Chapter_13

Organic Compounds Containing Nitrogen

1. Amines are derivatives of ammonia, obtained by replacement of one, two or three hydrogen atoms by alkyl/aryl groups. e.g.

- **2.** Nitrogen orbitals in amines are *sp*³-hybridised and the geometry of amines is pyramidal.
- Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl group in NH₂.
- 4. In IUPAC system, amines are named as **alkanamines**, derived by replacement of 'e' of alkane by word 'amine'.

5. Preparation of Amines

 Both aliphatic and aromatic primary amines can be prepared by the reduction of nitro compounds either catalytically with H₂ in the presence of Raney Ni, Pt or Pd or with active metal in acidic medium.

$$\begin{array}{c} C_6H_5NO_2 + 3H_2 & \xrightarrow{Sn + HCl} & C_6H_5NH_2 + H_2O \\ \hline \text{Nitrobenzene} & & \text{Or Fe + HCl} & Aniline \end{array}$$

 In Hofmann bromamide reaction, amides on treatment with Br₂/NaOH gives an amine (primary) having one carbon less than the parent amide.

$$R = C = NH_2 + Br_2 + 4NaOH \longrightarrow$$

$$R = NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

• In Gabriel phthalimide synthesis, a phthalimide is treated with ethanolic KOH and forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.

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This method produces only primary amines, without traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

 Ammonolysis of alkyl halides involves the process of cleavage of C—X bond by ammonia molecule.

$$\begin{array}{c} \overbrace{\mathsf{NH}_3}^+ + \overbrace{\mathsf{R}}^+ \overbrace{\mathsf{X}}^- &\longrightarrow \\ R \longrightarrow \\ (1^\circ) & (2^\circ) \\ (1^\circ) & (2^\circ) \\ (2^\circ) & (3^\circ) \\ (3^\circ) & \underset{\text{anmonium}}{\overset{\mathsf{RX}}} \\ R \longrightarrow \\ (3^\circ) & \underset{\text{RX}}{\overset{\mathsf{RX}}} \\ R$$

• Reduction of nitriles $R - C \equiv N \xrightarrow{H_2/Ni} R - CH_2 - NH_2$

$$\begin{array}{c} O \\ \parallel \\ R - C - NH_2 \xrightarrow{(i) \text{ LiAlH}_4} RCH_2 - \end{array}$$

$$- \ddot{\mathsf{C}} - \mathsf{NH}_2 \xrightarrow{(1) \sqcup \mathsf{AIH}_4} RCH_2 - \mathsf{NH}_2$$

6. Physical Properties

- 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen.
- 1° and 2° amines are engaged in intermolecular association due to H-bonding between nitrogen of one and hydrogen of another molecule. Therefore, the order of boiling point of amines is

1° amines > 2° amines > 3° amines.

7. Basic character of amines are stronger bases than ammonia due to + *I*-effect (electron donating power) of alkyl groups, due to which electron density on nitrogen atom increases and hence, they can easily donate their

electrons as compared to ammonia. Aromatic amines are weaker bases than ammonia due to electron withdrawing nature of aryl group.

- Larger the value of K_b or smaller the value of pK_b, stronger is the base.
- Order of basicity of amines in gaseous phase follows the expected order.
 Tertiary amine > Secondary amine > Primary amine > Ammonia
- Combined effect of + *I*-group, steric effect and solvation effect decides the basic character of amines in **aqueous phase**. If the alkyl group is small, i.e. CH₃, then there is no steric hindrance to H-bonding and hence, H-bonding predominates over + *I*-effect. Since, all these effects are favourables for 2° amine, therefore, order of basicity is 2° amine > 1° amine > 3° amine (in aqueous phase).
- If the alkyl group is bigger than —CH₃ group, there is steric hindrance to H-bonding and hence + *l*-effect predominates over H-bonding. Therefore, the order is 2° amine > 3° amine > 1° amine (in aqueous phase).
- In anilinium ion, there is only two resonating structures, therefore, it is less stable than aniline (five resonating structures).
- In case of substituted aniline, electron releasing groups like — CH₃, — OCH₃, — NH₂ increase basic strength and electron withdrawing groups like — NO₂, —X, — COOH decrease the basic strength.

8. Chemical properties

- Aliphatic and aromatic amines reacts with acid chlorides, anhydrides and esters by nucleophilic substitution reaction.
- Primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which have foul smell. This reaction is called **carbylamine reaction** or **isocyanide test**. This reaction is used to test primary amines.

e.g.
$$R \longrightarrow NH_2 + CHCl_3 + 3KOH \longrightarrow$$

1° amine Chloroform Potassium
hydroxide $R \longrightarrow NC + 3KCl + 3H_2O$
(Isocyanide)

 Primary aliphatic amines when treated with HNO₂ (NaNO₂ + HCl) gives alcohol whereas, primary, aromatic amines in this reaction give diazonium salt

 $(C_6H_5N_2^+Cl^-)$. • Hinsberg's reagent reacts with 1° and 2° amines to form

- sulphonamides, whereas 3° amines does not react.
 In aniline, electron density at *ortho-* and *para-* positions (due to NH₂) is high. Therefore, NH₂ group is *ortho* or *para* directing and powerful activating. To control its activity, aniline is subjected to acetylation before subjecting to electrophilic substitution reactions to get mono-substituted product.
- **9. Diazonium salts** have general formula *R*N₂ *X*. It can be prepared by the reaction of aniline with nitrous acid at 273-278 K.
 - **Chemical reactions** Reactions involving displacement of nitrogen.

$$\begin{array}{c} \overset{+}{\mathsf{N}} = \mathsf{NCI}^{-} & \xrightarrow{\mathsf{CuCI/HCI}} \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{CI} + \mathsf{N}_{2} \\ & \xrightarrow{\mathsf{(Sandmeyer reaction)}} \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{Br} + \mathsf{N}_{2} + \mathsf{Cu}X \\ & \xrightarrow{\mathsf{(Gattermann reaction)}} \mathsf{(Gattermann reaction)} \\ & \xrightarrow{\mathsf{HBF}_{4}} \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{F} + \mathsf{BF}_{3} + \mathsf{N}_{2} + \mathsf{HX} \\ & \xrightarrow{\mathsf{H}_{3}\mathsf{PO}_{2} + \mathsf{H}_{2}\mathsf{O}} \mathsf{C}_{6}\mathsf{H}_{6}\mathsf{H}_{2} + \mathsf{H}_{3}\mathsf{PO}_{3} + \mathsf{HCI} \\ & \xrightarrow{\mathsf{H}_{2}\mathsf{O}} \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{O}\mathsf{H} + \mathsf{N}_{2} + \mathsf{HX} \end{array}$$

• Benzene diazonium chloride coupled with phenol molecule having — OH group at *para*-position to give *p*-hydroxyazobenzene, hence, the reaction is known as **coupling reaction**.

The azo products obtained, are coloured and used as dyes.

