AMINES

QUESTIONS

1. Write IUPAC names of the following amines:

(ii) CH₃NHCH(CH₃)₂

(ix) H_2N (CH_2) $_6NH_2$

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

(vi)
$$\left[\begin{array}{c} \dot{N}(CH_3)_3 \\ \end{array}\right]$$
 Br

(vii)
$$\stackrel{\uparrow}{\text{NH}(\text{CH}_3)_2}\overline{\text{O}}\text{COCH}_3$$

2. Giving an example of each describe the following reactions :

- (i) Hoffman bromamide reaction
- (iv) Coupling reaction
- (vii) Acetylation of aniline.

- (ii) Gabriel phthalimide synthesis
- (v) Hoffman's ammonolysis
- (iii) Gatterman reaction
- (vi) Carbylamine reaction

3. Describe the method 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:

- (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) NH₄+, C₆H₅NH₃+, p-F-C₆H₅NH₃+. (Acid strength).

5. Identify A and B in the following reactions:

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

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

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:

$$\mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{I} \xrightarrow{\qquad \mathsf{NaCN} \qquad \mathsf{A} \xrightarrow{\qquad \mathsf{OH}^{-} \qquad \mathsf{B}} \mathsf{B} \xrightarrow{\qquad \mathsf{Br}_{2}/\mathsf{NaOH} \qquad \mathsf{CH}_{2}} \mathsf{B} \xrightarrow{\qquad \mathsf{NaCN} \qquad \mathsf{CH}_{3}} \mathsf{B} \xrightarrow{\qquad \mathsf{NaCN} \qquad \mathsf$$

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

(i)
$$\begin{array}{c|c} CH_2Br \\ \hline & \underline{ethanolic} \\ NaCN \end{array} \rightarrow B \begin{array}{c} H_2/Ni \\ \hline \end{array} \rightarrow C$$

(ii)
$$H_2$$
 + $(CH_3CO)_2O$ \rightarrow A HNO_3 \rightarrow 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 (iv) Aniline and benzylamine (vii) Ethanol and ethanamine
 - (ii) Secondary and tertiary amines (v) Methylamine and methanol
 - (iii) Ethylamine and aniline (vi) Methylamine and N, N-Dimethylamine
- 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 can not 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) Aniline is 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_h 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-tribronoaniline on reaction with bromine water.
 - (xiii) Sulphanillic and 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. Why does diazonium ion act as an electrophile? Give example of a reaction where diazonium ion acts as an electrophile.
- *13. 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.:
$$A = CH_3CH_2CH_2NH_2$$
 $B = CH_3CH_2NHCH_3$ $C = (CH_3)_3N$]

14. 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. :
$$A = CH_3 C = N$$
 $B = CH_3CH_2NH_2$ $C = CH_3CH_2N \stackrel{\text{def}}{=} C$

15. An organic compound [A] C₃H₆O₂ on reaction wish ammonia followed by heating yield B. Compound B on reaction with Br₂ and alc. NaOH gives compound C, (C₂H₇N). 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.