

## Organic Compounds Containing Nitrogen

### Synopsis

- \* The formula of Nitroalkanes is  $\text{RNO}_2$ .
- \* The formula of alkyl nitrite is  $\text{RONO}$ .
- \* Nitroalkanes and alkyl nitrites can be considered as the alkyl derivatives of nitrous acid.
- \* If the  $\text{NO}_2$  group is bonded to the alkyl carbon atom through the oxygen atom, the derivatives are called alkyl nitrites.
- \* Amines are organic derivatives of ammonia, and obtained by replacement of one, two or all the three hydrogen atoms by alkyl/or aryl groups.
- \* Nitrogen orbitals in amines are  $\text{sp}^3$  hybridised, and one hybrid orbital contains an unshared pair of electron.
- \* Geometry of the amines is 'Pyramidal', and the bond angle is less than  $109.5^\circ$ .
- \* Alkyl amines contain nitrogen atom bonded to  $\text{sp}^3$  carbon atom, and aryl amines contain nitrogen atom bonded to  $\text{sp}^2$  carbon atom of Benzene or Benzene like ring.
- \* Amines are classified as per the degree of substitution at Nitrogen atom as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) (unlike alkyl halides, alcohols in which classification is based on nature of carbon atom).
- \* In the common system amines are called alkyl amines or amino alkanes as one word.
- \* When two or more groups are the same the prefix di or tri is appended before the name.
- \* Due to "lone pair" of electrons on nitrogen - they act as bases.
- \* Treated as both Bronsted and Lewis base.
- \* Basicity of amines is related to their structure and the usual order of basic character is aliphatic amines > ammonia > aryl amines,

- \* More the number of alkyl groups on nitrogen atom, more is the basic character. Thus the greater the number of "electron releasing alkyl groups", the greater is the availability of nitrogen lone pair and strength of the base
- \* As a result of these three factors (a) opposing (b) and (c), the practical observations show that the order of basicity of amines is secondary > tertiary > primary >  $\text{NH}_3$ . Aniline, the aromatic amine is less basic than  $\text{NH}_3$  and aliphatic amines.
- \* Industrially aniline is prepared by the reduction of nitrobenzene with iron and water and small quantity of hydrochloric acid.
- \* Aniline reacts with Benzene sulphonyl chloride at high temperatures and gives N-Phenyl Benzene Sulphonamide.
- \* Isocyanide is known as carbylamine. It will have nauseating odour. This reaction is known as carbylamine reaction. This test is used for identification of primary amines (both aliphatic and aromatic) and  $\text{CHCl}_3$ .
- \* **Diazotisation:** In this reaction aniline reacts with nitrous acid at 0 to  $5^\circ\text{C}$  to form benzene diazonium chloride. As nitrous acid ( $\text{HNO}_2$ ) is unstable is generated in situ from a mineral acid ( $\text{HCl}$ ) and sodium nitrite.
- \* **Sulphonation:** Aniline reacts with concentrated sulphuric acid to form anilinium hydrogen sulphate which on heating at  $180^\circ\text{--}200^\circ\text{C}$  produces p-amino benzene sulphonic acid i.e sulphanilic acid.
- \* Aryl diazonium salts undergo coupling reactions with phenols or aryl amines to form azo compounds.
- \* Azo compounds are usually coloured because of extended conjugate system with aromatic rings and azo linkage  $-\text{N}=\text{N}-$ . Therefore these compounds are coloured and used as dyes.
- \* Removal of the diazo group provides convenient method for producing arenes, phenols, aryl halides, cylinders etc., for example Fluorides and iodides can not be

prepared by direct reaction of halogen. Further  $\text{CN}^-$  cannot be introduced in place of  $\text{Cl}^-$  by  $\text{SN}$  reaction.

- \* Primary amine formed reacts with excess alkyl halide to form secondary, tertiary amines, and finally quaternary ammonium salt.
- \* This reaction involves migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. Here isocyanates are formed as intermediates.
- \* Product is primary amine having one carbon atom less than the corresponding amide. Organic Compounds Obtained by replacing the 'H' atom of Hydrogen Cyanide by an alkyl Or aryl group are called cyanides
- \* Both aliphatic and aromatic primary amines on heating with chloroform and aqueous Potassium hydroxide form isonitrites.