

Chapter_10

Haloalkanes and Haloarenes

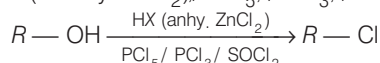
1. Haloalkanes and haloarenes are obtained by the replacement of a hydrogen atom of an alkane and arene respectively by a halogen atom (F, Cl, Br, I).

2. **Haloalkanes** are named as X-haloalkanes where, X represents the position of halogen atom.

e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ (1-iodopropane).

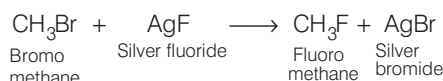
3. **Methods of preparation** These are as follows :

- Haloalkanes are obtained from alcohols by treating them with
 $\text{HX (+ anhy. ZnCl}_2\text{) / PCl}_5\text{, / PCl}_3\text{, / SOCl}_2\text{ etc.}$

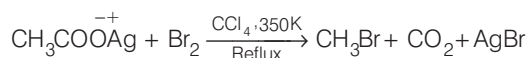


SOCl_2 is the best reagent as by products are gases (SO_2 and HCl).

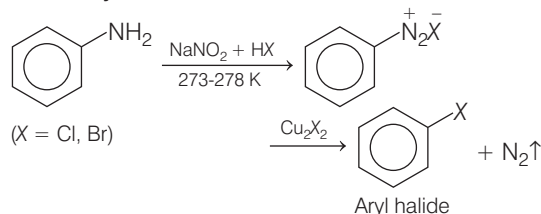
- Haloalkanes are also prepared by the action of halogen acid (HX) on alkene. The reaction follows **Markownikoff's rule**, which states that the negative part of the reagent goes to the carbon bearing less number of hydrogen atoms.
- Fluoroalkanes are prepared by treating alkyl chloride/bromide in the presence of a metallic fluoride such as AgF , Hg_2F_2 , CoF_2 or SbF_3 . This reaction is known as **Swarts reaction**.



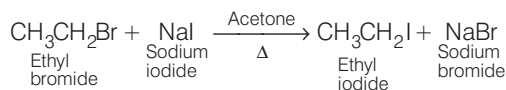
- Generally, bromoalkanes are prepared by the reaction known as **Borodine-Hunsdiecker reaction**.



- Sandmeyer's reaction**

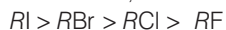


- Finkelstein reaction** (For preparation of alkyl iodides)



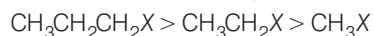
4 Physical properties

- For same alkyl group, the **boiling point** of alkyl halides decreases in the order,



This is because with the increase in size and mass of the halogen atom, the magnitude of van der Waals' forces of attraction increases.

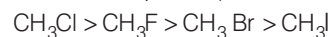
As the size of alkyl group decreases, boiling point decreases for the same halogen.



For isomers of RX having same number of C-atoms, more be the branching, lesser would be the boiling point.

- Density** : Fluoro and chloroalkanes are lighter than water while bromo, iodo and polychloro derivatives are heavier than water.

- From F to I, the electronegativity of halogen decreases, therefore, polarity in the $\text{C} - \text{X}$ bond and thus, dipole moment also decreases accordingly. However, fluorides have lower dipole moment than chlorides because of very small size of F. (Strong electron ... electron-repulsion).



- Alkyl halides are slightly soluble in water, because they do not form H-bonds with water.
- Due to better symmetry of *para* isomers as compared to *ortho* and *meta* isomers, *para* isomers have high melting points as compared to their *ortho* and *meta* isomers.

5. **Chemical properties** : With the increase in size of halogen atom, carbon-halogen bond length increases, hence, reactivity increases. Thus, $\text{R} - \text{I}$ is most reactive towards $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ reactions.

These are as follows:

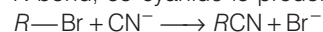
- $\text{S}_\text{N}1$ mechanism** involves formation of carbocation as intermediate. The reactant that gives more stable carbocation, is more reactive towards $\text{S}_\text{N}1$ reactions. The order of reactivity of alkyl halides towards these reactions is $3^\circ > 2^\circ > 1^\circ$.

These reactions give racemisation product, i.e. retention as well as inversion of configurations.

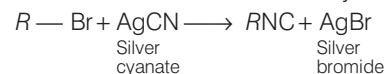
- $\text{S}_\text{N}2$ mechanism** involves formation of transition state. Less hindered alkyl halides readily undergo these reactions. These reactions result in the inversion of configuration.

The order of reactivity of alkyl halide will be $1^\circ > 2^\circ > 3^\circ$.

- In the presence of polar solvent, KCN readily ionises to furnish CN^- ions. As, $\text{C} - \text{C}$ bond is more stable than $\text{C} - \text{N}$ bond, so cyanide is predominantly formed.



However, AgCN does not ionise, so it attacks through N and results in the formation of isocyanide.



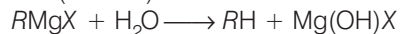
- Reaction of KNO_3 with RBr results in the formation of RONO_2 (nitrite) whereas, reaction of RBr with AgNO_3 results in the formation of RNO_3 (nitrate) predominantly.

6. Stereochemical Principles and Notation

- An object or molecule which is non-superimposable on its mirror image is called **chiral** and the property is called **chirality**.
- A **chiral** or **asymmetric carbon** is that, in which all the four valencies are satisfied by four different groups. Such a carbon bearing molecule is generally optically active.

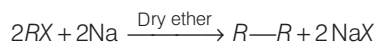
- An equimolar mixture of two enantiomers (*d* and *l*-forms) is called **racemic mixture**. It is represented as *dl* or \pm forms and will be optically inactive. The process of converting the *d* or *l*-form of an optically active compound into racemic mixture (*dl*) is called **racemisation**.

7. **Grignard reagents** are highly reactive species and react with water (a good source of proton) to give hydrocarbons. (alkanes)

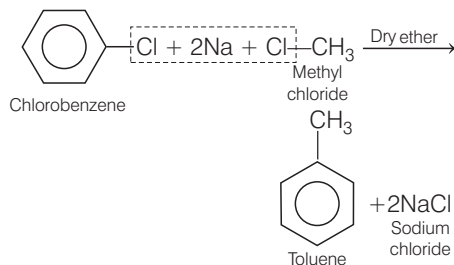


Hence, traces of moisture must be avoided during formation of a Grignard reagent.

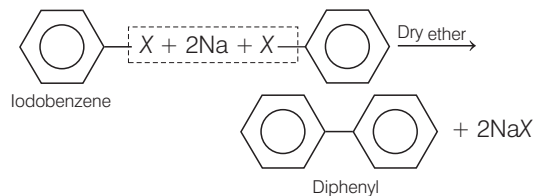
8. In electrophilic substitution reactions of benzene ring, Cl, Br, etc. are *ortho/para* directing groups and direct the incoming group at *ortho* and *para* positions of benzene ring.
9. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions, due to resonance effect (double bond character between C—Cl bond), sp^2 -hybridisation of C bearing halogen atom and instability of phenyl cation.
10. **Wurtz reaction** : Alkyl halides react with sodium metal in the presence of dry ether to give hydrocarbon containing double the number of carbon atoms present in the alkyl halide.



11. When aryl halide is heated with alkyl halide in the presence of sodium and dry ether, halogen atom is replaced by alkyl group and alkylarene is formed. This is called **Wurtz-Fittig reaction**.



12. When haloarenes 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**.



13. Carbon compounds having more than one halogen atom are usually referred to as **polyhalogen compounds** e.g. CH_2Cl_2 , $CHCl_3$, CHI_3 , CCl_4 , freons, DDT. Some polyhalogen compounds are as follows :

- Chloroform** : In the presence of sunlight, chloroform is slowly oxidised by air to produce a highly poisonous gas, carbonyl chloride or phosgene, $COCl_2$. That's why, it is stored in dark coloured bottles filled up to the brim.
- Freons** Chlorofluorocarbon compounds of methane and ethane are collectively known as **freons**.
- In stratosphere, freon is able to initiate chain reactions that can result in depletion of ozone layer. Since, freon has been found to be one of the factors responsible for the depletion of ozone layer, they are being replaced by other harmless compounds in many countries.
- DDT** : (*p*, *p'* dichlorodiphenyltrichloro ethane) is an insecticide, highly toxic and chemically stable. It is not metabolised rapidly by animals. In many countries DDT is used as an insecticide.

