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CHAPTER NOTES

Amines Class 12 Notes — CBSE Chemistry Chapter 13

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Amines Class 12 Notes — CBSE Chemistry Chapter 13

Chapter 13 — **Amines** — introduces nitrogen-containing organic compounds that are derivatives of ammonia. From the adrenaline in your body to the aniline used in dyes, amines are biologically and industrially vital. This chapter carries **5-7 marks** in Board exams. Focus on basicity comparison, diazonium salt reactions, and distinction tests.

Key Concepts

Classification

Type	Structure	Example
Primary (1°)	$R-NH_2$	CH_3NH_2 (methylamine), $C_6H_5NH_2$ (aniline)
Secondary (2°)	R_2NH	$(CH_3)_2NH$ (dimethylamine)
Tertiary (3°)	R_3N	$(CH_3)_3N$ (trimethylamine)

Preparation

1. Hofmann Ammonolysis: $RX + NH_3 \rightarrow RNH_2 + R_2NH + R_3N + R_4N^+X^-$ (mixture!)
(Excess $NH_3 \rightarrow$ mainly 1° amine)

2. Gabriel Phthalimide Synthesis (1° amine only):

Phthalimide + KOH $\rightarrow$ potassium phthalimide + $RX \rightarrow$ N-alkylphthalimide $\xrightarrow{(N_2H_4)}$ RNH_2 + phthalhydrazide

3. Reduction of Nitro Compounds:

$RNO_2 + 3H_2/Ni \rightarrow RNH_2$ (catalytic reduction)

$ArNO_2 + Sn/HCl \rightarrow ArNH_2$ (aniline — standard lab method)

4. Hoffmann Bromamide Degradation:

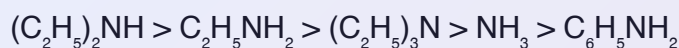
$RCOONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

(Amide $\rightarrow$ amine with ONE LESS carbon — very useful!)

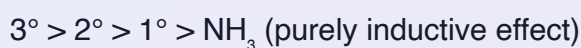
Gabriel synthesis: Only gives **primary amines**. Cannot be used for aromatic amines (ArNH_2) because aryl halides don't undergo $\text{S}_\text{N}2$ with potassium phthalimide.

Basicity of Amines

In aqueous solution (pK_b values):



In gas phase (no solvation):



Why aniline is a weak base: The lone pair on N is delocalised into the benzene ring (resonance), making it less available for protonation. Hence aniline is much weaker than aliphatic amines.

Effect of Substituents on Basicity

- **Electron-donating groups ($-\text{CH}_3$, $-\text{OCH}_3$) on ring:** Increase basicity of aromatic amines
- **Electron-withdrawing groups ($-\text{NO}_2$, $-\text{Cl}$) on ring:** Decrease basicity
- p-Toluidine ($\text{p-CH}_3\text{C}_6\text{H}_4\text{NH}_2$) > aniline > p-nitroaniline

Reactions of Amines

Distinction Tests (Hinsberg Test)

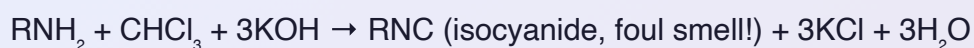
Hinsberg Reagent = $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (benzenesulphonyl chloride)

1° amine $\rightarrow$ sulphonamide (dissolves in NaOH — acidic H on N)

2° amine $\rightarrow$ sulphonamide (insoluble in NaOH — no acidic H)

3° amine $\rightarrow$ no reaction with Hinsberg reagent

Carbylamine Test (for 1° amines only)



Only 1° amines (aliphatic and aromatic) give this test.

Reaction with Nitrous Acid ($\text{NaNO}_2 + \text{HCl}$)

Amine Type	Reaction	Product
1° aliphatic	$\text{RNH}_2 + \text{HNO}_2$	$\text{ROH} + \text{N}_2\uparrow + \text{H}_2\text{O}$ (unstable diazonium $\rightarrow$ alcohol)
1° aromatic	$\text{ArNH}_2 + \text{HNO}_2$ (0-5°C)	$\text{ArN}_2^+\text{Cl}^-$ (diazonium salt — stable at 0-5°C!)
2° (both)	$\text{R}_2\text{NH} + \text{HNO}_2$	$\text{R}_2\text{N}-\text{N}=\text{O}$ (nitrosoamine — yellow oily liquid)
3° aliphatic	$\text{R}_3\text{N} + \text{HNO}_2$	$\text{R}_3\text{N}^+\text{H}\cdot\text{NO}_2^-$ (salt)
3° aromatic	$\text{Ar}_3\text{N} + \text{HNO}_2$	p-nitroso compound (electrophilic substitution on ring)

Diazonium Salts — The Most Versatile Intermediate!

Preparation: $\text{ArNH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow (0-5^\circ\text{C}) \text{ArN}_2^+\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}$ (diazotisation)

Reactions replacing N_2 :

$\text{ArN}_2^+\text{Cl}^- + \text{CuCl}/\text{HCl} \rightarrow \text{ArCl} + \text{N}_2$ (Sandmeyer — chloride)

$\text{ArN}_2^+\text{Cl}^- + \text{CuBr}/\text{HBr} \rightarrow \text{ArBr} + \text{N}_2$ (Sandmeyer — bromide)

$\text{ArN}_2^+\text{Cl}^- + \text{CuCN}/\text{KCN} \rightarrow \text{ArCN} + \text{N}_2$ (Sandmeyer — cyanide)

$\text{ArN}_2^+\text{Cl}^- + \text{KI} \rightarrow \text{ArI} + \text{N}_2 + \text{KCl}$ (no Cu catalyst needed!)

$\text{ArN}_2^+\text{Cl}^- + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{ArH} + \text{N}_2$ (replace NH_2 with H)

$\text{ArN}_2^+\text{Cl}^- + \text{HBF}_4 \rightarrow \text{ArF} + \text{N}_2 + \text{BF}_3$ (Balz-Schiemann — fluoride)

$\text{ArN}_2^+\text{Cl}^- + \text{H}_2\text{O} \rightarrow (\text{warm}) \text{ArOH} + \text{N}_2 + \text{HCl}$ (phenol)

Coupling reactions (N_2 retained):

$\text{ArN}_2^+ + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Ar}-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{OH}$ (azo dye — coloured!)

$\text{ArN}_2^+ + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{Ar}-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NH}_2$ (azo dye)

Why diazonium salts are so important: They allow introduction of groups ($-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$, $-\text{H}$) that cannot be directly introduced onto a benzene ring! They are the key intermediate for aromatic synthesis.

Important Definitions

Term	Definition
Amine	Organic derivative of ammonia where H atoms are replaced by alkyl/aryl groups
Diazotisation	Conversion of 1° aromatic amine to diazonium salt using $\text{NaNO}_2 + \text{HCl}$ at $0-5^\circ\text{C}$
Coupling Reaction	Reaction of diazonium salt with activated aromatic compound to form azo dye
Carbylamine Reaction	Test for 1° amine using $\text{CHCl}_3 + \text{KOH} \rightarrow$ foul-smelling isocyanide
Hofmann Degradation	Conversion of amide to amine with one less carbon using Br_2/NaOH

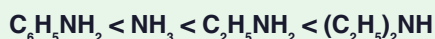
Solved Examples — NCERT Based

Example 1: Basicity Comparison

Q: Arrange in increasing order of basicity: $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, NH_3

Solution:

$\text{C}_6\text{H}_5\text{NH}_2$ is weakest (lone pair delocalised into ring). NH_3 is next. Among aliphatic: $2^\circ > 1^\circ$ in aqueous solution (balance of inductive and solvation effects).



Example 2: Conversion via Diazonium Salt

Q: Convert aniline to chlorobenzene.

Solution:

Step 1: $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow (0-5^\circ\text{C}) \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ (diazonium salt)

Step 2: $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{CuCl}/\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$ (Sandmeyer reaction)

Example 3: Hinsberg Test

Q: How can you distinguish between ethylamine, diethylamine, and triethylamine using Hinsberg reagent?

Solution:

Treat each with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (Hinsberg reagent):

Ethylamine (1°): Forms sulphonamide $\rightarrow$ dissolves in NaOH (due to acidic $-\text{NH}$)

Diethylamine (2°): Forms sulphonamide $\rightarrow$ does NOT dissolve in NaOH (no acidic H on N)

Triethylamine (3°): No reaction with Hinsberg reagent

Example 4: Gabriel Synthesis

Q: Prepare propan-1-amine using Gabriel synthesis.

Solution:

Phthalimide + KOH $\rightarrow$ potassium phthalimide

Potassium phthalimide + $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ $\rightarrow$ N-propylphthalimide

N-propylphthalimide + N_2H_4 (hydrazine) $\rightarrow$ **$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$** (propan-1-amine) + phthalhydrazide

Important Questions for Board Exams

1 Mark Questions

1. Why is aniline a weaker base than methylamine?
2. What is the carbylamine reaction?
3. What is diazotisation?
4. Name the reagent used in Hinsberg test.

2 Mark Questions

1. How do primary, secondary and tertiary amines react with nitrous acid?
2. Explain why $(\text{CH}_3)_3\text{N}$ is a weaker base than $(\text{CH}_3)_2\text{NH}$ in aqueous solution.
3. Write the Gabriel phthalimide synthesis reaction for methylamine.
4. Give the Hofmann bromamide degradation reaction.

3 Mark Questions

1. What are diazonium salts? How are they prepared? Write any 4 reactions.
2. How will you distinguish between 1°, 2° and 3° amines using Hinsberg test?
3. Compare the basicity of methylamine, dimethylamine, aniline and ammonia with reasons.

5 Mark Questions

1. What are amines? Discuss their classification and preparation (any 3 methods). Compare their basic character.
2. Describe the chemistry of diazonium salts: preparation, Sandmeyer reaction, coupling reactions, and importance in synthesis.

Quick Revision Points

- Amines: 1° (RNH_2), 2° (R_2NH), 3° (R_3N)
- Gabriel synthesis: only 1° amines, not aromatic amines
- Hofmann degradation: amide $\rightarrow$ amine (1 less C)
- Basicity (aq): $2^\circ > 1^\circ > 3^\circ > \text{NH}_3 \gg \text{aniline}$
- Aniline weak base: lone pair delocalised into ring
- Carbylamine test: 1° amines only $\rightarrow$ foul smell of isocyanide
- Hinsberg: 1° dissolves in NaOH, 2° doesn't, 3° no reaction
- Diazonium salt: $\text{ArNH}_2 + \text{NaNO}_2 + \text{HCl}$ at $0-5^\circ\text{C}$
- Sandmeyer: $\text{ArN}_2^+ + \text{CuX/HX} \rightarrow \text{ArX}$ (Cl, Br, CN)
- Coupling: diazonium + phenol/amine $\rightarrow$ azo dye

← Previous: Aldehydes, Ketones and Carboxylic Acids

Next: Biomolecules →



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