AMINES

METHOD OF PREPARATION

METHOD OF PREPARATION:

(1) AMMONOLYSIS OF ALKYL HALIDES AND ALCOHOL:

(a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis]:

Upon heating an aqueous ammonia solution in the presence of an alkyl halide, a mixture of the three amine types and quaternary ammonium salt is generated.

$$R - X \xrightarrow{NH_2} \rightarrow R - NH_2 \xrightarrow{R-X} \rightarrow R_2 - NH \xrightarrow{R-X} \rightarrow R_3N \xrightarrow{R-X} \xrightarrow{\Theta} R_4 \xrightarrow{N} X_4 \xrightarrow{N} X_4$$

If ammonia is taken in excess, 1° amine is the main product.

(b) Ammonolysis of alcohols:

When ROH and NH₃ are passed over Al_2O_3 or ThO₂ at 350° C all the three types of amines are formed.

$$R - OH \xrightarrow{NH_3} Al_3 O_3 / 400^{\circ}C \rightarrow R - NH_2 \xrightarrow{R - OH} Al_2 O_2 \rightarrow R_2 - NH \xrightarrow{R - OH} Al_2 O_3 \rightarrow R_3N$$

Note: (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.

(ii) If excess of ammonia is used, then main product will be primary amine.

(2) BY REDUCTION:

- (a) With RCONH₂: RCONH₂ $\frac{\text{LiAlH}_4}{\text{or Na/ C}_2\text{H}_2\text{OH}} \rightarrow \text{RCH}_2\text{NH}_2$
- (b) With RCN: $RCN + 4H \xrightarrow{Na/C_2H_2OH} RCH_2NH_2$

This chemical process is commonly known as the Mendius reaction. When alkyl isocyanides are reduced using sodium and ethanol, it results in the formation of secondary amines.

$$R - NC + 4H \xrightarrow{Na/C_2H_5OH} RNHCH_3$$

- (c) With Oximes: $R CH = N OH + 4H \xrightarrow{\text{LiAIH}_4}{\text{Na}/C_2H_5OH} \rightarrow RCH_2 NH_2 + H_2O$
- (d) With RNO₂ : RNO₂ + $6H \frac{Sn/HCI}{\Delta} \rightarrow RNH_2 + 2H_2O$ In lab method we use Sn/HCl while in industrial method we use Fe/ HCl.

Class-12th

Chemistry

(3) BY HYDROLYSIS OF:

(a) **R—NC:** Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.

R—NC + 2H₂O HCl \rightarrow RNH₂ + HCOOH

(b) RNCO: Alkyl isocyanate undergoes hydrolysis on heating with KOH.

 $R = N = CO + 2 KOH RNH_2 + K_2CO_3$

(4) FROM GRIGNARD REAGENT:

Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

$$R - Mg - I + Cl - NH_2 \rightarrow R - NH_2 + Mg < CI$$

(5) GABRIEL PHTHALIMIDE SYNTHESIS:

The process begins with the treatment of phthalimide with KOH to produce potassium phthalimide, which is subsequently subjected to alkyl iodide. Upon hydrolysis, alkyl phthalimide transforms into alkyl amine. This technique finds application in the production of highly pure aliphatic primary amines.



(6) BY HOFMANN'S BROMAMIDE REACTION (HOFMANN'S HYPOBROMITE REACTION): This method serves as a general approach to transform alkane amides into primary amines with one less carbon atom. The procedure involves heating ethanamide with an excess of KOH and bromine.

 $CH_3CONH_2 + Br_2 + 4KOH \quad -- \rightarrow \qquad CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$

MECHANISM:

Step 1 CH_3 — $CONH_2 + Br_2 + KOH --- \rightarrow$

 $CH_3CONHBr + KBr + H_2O$

N-bromo ethanamide

Chemistry



(7) CURTIUS REACTION:

Acid chloride on treatment with sodium aside give acid asides which on pyrolysis gives isocyanates which on hydrolysis gives corresponding amines.

 $\begin{array}{ccc} \mathsf{RCON}_3 & \frac{-N_2}{\Delta} \rightarrow & \mathsf{RCON}_3 & \frac{-N_2}{\Delta} \rightarrow & \mathsf{R}-\mathsf{N}=\mathsf{C}=\mathsf{O} & \frac{-N_2}{\Delta} \rightarrow & \mathsf{R}-\mathsf{NH}_2 \\ & \mathsf{A} \text{ cylaside} & & \mathsf{A} \text{ lkyl isocyanate} & & \mathsf{A} \text{ lkyl amide} \end{array}$

MECHANISM:



(8) SCHMIDT REACTION:

In presence of conc. H_2SO_4 alkanoic acid reacts with hydrazoic acid (N₃H) to yield alkylamine.

 $R-COOH + N_{3}H \xrightarrow{conc.H_{2}SO_{4}} R-NH_{2} + NH_{2} + N_{2} + CO_{2}$

MECHANISM:



(9) LOSSEN REARRANGEMENT REACTION:

In this reaction hydroxamic acid undergoes rearrangement and gives alkyl amine.



(10) REDUCTIVE AMINATION OF ALDEHYDE AND KETONE:

$$\sum C = 0 + NH_3 + H_2 \quad \frac{Ni}{\Delta} \rightarrow \sum CH - NH_2 + H_2O \ 1^{\circ} \text{ amine}$$

$$\sum C = 0 + RNH_2 + H_2 \quad \frac{Ni}{\Delta} \rightarrow \sum CH - NHR + H_2O \ 2^{\circ} \text{ amine}$$

$$\sum C = 0 + R_2NH + H_2 \quad \frac{Ni}{\Delta} \rightarrow \sum CH - NH_2 + H_2O \ 3^{\circ} \text{ amine}$$