Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter - 10)
Ganesh Kumar Date:- 10/09/2020

Haloalkanes and Haloarenes

From alkene:

i) Addition of hydrogen halide (HX):

Alkenes add HX (HCl, HBr or HI) to form alkyl halides. In the case of unsymmetrical alkenes, the addition takes place according to Markovnikov's rule. **[The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule)** gets attached to the carbon containing lesser number of hydrogen atoms"].

e.g. CH_3-CH=CH_2 + HBr ⟶ CH_3-CH_2-CH_2Br + CH_3-CHBr-CH_3

Propene — Bromopropane (minor) — 2- Bromopropane (major)

ii) Addition of halogen:

Alkenes add halogen to form vicinal dihalides (2 halogen atoms on adjacent C- atoms). For e.g. addition of bromine in CCl_4 to an alkene results in the formation of vicinal dibromides and also in the discharge of the reddish brown colour of Br_2 in CCl_4. So this is used as a test for unsaturation.

e.g. CH_2= CH_2 + Br_2 $\xrightarrow{CCl4}$ $CH_2Br - CH_2Br$

Ethene Bromine (1,2-dibromoethane)

Halogen Exchange Reactions:

a) *Finkelstein reaction*:

Alkyl chlorides or bromides when treated with NaI in dry acetone, alkyl iodides are formed. This reaction is known as Finkelstein reaction.

R-X + NaI $\xrightarrow{\text{Dry acetone}}$ R-I + NaX (where X = Cl, Br)

Alkyl chlorides — Alkyl iodide

b) *Swarts reaction*:

This method is used for the preparation of alkyl fluorides. Here alkyl chloride or bromide is treated with a metallic fluoride like AgF, Hg_2F_2, CoF_2 or SbF_3, to get alkyl fluoride.

$$\underset{\text{Alkyl chloride}}{R\text{-}X} + AgF \longrightarrow \underset{\text{Alkyl fluoride}}{R\text{-}F} + AgX \qquad \text{(where X = Cl or Br)}$$

Physical Properties

Melting and boiling points:

In haloalkanes, the C-X bond is polar due to the greater electronegativity of halogen atom. Due to greater polarity and higher molar mass, the inter molecular forces of attraction (dipole-dipole and vander Waals forces) are strong and so they have higher melting and boiling points than hydrocarbons of comparable molar mass.

For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because with the increase in size and mass of halogen atom, the magnitude of vander Waal forces increases.

The boiling points of isomeric haloalkanes decrease with increase in branching. This is because as branching increases, the surface area of the molecule decreases. So the vander forces decreases and hence the b.pt.

Among isomeric dihalobenzenes, the para-isomers are high melting as compared to their ortho and meta- isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta- isomers.

Solubility:

The haloalkanes are only very slightly soluble in water. This is because they cannot form hydrogen bonds with water (except alkyl fluorides).

****