FREE NOTES · NCERT + JEE/NEET LEVEL

Amines

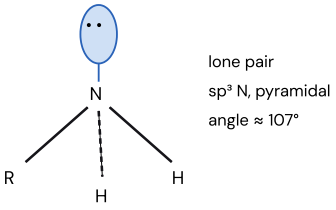
Structure, classification and naming, preparation, physical properties, basic character, chemical reactions and tests for 1°/2°/3° amines, diazonium salts and their uses.

01 Structure & classification
02 Preparation
03 Physical properties
04 Basic character
05 Reactions of amines
06 Hinsberg's test
07 Aniline: ring reactions
08 Diazonium salts
09 JEE Extra + Tricks
10 Solved questions
11 Mistakes & practice
12 Quick revision

01 Structure & classification

Amines are derivatives of NH_3 where H is replaced by alkyl/aryl groups. N is sp^3 with a lone pair ⇒ **pyramidal**.

- **1°**: $R–NH_2$, **2°**: R_2NH, **3°**: R_3N. (Different from alcohols: here we count groups on N.)
- Naming: alkanamine (ethanamine, N-methylethanamine, N,N-dimethylmethanamine). $C_6H_5NH_2$ = aniline (benzenamine).



Pyramidal shape of an amine

02 Preparation

Method	Reaction	Gives
Reduction of nitro compounds	$ArNO_2$ + Fe/HCl (preferred) or Sn/HCl or H_2/Pd	$ArNH_2$
Ammonolysis of halides	$R–X + NH_3$	Mixture 1°, 2°, 3°, quaternary salt
Reduction of nitriles	$RCN + LiAlH_4$ or H_2/Ni	RCH_2NH_2 (one C more)
Reduction of amides	$RCONH_2 + LiAlH_4$	RCH_2NH_2
Gabriel phthalimide	Phthalimide + KOH + RX, then hydrolysis	Pure 1° aliphatic amine (not aromatic)
Hoffmann bromamide	$RCONH_2 + Br_2 + 4NaOH$	RNH_2 (**one C less**)

03 Physical properties

- Lower aliphatic amines are gases with a fishy smell; aniline is a liquid that darkens in air (oxidation).
- 1° and 2° amines form H-bonds ⇒ b.p.: **1° > 2° > 3°** (3° has no N–H).
- Amines have lower b.p. than alcohols (N is less electronegative than O ⇒ weaker H-bonds).
- Small amines are water-soluble; solubility falls as alkyl size rises.

04 Basic character

The lone pair on N accepts a proton ⇒ amines are **Lewis bases**. Higher K_b / lower pK_b ⇒ stronger base.

- Aliphatic amines are stronger than NH_3 (+I of alkyl).
- In **water**, the order depends on +I, H-bonding (solvation) of the ammonium ion, and crowding:
  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- **Aniline is weaker than NH_3**: the lone pair is delocalised into the ring (resonance) and the anilinium ion has less resonance.
- On the ring, EDG ($-CH_3$, $-OCH_3$) increase basicity; EWG ($-NO_2$) decrease it. p-toluidine > aniline > p-nitroaniline.

05 Reactions of amines

Reaction	Reagent	Result
Salt formation	HCl	$RNH_3^+Cl^-$ (water-soluble)
Alkylation	R′X	2°, 3° amines, quaternary salt
Acylation	CH_3COCl / $(CH_3CO)_2O$, pyridine	Amide (1° and 2° only)
Benzoylation	C_6H_5COCl	N-benzoyl amide
Carbylamine	$CHCl_3$ + alc. KOH, heat	Isocyanide (foul smell): only **1° amines**
Nitrous acid	$NaNO_2$ + HCl	1° aliphatic: alcohol + N_2 gas; aromatic (273–278 K): **diazonium salt**

06 Hinsberg's test: telling 1°, 2°, 3° apart

Amine	+ Benzenesulphonyl chloride ($C_6H_5SO_2Cl$)
1°	N-alkylbenzenesulphonamide, **soluble in KOH** (acidic N–H)
2°	N,N-dialkyl sulphonamide, **insoluble in KOH** (no H on N)
3°	No reaction

Carbylamine test also picks out 1° amines.

07 Aniline: ring reactions

$-NH_2$ is strongly **activating**, ortho/para directing.

- **Bromine water** ⇒ white ppt of **2,4,6-tribromoaniline**. To get mono-bromo, first **acetylate** (acetanilide reduces activation), brominate, then hydrolyse.
- **Nitration:** direct nitration gives tarry oxidation products and ~47% **meta** product (the anilinium ion $-NH_3^+$ is meta directing in acid). Protect by acetylation ⇒ p-nitroaniline mainly.
- **Sulphonation:** conc. H_2SO_4 ⇒ anilinium hydrogensulphate ⇒ heat ⇒ **sulphanilic acid** (exists as a zwitterion).
- **No Friedel-Crafts:** aniline (a base) forms a salt with $AlCl_3$; N gets + charge and deactivates the ring.

08 Diazonium salts

$ArNH_2 + NaNO_2 + 2HCl$, **273–278 K** ⇒ $ArN_2^+Cl^-$ (diazotisation). Aryl diazonium salts are stable at low temperature (resonance); alkyl ones are not.

Reagent	Product	Name
CuCl/HCl, CuBr/HBr, CuCN/KCN	ArCl, ArBr, ArCN	Sandmeyer
Cu powder + HX	ArX	Gatterman
KI	ArI	
HBF_4, heat	ArF	Balz-Schiemann
H_3PO_2 or CH_3CH_2OH	ArH (benzene)	Removes $-NH_2$
H_2O, warm	Phenol	
HBF_4 then $NaNO_2$/Cu	Nitrobenzene	
Phenol (alkaline) / aniline (acidic)	p-Hydroxyazobenzene (orange) / p-aminoazobenzene (yellow)	**Coupling** (dyes; N_2 retained)

09 JEE Extra + Tricks

JEE LEVEL

- Basicity in water: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$; for methyl: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$. Aniline is a weak base (lone pair in resonance).
- Hinsberg test (benzenesulphonyl chloride): 1° ⇒ soluble in alkali; 2° ⇒ insoluble product; 3° ⇒ no reaction.
- Carbylamine test ($CHCl_3$ + KOH): only 1° amines give foul-smelling isocyanide.
- Hofmann bromamide: amide → amine with one carbon less. Gabriel phthalimide: only 1° aliphatic amines (not aromatic).
- Diazonium salts (0–5 °C): Sandmeyer (CuCl/CuBr/CuCN), Gattermann, coupling with phenol (orange dye) / aniline (yellow dye).
- Aniline + Br_2 water ⇒ 2,4,6-tribromoaniline; to get mono substitution, first acetylate ($-NHCOCH_3$).

10 Solved questions

Q1. Convert benzamide to aniline.

Hoffmann bromamide: $C_6H_5CONH_2 + Br_2 + 4NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$.

Q2. Why can't Gabriel synthesis make aniline?

Aryl halides don't undergo nucleophilic substitution with the phthalimide anion.

Q3. Arrange in order of basicity in water: CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$.

Q4. Convert aniline to benzonitrile.

$NaNO_2/HCl$ (273 K) → $C_6H_5N_2^+Cl^-$ → CuCN/KCN → C_6H_5CN.

11 Mistakes & practice

- Saying 3° amine is the strongest base in water (crowding and poor solvation lower it).
- Forgetting that Hoffmann bromamide removes one carbon.
- Expecting only o/p products in direct nitration of aniline.
- Doing diazotisation at room temperature (the salt decomposes).

1. Which amines give the carbylamine test?
2. Product of CH_3CONH_2 + Br_2 + NaOH?
3. Is aniline more or less basic than ammonia?
4. Why is aniline acetylated before bromination?
5. Reagent to replace N_2^+ by H?

ANSWERS

1) Only 1° · 2) CH_3NH_2 · 3) Less · 4) To reduce activation and get mono-substitution · 5) H_3PO_2

12 Quick revision: 5 minutes before the exam

PREPARATION

- Gabriel: pure 1° aliphatic.
- Hoffmann: one C less.
- Nitrile + $LiAlH_4$: one C more.

BASICITY

- 2° > 1° > 3° (methyl, water).
- Aliphatic > NH_3 > aniline.

TESTS

- Carbylamine: 1° only.
- Hinsberg: 1° soluble in KOH, 2° insoluble, 3° no reaction.

DIAZONIUM

- 273–278 K.
- Sandmeyer: CuX.
- Coupling ⇒ azo dyes.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.