QUESTION BANK

TOPIC- PREPARATION OF AMINES

Q1. Give reasons :

(a) Aniline is a weaker base than cyclohexylamine.

(b) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

(c) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Answer: (a) The lone pair of electrons on the N-atom in aniline are delocalised over the benzene ring. The electron density of the nitrogen decreases as a result.

However, because there are no -electrons in cyclohexylamine, the lone pair of electrons on the N-atom are readily available. As a result, aniline is a weaker base than cyclohexylamine.

(b) This is because the primary amine produced by ammonolysis acts as a nucleophile, producing additional 2° and 3° alkyl amine.

(c) Gabriel phthalimide synthesis gives pure primary amines without contamination.

Q.2 How 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?

Ans:

(i) $CH_3COOH \xrightarrow{SOCl_2} CH_3COCI \xrightarrow{NH_3(excess)} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$ (*ii*) $CH_3(CH_2)_4CN \xrightarrow{H_3O^+} CH_3(CH_2)_4COOH \xrightarrow{SOCl_2} CH_3(CH_2)_4COCI \xrightarrow{NH_3(excess)} CH_3(CH_2)_4CONH_2$ $CH_3(CH_2)_4NH_2 \leftarrow Br_2/NaOH$

$$(iii) CH_{3}OH \xrightarrow{PCl_{3}} CH_{3}CI \xrightarrow{KCN(alc)} CH_{3}CN \xrightarrow{H_{3}O^{+}} CH_{3}COOH$$

$$(iii) CH_{3}OH \xrightarrow{PCl_{3}} CH_{3}CI \xrightarrow{KCN(alc)} CH_{3}CN \xrightarrow{H_{3}O^{+}} CH_{3}COOH$$

$$(iii) CH_{3}CH_{2}NH_{2} \xrightarrow{HONO} CH_{3}CH_{2}OH \xrightarrow{K_{2}Cr_{2}O_{7}H_{2}SO_{4}} CH_{3}CHO$$

$$CH_{3}CONH_{2} \xleftarrow{H_{2}O} CH_{3}COONH_{4} \xleftarrow{NH_{3}} CH_{3}COOH \xleftarrow{K_{2}Cr_{2}O_{7}H_{2}SO_{4}} CH_{3}COOH \xleftarrow{K_{2}Cr_{2}O_{7}H_{2}SO_{4}} CH_{3}COOH \xleftarrow{H_{3}OH} CH_{3}NH_{2}$$

$$(v) CH_{3}COOH \xrightarrow{LiAlH_{4}} CH_{3}CH_{2}OH \xrightarrow{P+I_{2}} CH_{3}CH_{2}LH_{2}I \xrightarrow{KCN} CH_{3}CH_{2}CN$$

$$CH_{3}COOH \xleftarrow{H^{+}H_{2}O} CH_{3}OH \xrightarrow{P+I_{2}} CH_{3}CH_{2}LH_{2}I \xrightarrow{KCN} CH_{3}CH_{2}CN$$

$$(vi) CH_{3}NH_{2} \xrightarrow{HONO} CH_{3}OH \xrightarrow{P+I_{2}} CH_{3}I \xrightarrow{KCN} CH_{3}CN$$

$$(vii) CH_{3}NO_{2} \xrightarrow{Sn/HCI} CH_{3}OH \xrightarrow{P+I_{2}} CH_{3}I \xrightarrow{KCN} CH_{3}NC \xrightarrow{LiAlH_{4}} CH_{3}NHCH_{3}$$

$$(viii) CH_{3}CH_{2}COOH \xrightarrow{NH_{3}} CH_{3}CH_{2}CONH_{2} \xrightarrow{Br_{7}NaOH} CH_{3}CH_{2}NH_{2}$$

$$(viii) CH_{3}CH_{2}COOH \xrightarrow{NH_{3}} CH_{3}CH_{2}CONH_{2} \xrightarrow{Br_{7}NaOH} CH_{3}CH_{2}OH$$

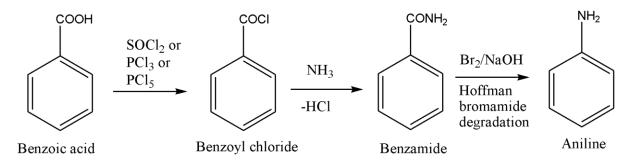
Q.3 Accomplish the following conversions:

(i) Benzoic acid to aniline

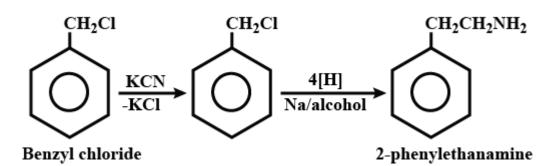
(ii) Benzyl chloride to 2-phenylethanamine

(iii) Chlorobenzene to p-chloroaniline

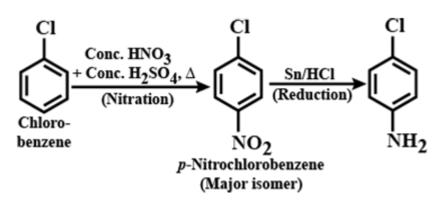
Answer-(i) Benzoic acid to aniline



(ii) Benzyl chloride to 2-phenylethanamine



(iii) Chlorobenzene to p-chloroaniline



Q.4 Convert the following:

(i) Ethannitrile to ethanamine

(ii) Ethanoic acid to methanamine

(iii) Ethyl alcohol to ethylamine

 $\begin{array}{c} CH_3 CN & \xrightarrow{H_2/N_i} CH_3 CH_2 NH_2 \\ \hline Na & (Hg)/C_2H_5 OH \end{array} \\ \hline Ethanenitrile & Ethanamine \end{array}$

Answer: (i)Ethane nitrile to ethanamine-

(ii) Ethanoic acid to methanamine

CH₃COOH -SO₂,-HCl CH₃COCl Ethanoic acid -SO₂,-HCl Ethanoyl chloride

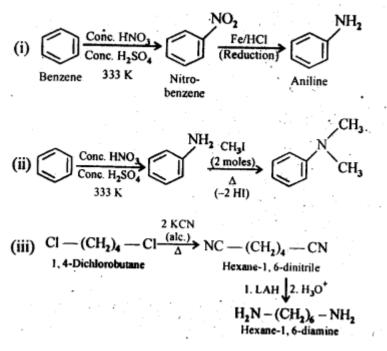
NH₃ (Excess) −NH₄Cl → CH₃CONH₂ Ethanamide → CH₃NH₂ bromamide → CH₃NH₂ Methanamine → CH₃NH₂

(iii)
$$C_2H_5OH + NH_3 \xrightarrow{ZnCl_2/NH_3} C_2H_5NH_2 + H_2O$$

Q.5 How will you convert :

- (i) Benzene into aniline
- (ii) Benzene into N,N-dimethylaniline
- (iii) CI-(CH₂)₄-CI into Hexane-1,6-diamine

Ans:



Q.6 Write short notes on the following:

- (i) Hofmann's bromamide reaction
- (ii) Ammonolysis
- (iii) Gabriel phthalimide synthesis

Answer: (i) Hoffmann's bromamide reaction:

When an amide is treated with bromine in alkali solution, it is converted to a primary amine that has one carbon atom less than the starting amide. This reaction is known as Hoffinann's bromamide degradation reaction.

$C_6H_5CONH_2 \xrightarrow{Br_2+NaOH} C_6H_5NH_2$

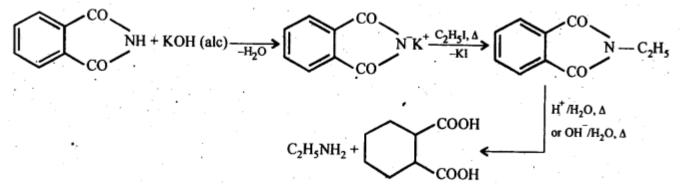
(ii) **Ammonolysis:** It is a process of replacement of either halogen atom in alkyl halides (or aryl halides) or hydroxyl group in alcohols (or phenols) by amino group. The reagent used for ammonolysis is alcoholic ammonia. Generally, a mixture of primary, secondary and tertiary amine is formed.

$$ROH + NH_{3} \xrightarrow{\text{Al}_{2}O_{3},\Delta} RNH_{2} + H_{2}O$$

$$R - NH_{2} \xrightarrow{+R-OH} R_{2}NH \xrightarrow{+R-OH} R_{3}N \xrightarrow{+R-OH} R_{4}N^{+}OH^{-}$$

$$(1^{\circ}) \xrightarrow{-H_{2}O} (2^{\circ}) \xrightarrow{-H_{2}O} (3^{\circ})$$

(iii)**Gabriel phthalimide synthesis:** It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide on treatment with ethanolic KOH gives potassium phathalimide which on heating with a suitable alkyl Or aralkyl halides gives N-substituted phthalimides, which on hydrolysis with dil HCI or with alkali give primary amines.



Q.7 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 C₆H₇N. Write the structures and IUPAC names of compounds A, B and C.

Answer:

From the available information, we find that 'B' upon heating with Br_2 and KOH forms a compound 'C'. The compound 'B' is

expected to be an acid amide. Since 'B' has been formed upon heating compound 'A' with aqueous ammonia, the compound 'A' is an aromatic acid.

It is benzoic acid. The reactions involved are given as follows:

