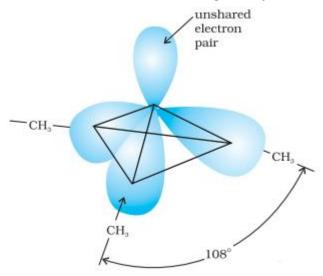
# **Amines**

# Structure of amines: Trigonal Pyramidal



Pyramidal shape of trimethylamine

# **Basicity of Amines**

# a) Aliphatic Amine:

Basic Strength:  $NH_3 < RNH_2 < R_2NH < R_3N$ ,

# b) Aromatic Amine:

Basic Strength:  $NH_3 > Ar- NH_2 > Ar_2- NH_2$ 

Benzene ring decreases the electron density over N atom due to resonance effect.

$$(a) \qquad (b) \qquad (c) \qquad (d)$$

# **Preparation of Amines**

#### a) From Alkyl halides:

$$\mathsf{RX} \xrightarrow{\mathsf{NH}_3} \mathsf{RNH}_2 \xrightarrow{\mathsf{RX}} \mathsf{R}_2 \mathsf{NH} \xrightarrow{\mathsf{RX}} \mathsf{R}_3 \mathsf{NH} \xrightarrow{\mathsf{RX}} \mathsf{R}_4 \overset{\oplus}{\mathsf{NHX}}^-$$

## b) From Nitro Compounds:

p-Nitrotoluene

p-Toluidine

#### c) From Nitriles:

### d) Hofmann Bromamide or Hofmann degradation:

$$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr$$

#### e) From carbonyl compounds (Reductive Amination)

$$CH_3CH = O + NH_3 \longrightarrow CH_3CH = NH \xrightarrow{H_2/Ni} CH_3CH_2$$
(an imine) (an ami

#### f) Curtius reaction:

O | | | 
$$R-C-CI$$
 +  $NaN_3$   $\longrightarrow$   $R-C-N-N = N$  | Acid chlorides | Sodium | Acyl azides |  $\Delta$  |  $\Delta$ 

#### g) Schmidt reaction:

$$RCO_2H + HN_3 \xrightarrow{conc H_2SO_4} RNH_2 + CO_2$$

g) Schmidt reaction:

$$RCO_2H + HN_3 \xrightarrow{conc H_2SO_4} RNH_2 + CO_2$$

h) Reduction of Alkyl isocyanide:

$$RNC + 4[H] \rightarrow R - NH - CH_3$$

i) Preparation of tertiary amine:

$$3RX + NH_3$$
 (In excess)  $\xrightarrow{\text{Ethanolic solution}} R_3N + 2HX$ 

### **Chemical Reactions**

a) Acylation:

 $RNH_2 + R'COCl \rightarrow R'CO NHR$  an N-substituted amide  $R_2NH + R'COCl \rightarrow R'CO.NR_2$  an N,N disubstituted amide

b) Benzoylation (Schotten Baumann Reaction)

Primary amine reacts with benzoyl chloride to give the acylated product

c) Carbylamine Reaction (Given Only by Primary Amines):

$$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$$
  
 $C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$ 

d) Action with Aldehyde and Ketone:

$$C_2H_5NH_2 + CH_3CHO \longrightarrow C_2H_5N = CHCH_3 + H_2O$$
  
Ethylamine Acetaldehyde Ethylidene ethylamine (Schiff's base)

e) Hofmann Mustard Oil Reaction:

$$C_2H_5NH_2 + S = C = S \longrightarrow S = C$$

$$SH$$

$$HgCl_2$$

$$C_2H_5N = C = S + HgS + 2HCI$$
Ethylisothiocyanate

- f) Reaction with Carbonyl Chloride:  $C_2H_5 NH_2 + COCl_2 \rightarrow C_2H_5NCO + 2HCl$
- **g) Hofmann Elimination:** When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene

$$\begin{array}{c} CH_3 \\ | \oplus \\ CH_3 - N - CH_2 - CH_2 - CH_3 \\ | \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ | \\ OH \xrightarrow{\Delta} CH_3 - N + CH_2 = CH - CH_3 + H_2O \\ | \\ CH_3 \end{array}$$

## h) The diazonium salts of amines:

$$RNH_2/Ar-NH_2 \xrightarrow{HONO} RN_2^+Cl^-$$

i) Reaction of Tertiary amines with Nitrous acid: When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.

$$2R_3N + HX + NaNO_3 \Longrightarrow R_3NHX + R_3N - N = OX^-$$
Tertiary aliphatic amine N-Nitrosoammonium compound

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

p-Nitroso-N, N-dimethyl aniline

## j) Coupling Reactions of Arene Diazonium Salts:

$$\begin{array}{c|c} O \\ \parallel \\ CH_3 - CO^-Na^+ \\ \hline N-N-Dimethylaniline \\ N-N-Dimethylaniline \\ \hline \end{array}$$

## k) Ring Substitution in Aromatic Amines:

## l) Aniline -X rearrangement:

Such compounds are not much stable so the group X migrates mainly at p-position.

#### 1. Fisher-Hepp rearrangement

### 2. Phenylhydroxylamine - p-aminophenol rearrangement.

# **Separation of a Mixture of Amines:**

## a) Hinsberg's Method

### **Primary amine:**

 $RNH_2 + C_6H_5SO_2Cl \frac{3}{4} \otimes C_6H_5 - SO_2 - NH - R + HCl$  $C_6H_5 - SO_2 - NH - R : N$ -alkyl benzene sulfonamides

Dissolves in NaOH due to acidic H-attached to Nitrogen)

### **Secondary amine**

$$R_2NH + C_6H_5SO_2CI \longrightarrow C_6H_5-SO_2-N$$
 + HCI (Insoluble is NaOH) R

### **Tertiary amine:**

Tertiary amines do not react with Hinsberg's reagent.

#### a) Hofmann's Method:

The mixture of amines is treated with diethyloxalate, which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react.

$$\begin{array}{cccc} COOC_2H_5 + 2RNH_2 & \longrightarrow CONHR + 2C_2H_5OH \\ & & & & & \\ COOC_2H_5 & & CONHR \\ diethyloxalate & & dialkyloxamide \\ & & & & & \\ COOC_2H_5 + R_2NH & \longrightarrow CONR_2 + C_2H_5OH \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

#### **Test for Amines**

**Primary amine** is treated with a strong base in presence in chloroform, an isocyanide is formed and this isocyanide thus formed has a very foul smell.

RNH<sub>2</sub> + CHCl<sub>3</sub> + 3KOH 
$$\longrightarrow$$
 R  $\longrightarrow$  R  $\longrightarrow$  N  $\stackrel{+}{=}$  C: + 3KCl + H<sub>2</sub>O an isocyanide (foul smelling)

**Secondary amine** is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solutions warmed with phenol and concentrated  $H_2SO_4$ , a brown or red colour is formed at first soon it changes to blue and then to green. The colour changes to red on dilution and further changes to greenish blue on treating with alkali.

Tertiary arylamines react with nitrous acid to form o-nitroso aromatic compound