13.10. An aromatic compound 'A'on treatment with aqueous ammonia and heating forms compound 'B' which on heating with $Br_2$ and KOH forms a compound 'C' of molecular formula $C_6H_7N$. Write the structures and IUPAC names of compounds A, B and C.
Ans:
Since the compound 'C' with molecular formula $C_6H_7N$ is formed from compound 'B' on treatment with $Br_2$ KOH, therefore, compound 'B' must be an amide and 'C' must be an amine.
The only amine having the molecular formula $C_6H_7N$, i. e., $C_6H_5NH_2$ is aniline.
Since 'C' is aniline, therefore, die amide from which it is formed must be benzamide ($C_6H_5CONH_2$). Thus, compound'B'is benzamide. Since compound 'B' is formed from compound 'A' with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.

13.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc. KOH}$ (ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

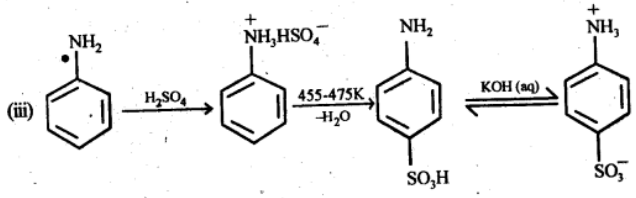
(iii) $C_6H_5NH_2 + H_2SO_4\ (\text{conc}) \longrightarrow$ (iv) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(v) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$ (vi) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

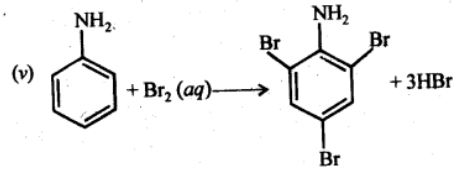
(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\Delta]{(i)\ HBF_4}$

Ans:

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{Cu^+} C_6H_6 + N_2 + H_3PO_3 + HCl$

(iii) 

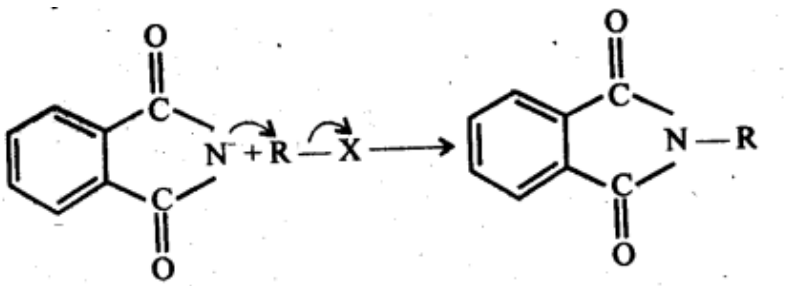

(iv) $C_6H_5N_2Cl + C_2H_5OH \xrightarrow{\text{Reduction}} C_6H_6 + CH_3CHO + N_2 + HCl$

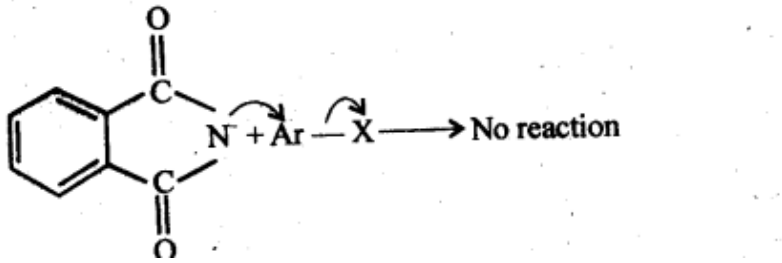
(v) 


(vi) $C_6H_5NH_2 + CH_3CO-O-COCH_3 \xrightarrow{CH_3COOH} C_6H_5NHCOCH_3 + CH_3COOH$

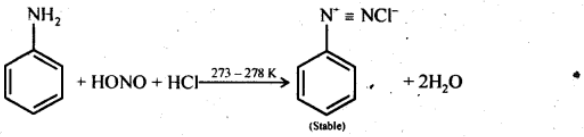
(vii) $C_6H_5N_2Cl \xrightarrow[-HCl]{HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} C_6H_5NO_2 + N_2 + NaBF_4$

13.12. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
Ans: The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound.
Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, i.e., aromatic, primary amines cannot be prepared by Gabriel phthalimide reaction.






13.13. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.
Ans: Both aromatic and aliphatic primary amines react with $HNO_2$ at 273-278 K to form aromatic and aliphatic diazonium salts respectively. But aliphatic diazonium salts are unstable even at this low temperature and thus decompose readily to form a mixture of compounds. Aromatic and aliphatic primary amines react with $HNO_2$ as follows




$$CH_3CH_2NH_2 + HONO + HCl \xrightarrow[-2H_2O]{273-278\ K} [CH_3CH_2 - N^+ \equiv NCl^-] \xrightarrow[273-278\ K]{Decomposes} CH_3CH_2OH + CH_2 = CH_2 + CH_3CH_2Cl + N_2$$

(Unstable)

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?
Ans:
(i) Loss of proton from an amine gives an amide ion while loss of a proton from alcohol give an alkoxide ion.

$R—NH_2—>R—NH^- + H^+$

$R—O—H—>R—O^- + H^+$.

Since O is more electronegative than N, so it wijl attract positive species more strongly in comparison to N. Thus, $RO^-$ is more stable than RNH®. Thus, alcohols are more acidic than amines. Conversely, amines are less acidic than alcohols.
(ii) Due to the presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of H-atom on the N-atom do not undergo H-bonding. As a result, primary amines have higher boiling points than tertiary amines of comparable molecular mass.
(iii) Aromatic amines are far less basic than ammonia and aliphatic amines because of following reasons:
(a) Due to resonance in aniline and other aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus it is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia and aliphatic amines.
(b) Aromatic amines arS more stable than corresponding

protonated ion; Hence, they hag very less tendency to combine with a proton to form corresponding protonated ion, and thus they are less basic.

********** END **********