# Unit 16 · Amines

STUDY NOTES

### WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: benzene → nitrobenzene → aniline → benzenediazonium chloride → p-hydroxyazobenzene; short: chlorobenzene from benzenediazonium chloride; long: the cycle P → Q → R (aniline) → S → T → P (benzene), with conditions; nitrobenzene → yellow dye
- **MCQ (1 mark)**
  - isomers of $C_3H_9N$ (four); a tertiary amine; diethyl oxalate separates 1°, 2°, 3°; excess chloroethane + $NH_3$ → quaternary salt
  - strongest base in water; 1° amine + $HNO_2$ → alcohol; carbylamine test (1° only); nitrile → 1° amine; methylamines 2° > 1° > 3°
  - aniline o, p director; why $-NH_2$ is protected; + benzenediazonium chloride → p-aminoazobenzene; isocyanide reduced → 2° amine
- **Short (5 marks, in parts)**: name and classify; aniline weaker than $NH_3$; basicity orders with reasons; ethanamine from ethanenitrile and bromoethane; 4-bromoaniline; scarlet dye; $C_2H_7N$ with no carbylamine smell; $C_3H_9N$ giving a yellow oil
- **Long (8 marks)**: Hofmann's separation; identify V–Z, P–S, A–E (C is 45 u: ethanamine); ethyne → benzene → … → p-nitroaniline; one C up and down (methanamine ⇄ ethanamine)

## Key terms

**Amine**: $NH_3$ with H replaced by alkyl or aryl; **aliphatic** (all alkyl), **aromatic** (N on the ring: aniline; $C_6H_5CH_2NH_2$ is aliphatic).

**1°, 2°, 3°**: how many groups on the **N** (not the C): R–$NH_2$ (amino), $R_2NH$ (imino), $R_3N$; $(CH_3)_3C–NH_2$ is **1°**.

**Quaternary ammonium salt**: $R_4N^+X^-$: no lone pair, a salt.

**pKaH**: pKa of $RNH_3^+$; **higher = stronger base**; pKaH + pKb = 14.00.

**Carbylamine reaction**: 1° amine + $CHCl_3$ + alc. KOH → **isocyanide** (foul smell).

**Diazotization**: $ArNH_2$ + $NaNO_2$ + HCl at **0–5 °C** → $ArN_2^+Cl^-$.

**Coupling**: $ArN_2^+$ + activated ring (para) → **azo dye**, –N=N–.

## Naming and isomers

| Formula | IUPAC (common) |
|---|---|
| $CH_3NH_2$ | methanamine (methylamine) |
| $CH_3CH_2CH_2NH_2$ | propan-1-amine (propylamine) |
| $CH_3CH(NH_2)CH_3$ | propan-2-amine (isopropylamine) |
| $(CH_3)_3CNH_2$ | 2-methylpropan-2-amine (tert-butylamine) |
| $CH_3CH_2NHCH_3$ | N-methylethanamine (ethylmethylamine) |
| $(CH_3)_2NCH_2CH_3$ | N,N-dimethylethanamine (3°) |
| $C_6H_5NH_2$ | benzenamine (aniline) |

- IUPAC: alkane, -e → **-amine**; 2°, 3°: largest group the parent, the others **N-** prefixes; **amino-** when a higher group takes the suffix (2-aminoethanoic acid)
- **chain** (butan-1-amine, 2-methylpropan-1-amine), **position** (propan-1-, -2-amine), **functional** (1°, 2°, 3° of one formula), **metamerism** (N-ethylethanamine, N-methylpropan-1-amine)
- $C_3H_9N$: **four**: propan-1-amine, propan-2-amine, N-methylethanamine, N,N-dimethylmethanamine

## Hofmann's separation (diethyl oxalate)

- **1°** (two N–H): $2\,C_2H_5NH_2 + (COOC_2H_5)_2 \longrightarrow (CONHC_2H_5)_2 + 2\,C_2H_5OH$: **solid** oxamide, filtered off
- **2°** (one N–H): $(C_2H_5)_2NH + (COOC_2H_5)_2 \longrightarrow C_2H_5OOC{-}CON(C_2H_5)_2 + C_2H_5OH$: liquid oxamic ester
- **3°** (no N–H): no reaction; distills first (lowest b.p.)
- back with KOH: $(CONHC_2H_5)_2 + 2\,KOH \longrightarrow (COOK)_2 + 2\,C_2H_5NH_2$
- $C_2H_5OOC{-}CON(C_2H_5)_2 + 2\,KOH \longrightarrow (COOK)_2 + (C_2H_5)_2NH + C_2H_5OH$

## Preparation of primary amines

- **haloalkane + alc. $NH_3$** (sealed tube): $C_2H_5Br + 2\,NH_3 \longrightarrow C_2H_5NH_2 + NH_4Br$; the amine reacts on ($\rightarrow$ 2°, 3°, $R_4N^+X^-$): **large excess of $NH_3$** for the 1°; excess RX $\rightarrow$ quaternary salt
- **nitriles** (one C more than RX): $CH_3CN + 4\,[H] \xrightarrow{\text{Na, ethanol}} CH_3CH_2NH_2$ (Mendius; or $LiAlH_4$, $H_2$/Ni)
- **Hofmann bromamide** (one C fewer): $CH_3CONH_2 + Br_2 + 4\,KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$
- **amide + $LiAlH_4$** (same C): $CH_3CONH_2 + 4\,[H] \longrightarrow CH_3CH_2NH_2 + H_2O$
- **nitroalkanes**: $RNO_2 + 6\,[H] \xrightarrow{\text{Sn, conc. HCl}} RNH_2 + 2\,H_2O$
- **one C up**: $CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$
- **one C down**: $C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH \xrightarrow{[O]} CH_3COOH \xrightarrow{NH_3,\ heat} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

## Physical properties

- $CH_3NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$, $C_2H_5NH_2$ (b.p. 17 °C) **gases**; ammonia-like, then **fishy** smell
- 1°, 2° **H-bond** (N–H···N, weaker than O–H···O): b.p. **alkane < amine < alcohol**; isomers **1° > 2° > 3°**
- butane −0.5, $(CH_3)_3N$ 3, $CH_3CH_2NHCH_3$ 37, propan-1-amine 48, propan-1-ol 97 (°C)
- lower ones soluble (H bonds with water); less as the chain grows; less dense than water

## Basicity

- lone pair on $sp^3$ N takes $H^+$: $RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$ (red litmus blue)
- **+I** of alkyl groups $\rightarrow$ stronger than $NH_3$; gas phase **3° > 2° > 1° > $NH_3$**
- in water also **hydration** of $RNH_3^+$ (3, 2, 1 N–H) and **crowding**: methylamines **2° > 1° > 3° > $NH_3$**; ethylamines 2° > 3° > 1°
- **aniline far weaker**: lone pair **delocalized** into the ring; protonation loses that resonance; ring $sp^2$ C –I
- order: **aliphatic amines > $NH_3$ > aniline**; $C_6H_5NH_2 < CH_3NH_2 \leq C_2H_5NH_2$ (ethyl pushes a little more; in water about equal, 10.66 and 10.65)

| Base | pKaH | pKb |
|---|---|---|
| $(CH_3)_2NH$ / $CH_3NH_2$ / $(CH_3)_3N$ | 10.73 / 10.66 / 9.80 | 3.27 / 3.34 / 4.20 |
| $(C_2H_5)_2NH$ / $(C_2H_5)_3N$ / $C_2H_5NH_2$ | 10.84 / 10.75 / 10.65 | |
| $NH_3$ | 9.25 | 4.75 |
| $C_6H_5NH_2$ | 4.87 | 9.13 |

## Reactions of aliphatic amines

- **acids** (acid–base, not addition): $C_2H_5NH_2 + HCl \longrightarrow C_2H_5NH_3^+Cl^-$; NaOH frees the amine; medicines as hydrochlorides
- **carbylamine** (1° only, aliphatic or aromatic): $C_2H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_2H_5NC + 3\,KCl + 3\,H_2O$
  - isocyanide reduced: $C_2H_5NC + 4\,[H] \longrightarrow C_2H_5NHCH_3$ (2° amine)
- **alkylation**: $C_2H_5NH_2 + C_2H_5Br \longrightarrow (C_2H_5)_2NH + HBr \rightarrow (C_2H_5)_3N \rightarrow (C_2H_5)_4N^+Br^-$
- **acylation** (1°, 2°; pyridine takes HCl): $C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5NHCOCH_3 + HCl$; 3° doesn't react

**Nitrous acid** ($NaNO_2$ + HCl, cold): $NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

- **1°**: $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$: brisk **$N_2$** bubbles
- **2°**: $(C_2H_5)_2NH + HNO_2 \longrightarrow (C_2H_5)_2N{-}NO + H_2O$: **yellow oil** (N-nitrosamine; Liebermann's test)
- **3°**: $R_3N + HNO_2 \longrightarrow R_3NH^+NO_2^-$: clear, no change (warm: nitrosamine + **aldehyde**)
- Hinsberg ($C_6H_5SO_2Cl$, KOH): 1° sulphonamide dissolves in alkali, 2° doesn't, 3° no reaction
- uses: rubber accelerators, medicines (adrenaline, ephedrine, procaine), quaternary salts as surfactants, nylon (hexane-1,6-diamine)

## Aniline

### Preparation

- $C_6H_5NO_2 + 6\,[H] \xrightarrow{\text{Sn, conc. HCl}} C_6H_5NH_2 + 2\,H_2O$ (then NaOH); industry $H_2$/Ni
- $C_6H_5OH + NH_3 \xrightarrow[\text{about 300 °C}]{\text{anhyd. } ZnCl_2} C_6H_5NH_2 + H_2O$
- $C_6H_5Cl + 2\,NH_3 \xrightarrow[\text{200 °C, 60 atm}]{Cu_2O} C_6H_5NH_2 + NH_4Cl$

**Physical**: colorless oily liquid, turns **yellow** → **brown** in air; b.p. 184 °C; 1.02 g/cm$^3$; sparingly soluble (3.6 g/100 mL); toxic (methemoglobin)

### Reactions

- alkylation: $C_6H_5NH_2 + CH_3Br \longrightarrow C_6H_5NHCH_3 + HBr \rightarrow C_6H_5N(CH_3)_2 \rightarrow C_6H_5N^+(CH_3)_3Br^-$
- acylation → **acetanilide**: $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$
- **diazotization**: $C_6H_5NH_2 + NaNO_2 + 2\,HCl \xrightarrow{\text{0-5 °C}} C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O$; ring spreads the charge (aliphatic ones lose $N_2$ at once); warm → phenol
- carbylamine: $C_6H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_6H_5NC + 3\,KCl + 3\,H_2O$

**Coupling** (para; –N=N– joins two rings: colored)

| With | Conditions | Dye |
|---|---|---|
| aniline | 0–5 °C, faintly acidic | **4-aminoazobenzene**, yellow |
| phenol | cold NaOH | **4-hydroxyazobenzene**, orange |
| naphthalen-2-ol | cold NaOH | 1-phenylazo-2-naphthol, scarlet (test) |

- $C_6H_5N_2{}^+Cl^- + C_6H_5NH_2 \longrightarrow C_6H_5N{=}NC_6H_4NH_2 + HCl$
- $C_6H_5N_2{}^+Cl^- + C_6H_5OH + NaOH \longrightarrow C_6H_5N{=}NC_6H_4OH + NaCl + H_2O$

**Ring**: $-NH_2$ +R: strongly **activating, o and p**

- $C_6H_5NH_2 + 3\,Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3\,HBr$ (bromine water, white ppt, no catalyst)
- **protect** first (acetanilide): conc. $HNO_3$ oxidizes aniline (tar); too activating; in strong acid $C_6H_5NH_3{}^+$ is **meta** (direct nitration: 47% meta, 51% para)
- aniline → acetanilide → $Br_2/CH_3COOH$ → 4-bromoacetanilide → hydrolysis → **4-bromoaniline**; the same with the nitrating mixture below 10 °C → **4-nitroaniline**
- sulphonation: $C_6H_5NH_2 + H_2SO_4 \longrightarrow C_6H_5NH_3{}^+HSO_4{}^- \rightarrow 453–473\ K \rightarrow$ **sulphanilic acid** (zwitterion $^+H_3N–C_6H_4–SO_3{}^-$) + $H_2O$

**Uses**: MDI → polyurethane foam; rubber chemicals; azo dyes; sulpha drugs, paracetamol; pesticides

## Chains (model paper)

- the cycle: $C_6H_6 \xrightarrow{HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow[\text{0-5 °C}]{NaNO_2/HCl} C_6H_5N_2Cl \xrightarrow[\text{warm}]{H_2O} C_6H_5OH \xrightarrow[\text{heat}]{\text{Zn dust}} C_6H_6$
- $C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2$ (Sandmeyer); $C_6H_5Cl \xrightarrow{NH_3/Cu_2O} C_6H_5NH_2$
- $3\,C_2H_2 \xrightarrow{\text{red–hot Fe}} C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow$ aniline → (protect) → p-nitroaniline
- A–E (C 45 u, ethanamine): $CH_3CH_2COOH \xrightarrow{NH_3,\ heat} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH \xrightarrow{NaOH/I_2} CHI_3$

### COMMON MISTAKES

✗ $(CH_3)_3CNH_2$ is sec-butylamine
✓ **tert**-butylamine, 2-methylpropan-2-amine (and 1°).

✗ haloalkane + $NH_3$ 1 : 1 gives the 1° amine
✓ a mixture; **large excess of $NH_3$**.

✗ $RCONH_2 + 2[H] \rightarrow$ amine
✓ + **4**[H] → $RCH_2NH_2 + H_2O$.

✗ 1° amine + $HNO_2$ gives $H_2$
✓ alcohol + $\mathbf{N_2}$ + $H_2O$.

✗ 3° amine + $HNO_2$ → nitrosamine + alcohol
✓ cold: soluble **salt**; warm: nitrosamine + **aldehyde**.

✗ carbylamine with 2KOH
✓ **3**KOH.

✗ amine + HCl an addition reaction
✓ **acid–base** (salt).

✗ bases lose electrons
✓ **donate a lone pair** / accept $H^+$.

✗ sulphonation of aniline with pyridine
✓ conc. $H_2SO_4$, **453–473 K**, no pyridine.

✗ 2° > 1° > 3° for all amines
✓ methylamines only; ethylamines 2° > 3° > 1°.

✗ Hoffmann
✓ **Hofmann**.