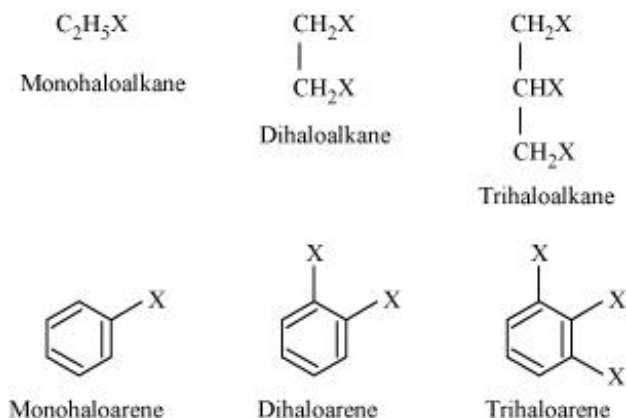


Haloalkanes and Haloarenes

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



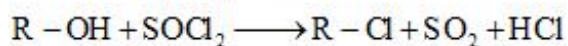
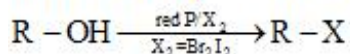
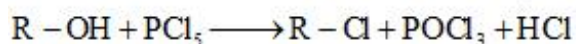
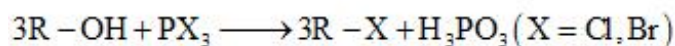
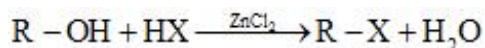
(i) Alkyl halides or haloalkanes ($R-X$) \rightarrow They form homologous series of general formula $C_nH_{2n+1}X$. They are further classified into primary, secondary, and tertiary.

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

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

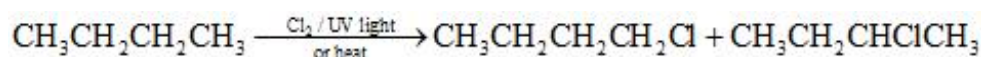
Methods of preparation:

• From alcohols –

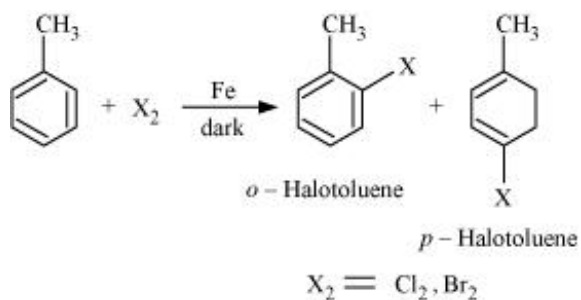


• From hydrocarbons –

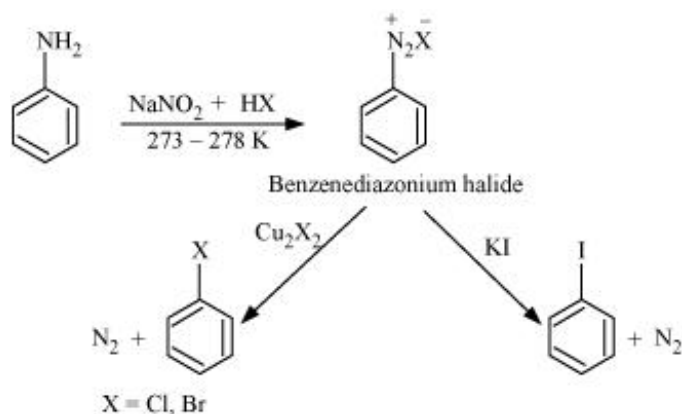
By free radical halogenations- Yields a complex mixture of isomeric mono- and polyhaloalkanes



- By electrophilic substitution

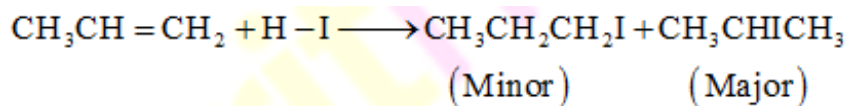


- Sandmeyer's reaction –**



- From alkenes –**

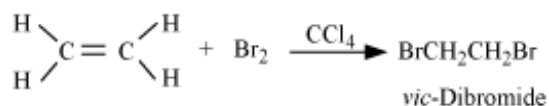
Addition of hydrogen halides to unsaturated hydrocarbons (Markovnikov's rule)



- Addition of halogens

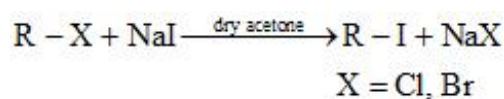
(Method used for detecting double bond in a molecule)

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

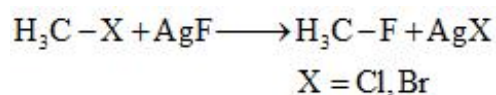


- Halogen exchange –**

Finkelstein reaction

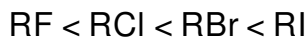


- Swarts reaction (synthesis of alkyl fluoride) –**

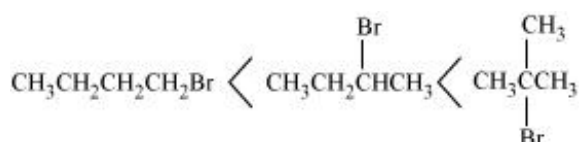


Physical properties:

- 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:



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



Hence, order of boiling points is opposite.

- Density –

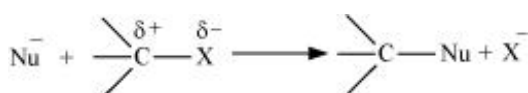
The density of halides increases with increase in the number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

- Solubility –

Soluble in organic solvents, but only slightly soluble in water

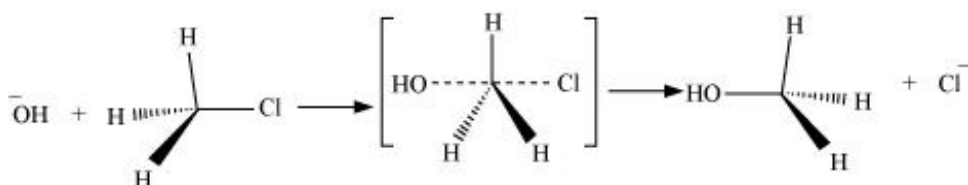
Reactions of haloalkanes –

- **Nucleophilic substitution reaction:**



Mechanism

- Substitution nucleophilic bimolecular ($\text{S}_{\text{N}}2$) (Inversion of configuration)



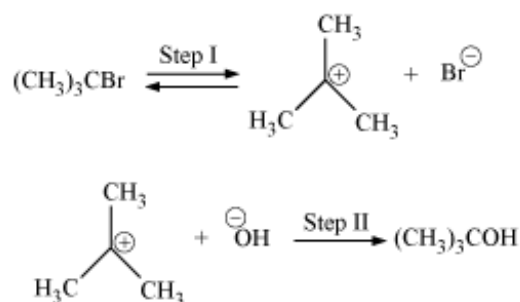
The increasing order of reactivity is



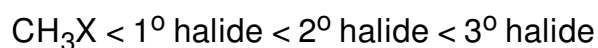
(Due to increase in hindrance by bulky substituent in the case of 2° and 3° halides)

- Substitution nucleophilic unimolecular ($\text{S}_{\text{N}}1$) (Two-step mechanism)

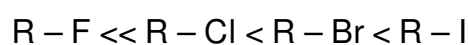
Step I is the slowest; it is reversible and rate-determining step



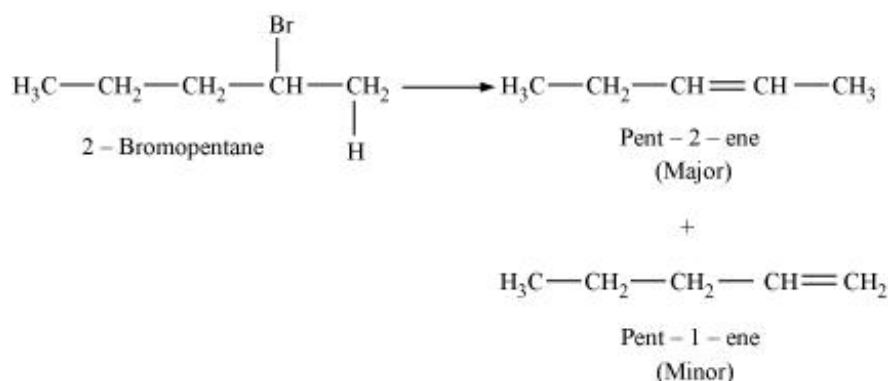
The increasing order of reactivity



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

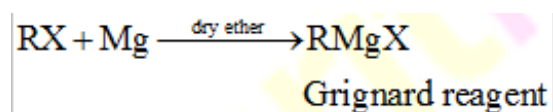


- Elimination reactions (β – elimination):**



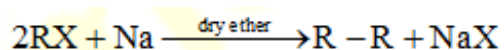
- Reaction with metals:**

- Grignard reagent –



- Wurtz reaction –

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



Nucleophilic substitution reaction:

- Aryl halides are less reactive towards nucleophilic substitution due to

i. Resonance effect

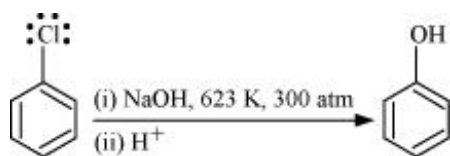
ii. sp^2 hybridisation

iii. Instability of phenoxide ion

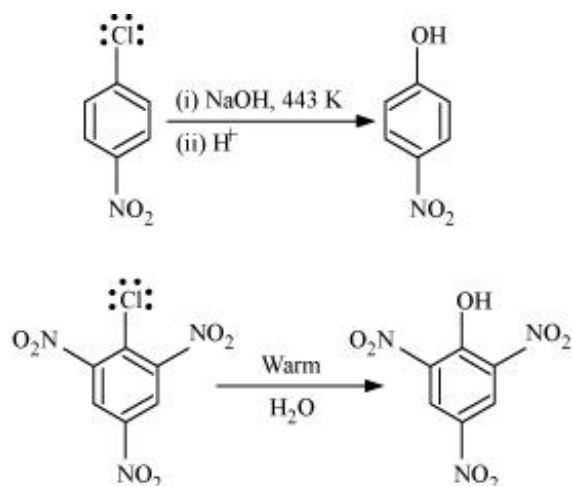
iii. Instability of phenyl cation

iv. Repulsion

- Replacement by alkyl group



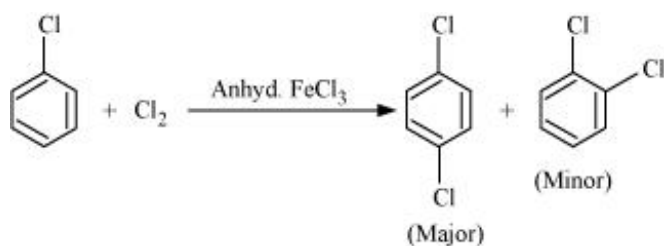
Presence of electron-withdrawing group at *o*- and *m*-positions increases the reactivity of haloarenes.



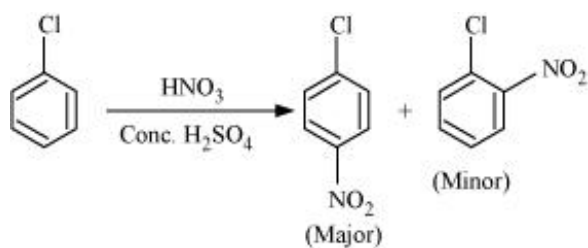
- **Electrophilic substitution reaction:**

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

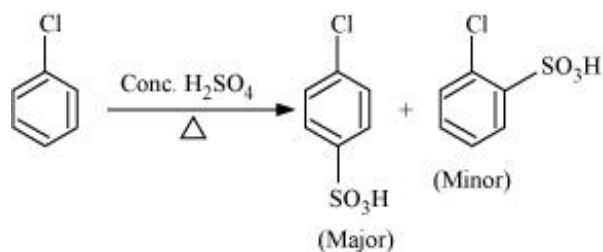
Halogenation



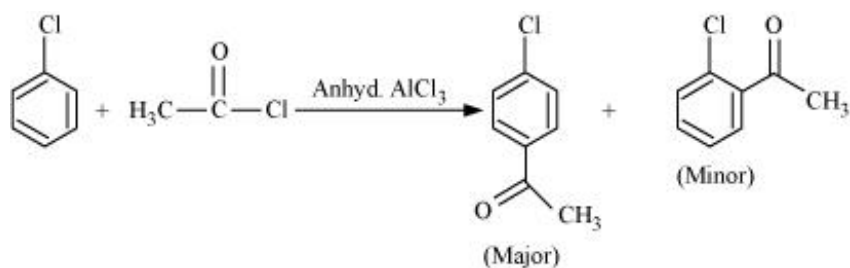
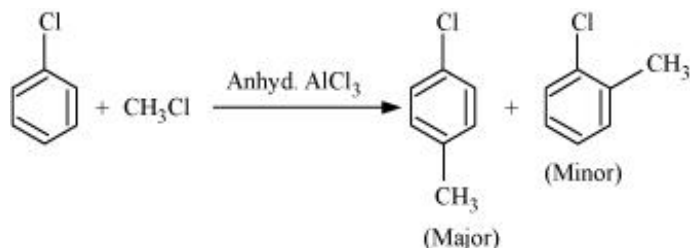
Nitration



Sulphonation

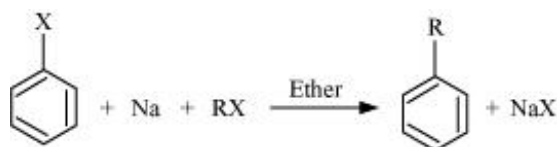


Friedel-Crafts reaction

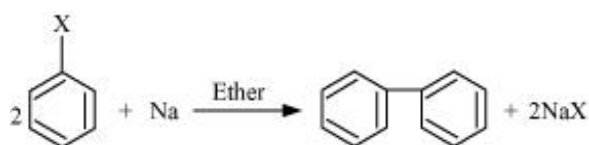


- **Reaction with metals:**

Wurtz-Fitting reaction

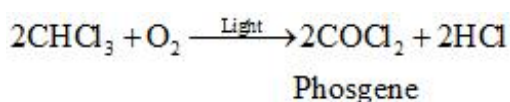


Fitting reaction



Polyhalogen compounds:

- **Dichloromethane (CH₂Cl₂)** – Industrially used as a solvent
- **Trichloromethane (Chloroform, CHCl₃)** –
 - Used as a solvent for fats, alkaloids, iodine
 - Causes damage to liver, kidneys and skin
 - Stored in closed, dark-coloured container as it is oxidised to an extremely poisonous gas, phosgene, when exposed to light.



- **Triiodomethane (iodoform, CHI_3) –**

- Earlier, used as an antiseptic
- Its antiseptic properties are due to the liberation of free iodine

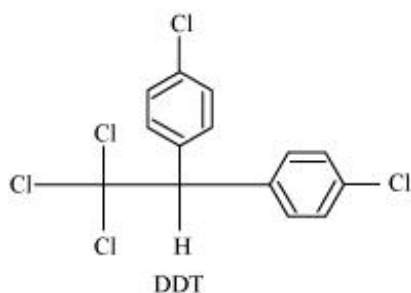
- **Tetrachloromethane –**

- 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) –**



The first chlorinated organic insecticide