

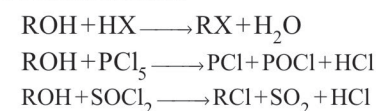
MIND MAP-10

HALOALKANES AND HALOARENES

Haloalkanes

Preparation:

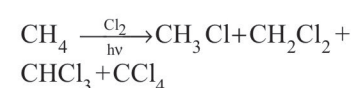
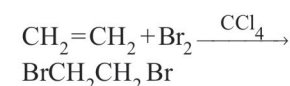
• From alcohols:



From hydrocarbons:

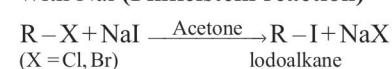


Order of reactivity $\text{HI} > \text{HCl} > \text{HF}$
In case of unsymmetrical alkenes addition occurs according to Markownikoff's rule only in case of HBr in presence of peroxides addition occurs according to anti Markownikoff's rule

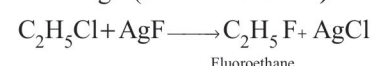


From halogen exchange

With NaI (**Finkelstein reaction**)



with AgF (**Swarts reaction**)



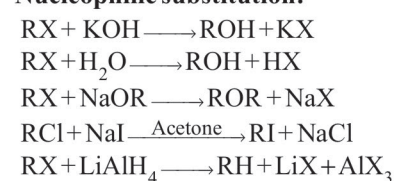
Properties:

Physical properties

- Lower alkyl halides are colourless with sweet smell or pleasant oily liquid, except CH_3F , CH_3Cl , $\text{CH}_3\text{-CH}_2\text{-F}$, $\text{CH}_3\text{-CH}_2\text{-Cl}$ which are gaseous in nature.
- Alkyl halides having 18-carbon or more than it are solid in nature.
- These are completely soluble in organic solvents but insoluble in H_2O
- Reactivity order is $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
- For same halide group, reactivity order is $3^\circ (\text{halide}) > 2^\circ (\text{halide}) > 1^\circ (\text{halide})$
- Polarity order is $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$
- Melting & Boiling points, for same alkyl group the order is $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
- Fluorides and chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to higher density of bromine than oxygen.

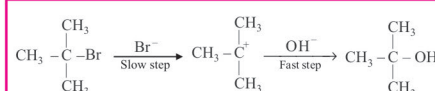
Chemical properties:

• Nucleophilic substitution:

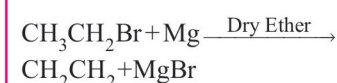
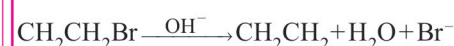


• These reactions are of two types:

- * **$\text{S}_\text{N}1$ type** (Unimolecular nucleophilic reactions) proceeds in two steps:



- * Rate, $r = k[\text{RX}]$. It is a first order reaction.
- * Reactivity order of alkyl halide towards $\text{S}_\text{N}1$ mechanism $3^\circ > 2^\circ > 1^\circ$
- * Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $\text{S}_\text{N}1$ mechanism.
- * In $\text{S}_\text{N}1$ reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation
- **$\text{S}_\text{N}2$ type** (Bimolecular nucleophilic substitution), these reactions proceed in one step.
- * It is a second order reaction with $r = k[\text{RX}][\text{Nu}]$.
- * During $\text{S}_\text{N}2$ reaction, inversion of configuration occurs
- * Reactivity of halides towards $\text{S}_\text{N}2$ mechanism is $1^\circ > 2^\circ > 3^\circ$
- * Rate of reaction in $\text{S}_\text{N}2$ mechanism depends on the strength of the attacking nucleophile.
- * Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $\text{S}_\text{N}2$ mechanism.



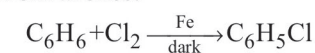
Grignard reagents are highly reactive and react with any source of proton (H_2O , alcohols, amines etc.) to give hydrocarbons.)



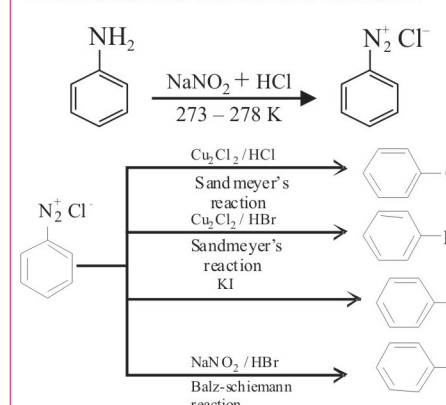
Haloarenes

Preparation:

From arenes:



From benzene diazonium chloride:



Polyhalogen compound:

- **Dichloromethane (CH_2Cl_2)**: It is useful as solvent in industries. Mostly it is used as solvent in the production of chemicals used in removal of colour.

* It is Harmful to nervous system. If it comes in direct contact with eye it damages the cornea. In addition, if it comes in direct contact with skin, red rashes are formed.

- **Tetrachloromethane (CCl_4)**: It is used in the manufacture of refrigerants and propellants for aerosol cans.

* Used as a cleaning solvent, degreasing agent and as fire extinguisher.

* It causes permanent damage to nerve cells.

* In atmosphere, it depletes the ozone layer.

- **Freons**: Chlorofluorocarbon compounds of methane and ethane are collectively known as freons and it is manufactured by **swarts reaction** using tetrachloromethane.

* Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.

* Freon is able to initiate radical chain reactions that can disturb the natural ozone balance.

- **DDT**: It is a powerful insecticide.

* It is a persistent organic pollutant that is readily adsorbed to soils and sediments, which can act both as sinks and as long-term sources of exposure affecting organisms.

* It is not metabolised very rapidly by animals.

Properties :

Physical properties:

- * Aryl halides are colourless liquids or colourless solids with characteristic odour.
- * Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order $\text{Ar-I} > \text{Ar-Br} > \text{Ar-Cl} > \text{Ar-F}$
- * The melting point of *p*-isomer is more than *o*- and *m*-isomer. This is because of more symmetrical nature of *p*-isomer.
- * Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexyl chloride.

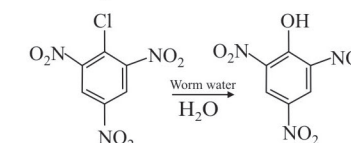
Chemical properties :

• Nucleophilic substitution reactions:

Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

- * Due to resonance, C-X bond has partial double bond character.
- * Stabilisation of the molecule by delocalisation of electrons.
- * Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.

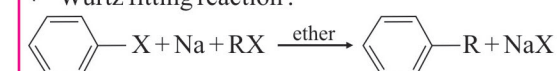


• Electrophilic substitution reactions:

Haloarenes are *o*, *p*-directing, due to +I effect of halogen group electronegativity increases at ortho and para positions e.g., halogenation, nitration, sulphonation, Friedel-Crafts reaction etc.

Reaction with metals:

- * Wurtz fitting reaction :



Fitting reaction :

