Exercises ONLY the CM mark grustions

- 13.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.
 - (i) $(CH_3)_2CHNH_2$
- (ii) $CH_3(CH_2)_2NH_2$
- (iii) CH₃NHCH(CH₃)₂

- (iv) (CH₃)₃CNH₂
- (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$
- (vii) m-BrC₆H₄NH₂
- 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) Aniline and N-methylaniline.
- 13.3 Account for the following:
 - (i) pK_b of aniline is more than that of methylamine.
 - (ii) Ethylamine is soluble in water whereas aniline is not.
 - (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated
 - (iv) Although amino group is o- and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of
 - (v) Aniline does not undergo Friedel-Crafts reaction.
 - (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic
 - (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines. Arrange the following:
 - (i) In decreasing order of the pK_b values: $\mathrm{C_2H_5NH_2},~\mathrm{C_6H_5NHCH_3},~\mathrm{(C_2H_5)_2NH}$ and $\mathrm{C_6H_5NH_2}$
 - (ii) In increasing order of basic strength:
 - $C_6H_5NH_2, \ C_6H_5N(CH_3)_2, \ (C_2H_5)_2NH \ and \ CH_3NH_2$ (iii) In increasing order of basic strength:
 - (a) Aniline, p-nitroaniline and p-toluidine

Chemistry 400

13.6

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(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$. in decreasing order of basic strength in gas phase: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3 (v) In increasing order of boiling point: C_9H_5OH , $(CH_3)_2NH$, $C_2H_5NH_9$ (vi) In increasing order of solubility in water: $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$. \$5 Now will you convert: (i) Ethanoic acid into methanamine (ii) Hexanenitrile into 1-aminopentane (iii) Methanol to ethanoic acid (iv) Ethanamine into methanamine (v) Ethanoic acid into propanoic acid (vi) Methanamine into ethanamine (vii) Nitromethane into dimethylamine (viii) Propanoic acid into ethanoic acid? 13.6/Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved. 13.7 Write short notes on the following: (ii) Diazotisation (i) Carbylamine reaction X(iv) Coupling reaction (iii) Hofmann's bromamide reaction (vi) Acetylation (v) Ammonolysis (vii) Gabriel phthalimide synthesis. 13.8 Accomplish the following conversions: (i) Nitrobenzene to benzoic acid (ii) Benzene to m-bromophenol (iii) Benzoic acid to aniline (iv) Aniline to 2,4,6-tribromofluorobenzene (v) Benzyl chloride to 2-phenylethanamine (vi) Chlorobenzene to p-chloroaniline (vii) Aniline to p-bromoaniline (viii) Benzamide to toluene (ix) Aniline to benzyl alcohol. 13.9 Give the structures of A, B and C in the following reactions: (i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH} B \xrightarrow{NaOH+Br_2} C$ (ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$ (iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LIAJH_4} B \xrightarrow{HNO_2} C$ (iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2 + HCl} B \xrightarrow{H_2O/H^+} C$ (v) $CH_3COOH \xrightarrow{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$ (vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2} B \xrightarrow{C_6H_5OH} C$

- 13.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating with Br₂ and KOH forms a compound to the string with Br₂ and KOH forms a compound to the string with Br₂ and the string with Br₃ and the string with Br₄ and the string with Br₄ and the string with Br₅ and the string with Br₅ and the string with Br₆ and the string with Br₆ and the string with Br₇ and the string with Br₇ and the string with Br₈ and the string with Br₈ and Br₉ an An aromatic compound 'A' on treatment with Br₂ and KOH forms a compound 'B' which on heating with Br₂ and IUPAC names of compound 'C' of the structures and IUPAC names of compound to the structure and the structures are structured to the structure and IUPAC names of compound to forms compound 'B' which on nearing with the structures and IUPAC names of compounds of molecular formula C_6H_7N . Write the structures and IUPAC names of compounds A, B and C.
- 13.11 Complete the following reactions:

(i)
$$C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$$

(ii)
$$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$$

(iii)
$$C_6H_5NH_2 + H_2SO_4$$
 (conc.) \rightarrow

(iv)
$$C_6H_5N_2Cl + C_2H_5OH \rightarrow$$

(v)
$$C_6H_5NH_2 + Br_2 (aq) \rightarrow$$

(vi)
$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$$

(vii)
$$C_6H_5N_2Cl \xrightarrow{(i)HBF_4} (ij)NaNO_2/Cu, \Delta$$

- 13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide
- 13.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous
- 13.14 Give plausible explanation for each of the following:
 - (i) Why are amines less acidic than alcohols of comparable molecular masses?
 - (ii) Why do primary amines have higher boiling point than tertiary amines?
 - (iii) Why are aliphatic amines stronger bases than aromatic amines?

Answers to Some Intext Questions

- **13.4** (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$
 - (ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$
 - (iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$