

Nitrogen compounds (A Level)

A-Level Chemistry 9701 · Topic 34 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Primary and secondary amines

3. Amides

2. Phenylamine and azo dyes

4. Amino acids and peptides

thelucidstem.com

1 Primary and secondary amines

Syllabus 34.1

An **amine** is ammonia with one or more H atoms replaced by alkyl or aryl groups: a **primary** amine is RNH_2 , a **secondary** amine is R_2NH . Primary alkyl amines are made by heating a **halogenoalkane with excess ammonia in ethanol in a sealed tube**, by **reducing an amide** with LiAlH_4 or by **reducing a nitrile** with LiAlH_4 or H_2/Ni . Because the amine product is itself a nucleophile, it can react with more halogenoalkane to give a **secondary amine**. The lone pair on nitrogen accepts H^+ , so amines are **bases**; ethylamine is stronger than ammonia because the **electron-donating alkyl group** makes the lone pair more available, while phenylamine is much weaker because its lone pair is **delocalised into the benzene ring**.

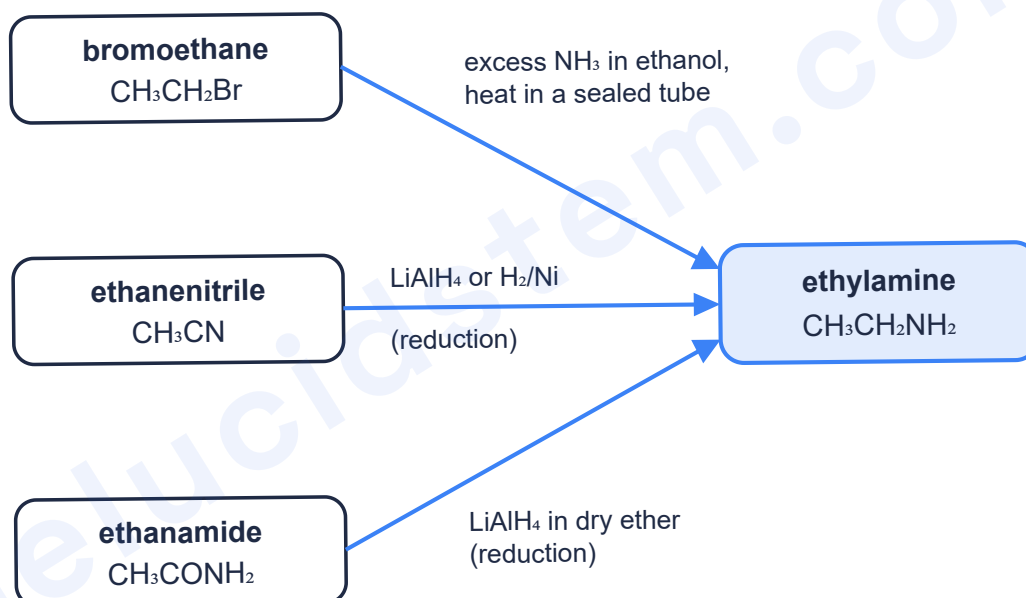


Fig. 1: three routes to the primary amine ethylamine

Three routes in, one lone pair out.

- ✓ $RX + \text{excess } NH_3$, ethanol, sealed tube.
- ✓ **Nitrile or amide** + $LiAlH_4$ (nitrile also H_2/Ni).
- ✓ $RNH_2 + RX$ gives the secondary amine R_2NH .
- ✓ **Basicity:** ethylamine $> NH_3 >$ phenylamine.

Watch out!

Basicity is about how **available the lone pair on N** is to accept H^+ , not about how many H atoms there are. Alkyl groups **push** electron density onto N (stronger base); a benzene ring **pulls** the lone pair into its delocalised system (weaker base). In the halogenoalkane route, forgetting the **excess** ammonia means a mixture of primary, secondary and tertiary amines and quaternary salts.

2 Phenylamine and azo dyes

Syllabus 34.1

Phenylamine, $C_6H_5NH_2$, is made by **reducing nitrobenzene** with **tin and concentrated HCl**, heated under reflux, then adding **NaOH** to release the free amine from its salt. Its N lone pair is partly delocalised into the ring, which makes it a weak base but **activates the ring**: with **aqueous bromine** at room temperature it gives a **white precipitate of 2,4,6-tribromophenylamine**. With **nitrous acid** ($NaNO_2 + HCl$) **below 10 °C** it forms **benzenediazonium chloride**, which **couple with phenol in alkaline solution** to give an **azo dye** containing $-N=N-$. The azo link joins two benzene rings into one **extended delocalised system**, which absorbs visible light, so azo compounds are used as **dyes** and indicators.

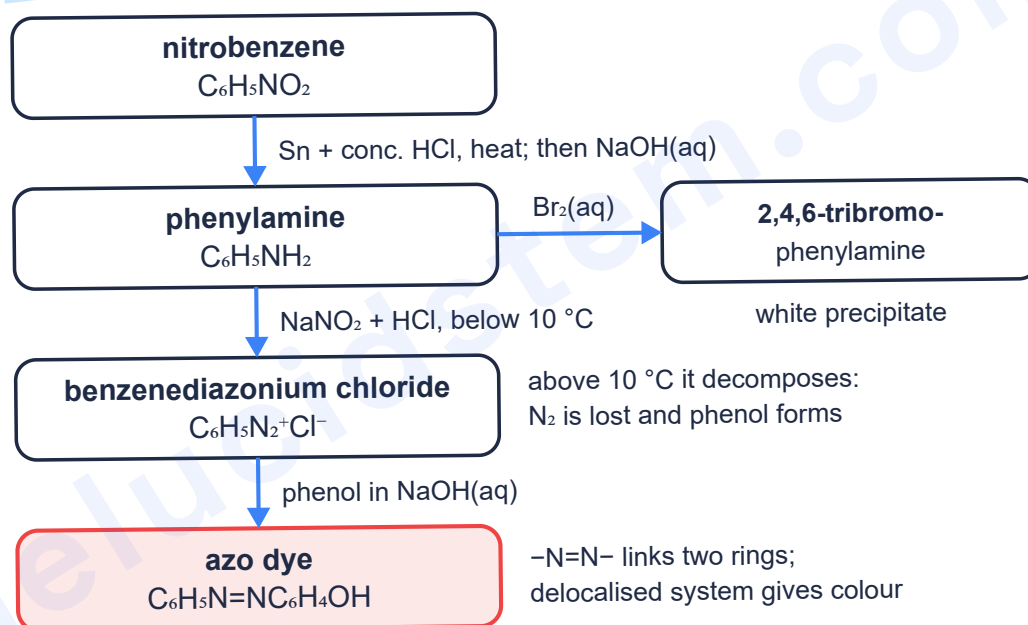


Fig. 1: from nitrobenzene to an azo dye, with the bromine test on phenylamine

Reduce, diazotise, couple.

- ✓ **Nitrobenzene:** $\text{Sn} + \text{conc. HCl}$, reflux, then NaOH .
- ✓ **$\text{Br}_2(\text{aq})$:** white 2,4,6-tribromophenylamine, no catalyst.
- ✓ **HNO_2 :** $\text{NaNO}_2 + \text{HCl}$, below 10°C .
- ✓ **Couple** with phenol in $\text{NaOH}(\text{aq})$: $-\text{N}=\text{N}-$ dye.

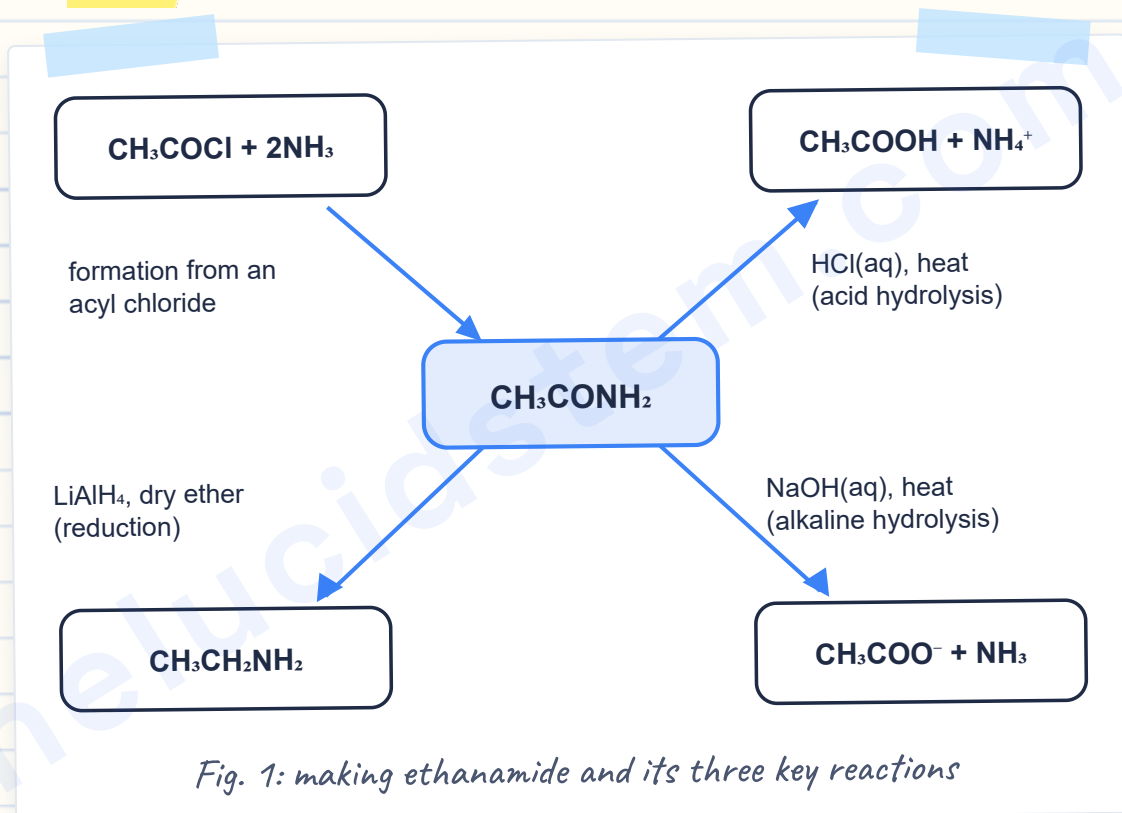
Watch out!

The reducing agent for nitrobenzene is **tin and concentrated HCl**, followed by **NaOH** ; do not write NaBH_4 or LiAlH_4 . Diazotisation must be kept **below 10°C** (but not frozen), otherwise phenol and N_2 form. Coupling with phenol needs **alkaline** conditions. Phenylamine with bromine water needs **no catalyst** and gives **three Br atoms** on the ring.

3 Amides

Syllabus 34.2

An **amide** contains the -CONH- group. Amides are made by reacting an **acyl chloride** with **ammonia** (giving RCONH_2) or with a **primary amine** (giving an N-substituted amide, RCONHR'); the reaction is fast at room temperature and gives steamy HCl , which reacts with more base. Amides are **hydrolysed** by heating under reflux: with **aqueous acid** the products are the **carboxylic acid** and an **ammonium salt**, with **aqueous alkali** they are the **carboxylate salt** and **ammonia or the amine**. Amides are **much weaker bases than amines**, effectively neutral, because the N lone pair is **delocalised over the C=O group**. LiAlH_4 **reduces** an amide to an amine.



Acyl chloride in, acid or alkali out.

- ✓ $\text{RCOCl} + 2\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{NH}_4\text{Cl}$.
- ✓ **Acid hydrolysis:** $\text{RCOOH} + \text{ammonium ion}$.
- ✓ **Alkaline hydrolysis:** $\text{RCOO}^- + \text{NH}_3$ or amine.
- ✓ **LiAlH_4 :** amide to amine; amides are neutral.

Watch out!

Learn the hydrolysis products by condition: **acid** gives the free **carboxylic acid** and the nitrogen as an **ammonium ion**; **alkali** gives the **carboxylate salt** and the free **ammonia or amine**. Amides are **not** basic like amines: their N lone pair is delocalised onto the C=O. Reduction needs LiAlH_4 ; NaBH_4 does not reduce amides.

thelucidstem.com

4 Amino acids and peptides

Syllabus 34.3

An **α -amino acid** has the general formula **$RCH(NH_2)COOH$** . In the solid and in neutral solution the $COOH$ group donates H^+ to the NH_2 group, forming a **zwitterion**, $H_3N^+CH(R)COO^-$; the strong ionic attractions between zwitterions give amino acids **high melting points** and solubility in water. The pH at which the amino acid has no overall charge is its **isoelectric point**. In **acid** the COO^- is protonated, giving the positive ion $H_3N^+CH(R)COOH$; in **alkali** the NH_3^+ loses H^+ , giving the negative ion $H_2NCH(R)COO^-$. Amino acids join by **condensation**, losing water, to form **peptide (amide) bonds**, $-CONH-$; peptides are **hydrolysed** back to amino acids by heating with acid or alkali. In **electrophoresis**, ions move in an electric field at a set pH: the direction depends on the **sign of the charge**, and the speed on the **size of the charge and of the ion**.

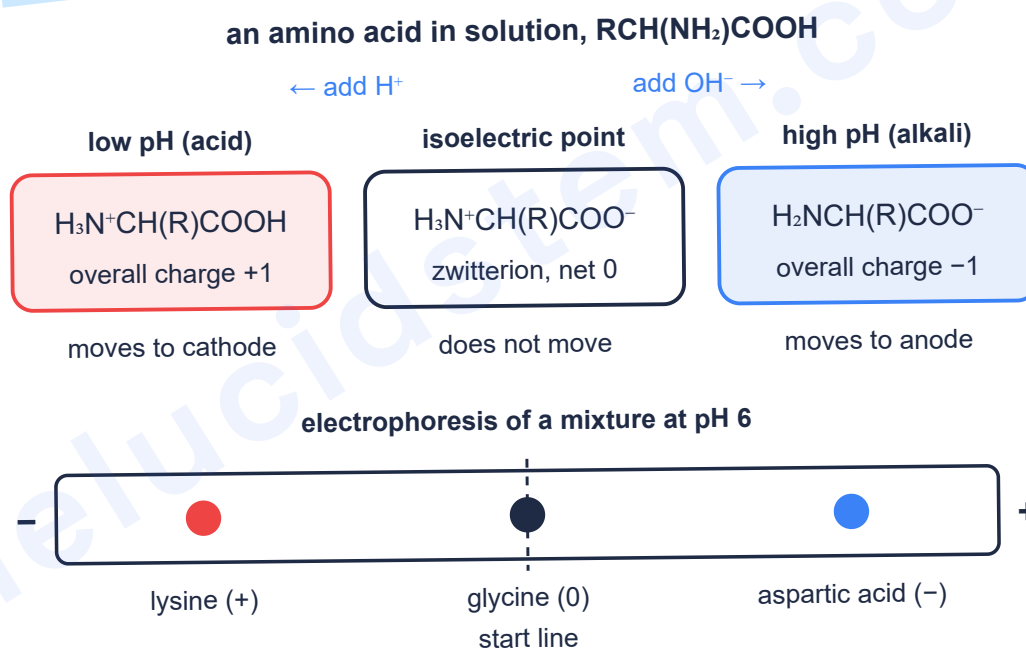


Fig. 1: the charge on an amino acid changes with pH, which is the basis of electrophoresis

Protonate in acid, deprotonate in alkali.

- ✓ **Zwitterion:** $\text{H}_3\text{N}^+\text{CH}(\text{R})\text{COO}^-$, high m.p.
- ✓ **Acid:** +1, to the cathode. **Alkali:** -1, to the anode.
- ✓ **Peptide bond:** $-\text{CONH}-$, condensation, lose H_2O .
- ✓ **Electrophoresis:** charge sets direction; charge and size set speed.

Watch out!

In acid, an amino acid is **positive** (NH_3^+ , COOH) and moves to the **cathode**; in alkali it is **negative** (NH_2 , COO^-) and moves to the **anode**. The peptide bond is an **amide** link made by **condensation**, not addition. Two different amino acids give **two** dipeptides, not one, because the order matters.

thelucidstem.com