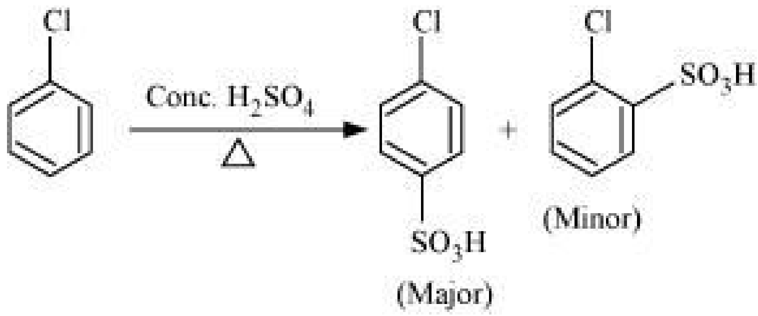
Halogenation



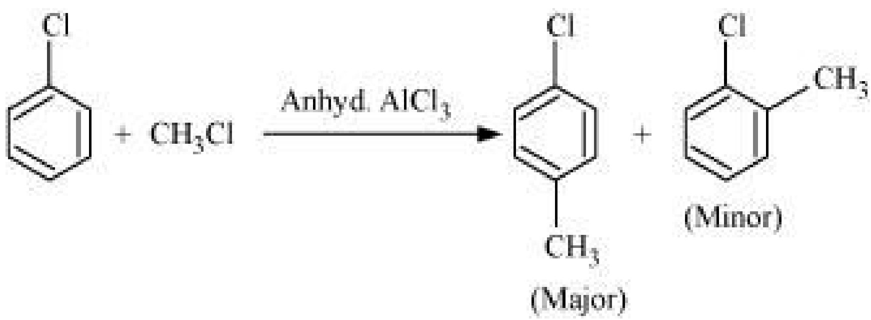
Nitration

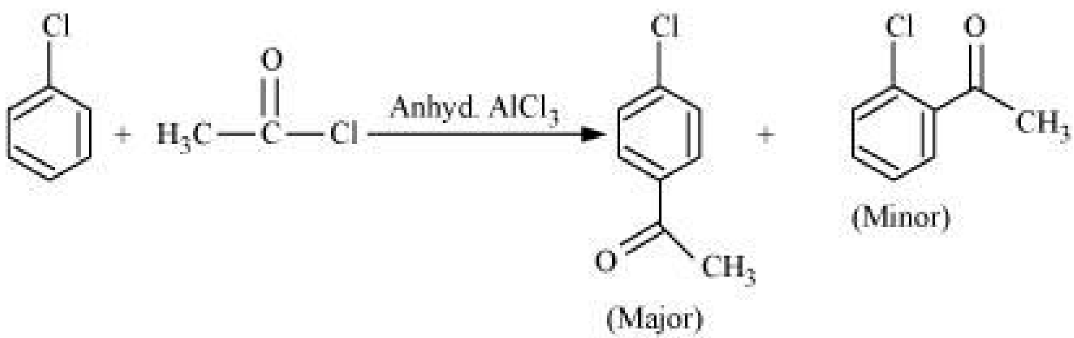


Sulphonation



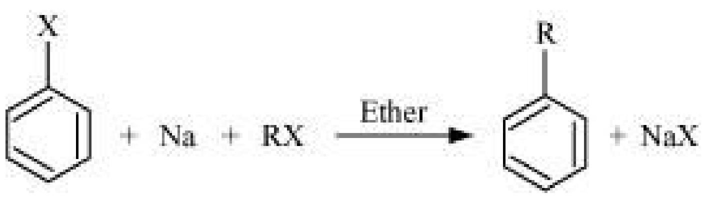
Friedel-Crafts reaction



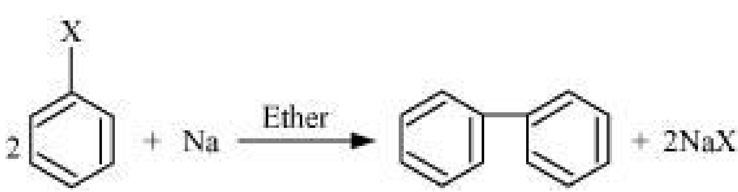


- **Reaction with metals:**

  Wurtz–Fitting reaction



Fitting reaction



Polyhalogen compounds:

- **Dichloromethane (CH_2Cl_2)** – Industrially used as a solvent

- **Trichloromethane (Chloroform, $CHCl_3$)** –

    - Used as a solvent for fats, alkaloids, iodine

    - Causes damage to lever, kidneys and skin
    - Stored in closed, dark-coloured container as it is oxidised to an extremely poisonous gas, phosgene, when exposed to light.

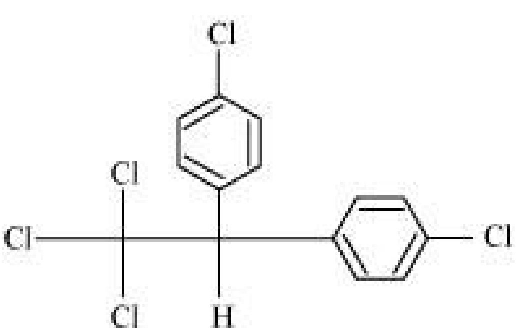
$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

- **Triiodomethane (iodoform, CHI_3)** –
    - Earlier, used as an antiseptic
    - Its antiseptic properties are due to the liberation of free iodine

- **Tetrachloromethane** –
    - Used in the manufacture of refrigerants, chlorofluorocarbons
    - Causes liver cancer in humans
    - Causes depletion of ozone layer

- **Freons** – Collective chlorofluorocarbon compounds of methane and ethane
    - Stable, unreactive, non-toxic, non-corrosive and easily liquefiable gas
    - Used as refrigerants
    - Upset the natural ozone balance

- ***p*, *p*'-Dichlorodiphenyltrichloroethane (DDT)** –



DDT

The first chlorinated organic insecticide