Chapter - 13

AMINES

- 1. Write IUPAC names of the following:
 - $\begin{array}{ccc} \text{(i)} & \text{CH}_3\text{CH}_2\text{CH--NH}_2\\ & \text{I}\\ & \text{CH}_3 \end{array}$

(ii) CH₃NHCH(CH₃)₂

(iii) (CH₃)₃ N

(iv) C₆H₅NHCH₃

(v)
$$C_6H_5NH-C-CH_3$$

(vi)
$$N(CH_3)_3$$
 Br

- 2. Giving an example of each, describe the following reactions :
 - (i) Hoffman bromamide reaction
 - (ii) Gabriel phthanlimide synthesis
 - (iii) Gatterman reaction
 - (iv) Coupling reaction
 - (vi) Carbylamine reaction
 - (vii) Acetylation of aniline.

- 3. Describe the Hinsberg's test for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.
- 4. Arrange the following in the increasing order of given property indicated.
 - (i) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3 , (Basic strength in aqueous solution).
 - (ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2 . (Basic strength in gaseous phase).
 - (iii) Aniline, p-toluidine, p-nitroaniline. (Basic strength).
 - (iv) C₂H₅OH, (CH₃)₂ HN, C₂H₅NH₂ (Boiling point)
- 5. Identify A and B in the following reactions:

(i)
$$CH_3CH_2CI + NH_3$$
 (Excess) $\xrightarrow{373K}$ A

(ii)
$$CH_3CH_2CI + NH_3 \xrightarrow{373K} OH^-$$

- 6. How will you bring about the following conversions?
 - (i) benzene to Aniline
 - (ii) aniline to benzene
 - (iii) ethanoic acid to ethanamine
 - (iv) p-toluidine to 2-bromo-4-methylaniline.
 - (v) methylbromide to ethanamine
 - (vi) benzenediazonium chloride to nitrobenzene
 - (vii) ethylamine to methylamine
 - (ix) benzene to sulphanilic acid
 - (x) hexanenitrile to 1-aminopentane.
- 7. Write the products formed in the following sequence of reactions :-

$$\mathsf{CH_3CH_2I} \xrightarrow{\mathsf{NaCN}} \mathsf{A} \xrightarrow{\mathsf{OH}^-} \mathsf{B} \xrightarrow{\mathsf{Br_2/NaOH}} \mathsf{C}$$

8. Identify the missing reagent/product in the following reactions :

(i)
$$\frac{CH_2Br}{\text{ethanolic}} B \xrightarrow{H_2/Ni} C$$

(ii)
$$H_2$$
 + $(CH_3CO)_2O$ \rightarrow A H_2SO_3 B H^+/H_2O \rightarrow C

(iii)
$$C_6H_5N_2^+CI^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$$

(iv)
$$C_6H_5NO_2 \xrightarrow{Fe/HCI} A \xrightarrow{H_2SO_4} B \xrightarrow{heat} C$$

(v)
$$CH_3COCI$$
 A Br_2/Fe B H_2O/OH C

- 9. Give one chemical test to distinguish between the following pairs of compounds :
 - (i) methylamine and dimethylamine
 - (ii) secondary and tertiary amines
 - (iii) ethylamine and aniline
 - (iv) aniline and benzylamine
 - (v) methylamine and methanol
 - (vi) methylamine and N, N-dimethylamine
 - (vii) ethanol and ethanamine

10. Explain why:

- (i) The C-N-C bond angle in trimethyl amine is 108°
- (ii) the quaternary ammonium salts having four different alkyl groups are optically active
- (iii) alkylamines are more basic than ammonia
- (iv) aniline cannot be prepared by Gabriel phthalimide synthesis
- (v) Garbriel phthalimide synthesis is preferably used for synthesising primary amines.
- (vi) ethylamine is soluble in water but aniline is not
- (vii) amines are soluble in dilute HCl.
- (viii) amines have lower boiling point than alcohols of comparable molecular masses.
- (ix) 1° amines have higher boiling points than 2° amines which in turn, are higher boiling than 3° amines.
- (x) The pK_b value of benzeneamine is 9.33 while that of ammonia is 4.75.
- (xi) aniline does not undergo Friedel-Crafts reaction.
- (xii) aniline readily forms 2, 4, 6-tribromoaniline on reaction with bromine water.
- (xiii) sulphanilic acid is soluble in water.
- (xiv) methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (xv) diazonium salt of aromatic amines are more stable than the diazonium salts of aliphatic amines.
- (xvi) Although amino group is o, p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
- 11. Why do amines act as nucleophiles? Give example of a reaction in which methylamine acts as a nucleophile.
- *12. Three isomeric amines A, B and C have the molecular formula C₃H₉N. Compound A on reaction with benzene sulphonyl chloride forms a product which is soluble in NaOH. Compound B on reaction with benzene sulphonyl chloride forms a product which is insoluble in NaOH and compound C

does not react with benzene sulphonyl chloride. Identify A, B and C.

[Ans. : (A) $CH_3CH_2CH_2NH_2$ (B) $CH_3CH_2NHCH_3$ (C) $(CH_3)_3N$]

13. An organic compound A (C₂H₃N) is used as a solvent of choice for many organic reactions because it is not reactive in mild acidic and basic conditions. Compound A on treatment with Ni/H₂ forms B. When B is treated with nitrous acid at 273K, ethanol is obtained. When B is warmed with chloroform and NaOH, a foul smelling compound C formed. Identify A, B and C.

[Ans. : (A) CH_3CN (B) $CH_3CH_2NH_2$ (C) CH_3CH_2NC

14. An organic compound [A] $C_3H_6O_2$ on reaction with ammonia followed by heating yield B. Compound B on reaction with Br_2 and alc. NaOH gives compound C (C_2H_7N). Compound C forms a foul smelling compound D on reaction with chloroform and NaOH. Identify A, B, C, D and the write the equations of reactions involved.

 $\label{eq:hint:} \textbf{(A)} \ \mathsf{CH_3CH_2COOH} \qquad \qquad \textbf{(B)} \ \mathsf{CH_2CH_2CONH_2}$

(C) $CH_3CH_2NH_2$ (D) $CH_3CH_2NC.$]