

9. AMINES

(Amines, Diazonium Salts, Cyanides and Isocyanides)



STUDY NOTES

1. Amines, Diazonium Salts, Cyanides and Isocyanides:

- i) **Common name** : • Amines, Diazonium Salts, Cyanides and Isocyanides
- ii) **IUPAC name** : • Amines, Diazonium Salts, Nitrile and Carbylamine
- iii) **General Formula** : • Primary Amines: $R-NH_2$ (or) $C_nH_{2n+1}-NH_2$
 • Diazonium Salts: $Ar-N_2^+ Cl^-$
 • Cyanides: $R-CN$ (or) $R-C \equiv N$
 • Isocyanides: $R-NC$ (or) $R-N \equiv C$
- iv) **Amine Ex** : • CH_3NH_2 (Methanamine-), $C_2H_5NH_2$ (Ethanamine)
- v) **Diazonium Salts Ex** : • $C_6H_5N_2^+ Cl^-$ (Benzenediazoniumchloride)
- vi) **Cyanides Ex** : • CH_3CN (Ethanenitrile), C_2H_5CN (Propanenitrile)
- vii) **Isocyanides Ex** : • CH_3NC (Methylisocyanide), C_2H_5NC (Ethylisocyanide)
 Methylcarbylamine (Isocyanomethane),
 Ethylcarbyl amine (Isocyanoethane)
 C_6H_5NC (Phenylisocyanide; Isocyanobenzene)

I) AMINES

2. 1. Classification of Amines:

Based on number of alkyl/aryl groups attached to nitrogen

Primary (1°) $\rightarrow R-NH_2$

Secondary (2°) $\rightarrow R_2NH$

Tertiary (3°) $\rightarrow R_3N$

Based on nature of groups:

- Aliphatic amines (alkyl amines)
- Aromatic amines (arylamines)

2.2. Structure of Amines:

Amines are derivatives of ammonia (NH_3)

Nitrogen is sp^3 hybridised

Shape: trigonal pyramidal

Lone pair present $\rightarrow$ basic nature

3. Nomenclature:**Common Names:**

Named as alkyl + amine

Ex: $\text{CH}_3\text{NH}_2 \rightarrow$ methylamine

IUPAC Naming: Replace “-e” of alkane with **-amine**

Ex: $\text{CH}_3\text{NH}_2 \rightarrow$ methanamine

4. Preparation of Amines:

i) Reduction of Nitro Compounds: Nitro $\rightarrow$ amine (using H_2 /Pd or Fe/HCl)

ii) Ammonolysis of Alkyl Halides: Alkyl halide + $\text{NH}_3 \rightarrow$ amine

iii) Reduction of Nitriles: Nitrile $\rightarrow$ primary amine

iv) Reduction of Amides: Amide $\rightarrow$ amine

v) Gabriel Phthalimide Synthesis: Gives **only primary amines**

vi) Hoffmann Bromamide Degradation: Amide $\rightarrow$ amine (one carbon less)

5. Physical Properties of Amines:

Lower amines $\rightarrow$ gases, higher $\rightarrow$ liquids/solids

Show **hydrogen bonding**

Boiling point: $1^\circ > 2^\circ > 3^\circ$ amines

Solubility: lower amines soluble in water

6. Chemical Reactions of Amines:**(i) Basicity of Amines:****(a) Alkanamines vs Ammonia**

Alkyl groups donate electrons (+I effect) $\rightarrow$ increase basicity

Order in aqueous solution: $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ (Methyl substituted Amines)

Reason: Balance of +I effect + solvation

(b) Arylamines vs Ammonia

Less basic than ammonia

Lone pair delocalised in benzene ring (resonance)

(ii) Alkylation:

Amines + alkyl halides $\rightarrow$ higher amines

(iii) Acylation:

Formation of amides (important for identification)

(iv) Carbylamine Reaction:

Only **primary amines** give isocyanides (foul smell test)

(v) Reaction with Nitrous Acid (HNO_2):

- **1° aliphatic amine** $\rightarrow$ alcohol + N_2 gas
- **1° aromatic amine** $\rightarrow$ diazonium salt
- **2° amine** $\rightarrow$ nitroso compounds
- **3° amine** $\rightarrow$ no reaction

(vi) Reaction with Arylsulphonyl Chloride (Hinsberg Test):

Used to distinguish **1°, 2°, 3° amines**

(vii) Electrophilic Substitution (Aromatic Amines): $-\text{NH}_2$ is **activating group**

(a) Bromination: Gives tribromoaniline

(b) Nitration: Gives nitro derivatives

(c) Sulphonation: Forms sulphonated products

II) DIAZONIUM SALTS

7.1 Preparation of Diazonium Salts:

From **primary aromatic amines**

Reaction with nitrous acid at **273–278 K**

7.2 Physical Properties of Diazonium Salts :

- Stable only at **low temperature**
- Explosive when dry

7.3 Chemical Reactions of Diazonium Salts :

a) Reactions involving displacement of nitrogen:

Nitrogen gas is replaced by other groups:

$\text{Cl}, \text{Br} \rightarrow$ Sandmeyer reaction

$\text{F} \rightarrow$ Balz–Schiemann reaction

$\text{OH} \rightarrow$ phenol

$\text{H} \rightarrow$ benzene

b) Reactions involving retention of diazo group:

Coupling Reactions

Reaction with phenols/anilines

Forms **azo compounds** ($-\text{N}=\text{N}-$)

7.4 Importance of Diazonium Salts:

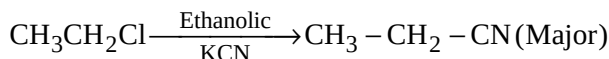
Preparation of Phenols, Aryl halides, Dyes (azo dyes)

Important intermediates in **organic synthesis**

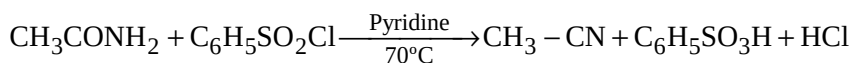
III) CYANIDES

8.1 Preparation of Cyanides:

From Alkylhalides & Ethanolic KCN



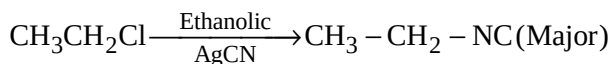
8.2 From Amides with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$



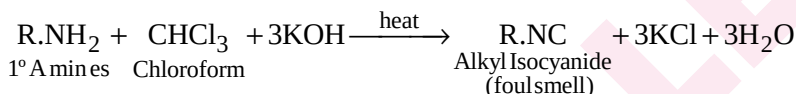
IV) ISOCYANIDES

9.1 Preparation of Isocyanides:

From Alkylhalides with ethanolic AgCN



9.2 From 1° amine with CHCl_3 & Alk.KOH



10. Daily life uses:

- **Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)** -Used in dyes, rubber, pharmaceuticals
- **Amines (general)** -Used in medicines, drugs, agrochemicals
- **Azo dyes (colour festival)** derived from amines- Used for textile coloring

Quick Revision Points

- Amine $\rightarrow$ NH_2 , Types $\rightarrow$ 1°, 2°, 3°
- Basicity $\rightarrow$ 2° > 1° > 3°
- Reactions $\rightarrow$ Alkylation, Acylation
- Diazonium $\rightarrow$ Very important
- Amines are **basic due to lone pair on nitrogen**
- **Primary amines $\rightarrow$ carbylamine test positive**
- Arylamines are **less basic (resonance effect)**
- Diazonium salts are **highly reactive intermediates**
- Used in **dye industry and aromatic substitutions**
- **Methyl substituted Amines (Order of basic strength in aqueous solution):**
 $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- **Ethyl substituted Amines:** $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$ $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)\text{NH}_2 > \text{NH}_3$
- Nature $\rightarrow$ Basic (lone pair)
- Aniline $\rightarrow$ Less basic (resonance)
- Tests $\rightarrow$ Hinsberg, Carbylamine