

# XII UNIT 13

**Organic Compounds Containing Nitrogen** 



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## **Basic Character and Preparation of Amines (All Methods)**

#### 1. BASIC NATURE OF AMINES

- 1. Aniline is less basic than ammonia. The phenyl group exerts- I (inductive effect, i.e., it withdraw electrons. This results in the lower availability of electrons on nitrogen for protonation.
- 2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.

$$\begin{array}{c|c}
O & O \\
\parallel & + \\
H_3C - C - NH_2 \longleftrightarrow H_3C - C = NH_2
\end{array}$$

3. The compound with least `s' character (sp³ hydrolized) is most basic and with more `s' character (sp-hydrilized) is least basic. Examples in decreasing order of basicity are :

$$CH_3\ddot{N}H_2 > CH_3 - \ddot{N} = CHCH_3 > CH_3 - C = \ddot{N}$$
(i)  $(sp^3)$   $(sp^2)$   $(sp)$ 

- (ii)  $CH_3CH_2CH_2NH_2 > H_2C = CHCH_2NH_2 > HC = CCH_2NH_2$
- (iii)  $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$

Electron withdrawing (C<sub>6</sub>H<sub>5</sub>—) groups cause decrease in electron density on nitrogen atom and there by decreasing basicity.

- (v)  $CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$
- 2. METHODS OF PREPARATION
- **1. Hafmann's bromamide reaction :** Amines (only primary) can also be prepared by Hoffmann degradation. In this method the amine will have one carbon atom less than the amide. The reaction proceeds via formation of nitrene.

O | | R - C - NH<sub>2</sub> + Br<sub>2</sub> + 4KOH 
$$\longrightarrow$$
 RNH<sub>2</sub> + K<sub>2</sub>CO<sub>3</sub> + 2KBr + 2H<sub>2</sub>O

Mechanism of above reaction has been proposed as given below:

$$Br_2 + KOH \longrightarrow K^+O^-Br + HBr$$

Mechanism

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$$

$$\begin{array}{c}
O \\
R - C - NH_2 + {}^{-}OBr \longrightarrow R - C - N - Br + OH^{-}
\end{array}$$

(a) N-bromoacetone

$$R - \stackrel{O}{\stackrel{}{\cup}} - N - Br \mid OH^{-} - H_{2}O$$

$$R - \stackrel{O}{\stackrel{}{\cup}} N - Br + H_{2}O$$

$$R - \stackrel{O}{\stackrel{}{\cup}} N - Br + H_{2}O$$

$$R - \stackrel{O}{\stackrel{}{\cup}} N - Br + H_{2}O$$

$$R - NH_2 + CO_2 \leftarrow R - N = C = O$$
 (Isocyanate)

2. Curtius, Schmidt and Lossen Rearrangment: These reaction are basically rearrangement reactions in which carbon migrates from carbon to nitrogen with the formation of an

isocyanate. In these migration i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be

- Br in Hoffmann rearrangement.
- N<sub>2</sub> in Curtius and Schmidt rearrangement.

The isocyanate formed on hydrolysis gives amine.

(a) Curtius Reaction: Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates on hydrolysis gives corresponding amines.

 $RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$ 

$$R - C - N = N = N \iff R - C = N - N_{2}$$

$$R - C - N = N = N \implies R - N = C = 0$$

$$R - N = N = N = N \implies R - N \implies$$

$$R - N = C - OH \xrightarrow{H_2O} R - N = C - O^-$$

$$OH OH$$

$$R - NH - C - OH \xrightarrow{-CO_2} R - NH_2 + CO_2$$

(b) Schmidt Reaction: Carboxylic acid reacts with hydrozoic acid in presence of concentrated H<sub>2</sub>SO<sub>4</sub> to give isocyanates.

$$R - C + H^{+} \longrightarrow R - C \oplus \underbrace{NH_{3}}_{OH} R - C - OH$$

$$H - N - N^{+} \equiv N$$

$$-H_{2}O$$

$$R - N = C = O$$

$$S - C \oplus A$$

$$R - R - R \oplus A$$

$$R - R$$

(c) Lossen Reaction: Hydroxylamine on treatement with acid chloride gives acyl derivatives of hydroxyl amine the acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroximic acid.

$$R - COCl + NH_{2}OH \longrightarrow R - C = N + HCl$$

$$O \qquad O$$

$$| | | \qquad |$$

$$R - C - NHOH \qquad R - C = N - OH$$

Keto form the Multiple of the Hydroximic form (enol form)

The hydroxamic form (keto form) forms o-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.

$$R - \stackrel{\mathsf{H}}{\mathsf{C}} - \mathsf{N} - \mathsf{OH} + R - \stackrel{\mathsf{O}}{\mathsf{C}} - \mathsf{CI} \longrightarrow R - \stackrel{\mathsf{H}}{\mathsf{C}} - \overset{\mathsf{O}}{\mathsf{N}} - \mathsf{O} - \stackrel{\mathsf{C}}{\mathsf{C}} - R$$

$$R + \mathsf{N}_{2} \stackrel{\mathsf{H}_{2}\mathsf{O}}{\longleftarrow} R - \mathsf{N} = \mathsf{C} = \mathsf{O} \longleftarrow R - \stackrel{\mathsf{G}}{\longleftarrow} \overset{\mathsf{O}}{\mathbin{\mathbb{N}}} \overset{\mathsf{O}}{\longleftarrow} \overset{\mathsf{O}}{\mathbin{\mathbb{N}}} \overset{\mathsf{O}}{\longleftarrow} \overset{\mathsf{O}}{\mathbin{\mathbb{N}}} \overset{\mathsf{O}}{\longleftarrow} - \mathsf{R}$$

3. By reduction of nitroethane:

$$C_2H_5NO_2 + 6[H] \xrightarrow{Sn + HCl} C_2H_5NH_2 + 2H_2O$$
Nitroethane Ethylamine

4. By reduction of methyl cyanide:

**5.** By reduction of acetamide: Ethylamine is obtained by reduction of acetamide with sodium and absolute alcohol or LiAlH4 in ether or hydrogen in presence of nickel catalyst.

$$CH_3CONH_2 + 4[H] \xrightarrow{Na + C_2H_5OH} CH_3CH_2NH_2 + H_2O$$
Methyl cyanide Ethylamine

**6. By reduction of aldoxime :** Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or LiAlH<sub>4</sub> in ether yields ethylamine.

$$CH_3CH = NOH + 4[H]$$
  $\longrightarrow$   $CH_3CH_2NH_2 + H_2O$   
Acetaloxime Ethylamine

**7.** By the hydrolysis of ethyl isocyanate: Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.

$$C_2H_5NCO + 2KOH \longrightarrow C_2H_5NH_2 + K_2CO_3$$
  
Ethyl  
isocyanate Ethylamine

**8.** By the acid hydrolysis of ethyl isocyanide: Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.

$$C_2H_5NC + 2H_2O \longrightarrow C_2H_5NH_2 + HCOOH$$

Ethyl isocyanate Ethylamine Formic acid

#### 9. By Schmidt reaction:

In this reaction the acyl azide (RCON)<sub>2</sub> and alkyl isocyanate (R—NCO) are formed as an intermediate.

10. By the action of chloramine on Grignard reagent: When chloramine reacts with ethyl magnesium iodide, the formation of ethylmine occurs.

$$C_2H_5COOH$$
 +  $N_3H$   $\longrightarrow$   $C_2H_5NH_2 + N_2 + CO_2$   
Propionic acid Hydrazoic acid Ethylamine

#### 11. By Gabriel's phthalimide reaction:

$$\begin{array}{c} CO \\ CO \\ CO \\ NH \\ \hline \begin{array}{c} KOH \\ -H_2O \\ \end{array} \\ \begin{array}{c} CO \\ CO \\ \end{array} \\ NK \\ \hline \begin{array}{c} C_2H_5I \\ \\ \end{array} \\ \begin{array}{c} C_2H_5I \\ \end{array} \\ \begin{array}{c} COOH \\ COOH \\ \end{array}$$
\\ \\ \begin{array}{c} COOH \\ COOH \\ \end{array} \\ \begin{array}{c} COOH \\ COOH \\ \end{array}\\ \begin{array}{c} COOH \\ COOH \\ \end{array}\\ \\ \begin{array}{c} COOH \\ COOH \\ \end{array}\\ \\ \begin{array}{c} COOH \\ COOH \\ \end{array}

**12.** Laboratory preparation of ethylamine: Ethylamine is prepared in the laboratory by Hoffmann's bromide reaction. Propionamides are heated with bromine and potassium hydroxide solution.

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$$C_2H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_2H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
Propionamide Ethylamine

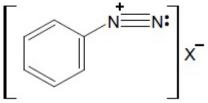
## **Diazonium Salt and Diazotisation**

#### **Diazonium Salt:**

When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.

$$NH_2$$
  $N_2$   $CI$   $+ HNO_2 + HCI$   $0^{\circ}C$   $+ H_2O$ 

This reaction is known as diazotisation. Diazonium salts have the structure



#### Mechanism of diazotisation:

#### Illustration:

Why ice cold condition have to be maintained in the diazotisation reaction of aniline?

Ans: Because benzene diazonium chloride is unstable and decomposes to give phenol above 278k.

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