

Nitrogen compounds

A-Level Chemistry 9701 · Topic 19 revision notes

Everything from the 2 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 amines

2. Nitriles and hydroxynitriles

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1 Primary amines

Syllabus 19.1

A **primary amine** has an NH_2 group joined to one carbon atom, for example **ethylamine** (ethanamine), $\text{CH}_3\text{CH}_2\text{NH}_2$. It is made by heating a halogenoalkane with **excess ammonia in ethanol under pressure** (in a sealed tube): $\text{CH}_3\text{CH}_2\text{Br} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$. This is **nucleophilic substitution**: the lone pair on N attacks the δ^+ carbon. The amine product still has a lone pair, so it can attack more halogenoalkane, giving **secondary and tertiary amines** and finally a **quaternary ammonium salt**; a large excess of ammonia makes that less likely. The same lone pair accepts a proton, so amines are **bases**: $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+\text{Cl}^-$. The electron-donating ethyl group makes ethylamine a **slightly stronger base than ammonia**.

each product is itself a nucleophile and can react again

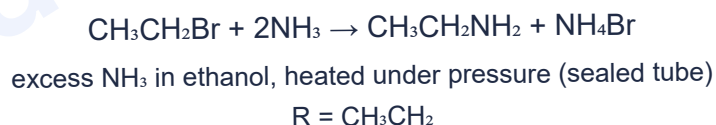
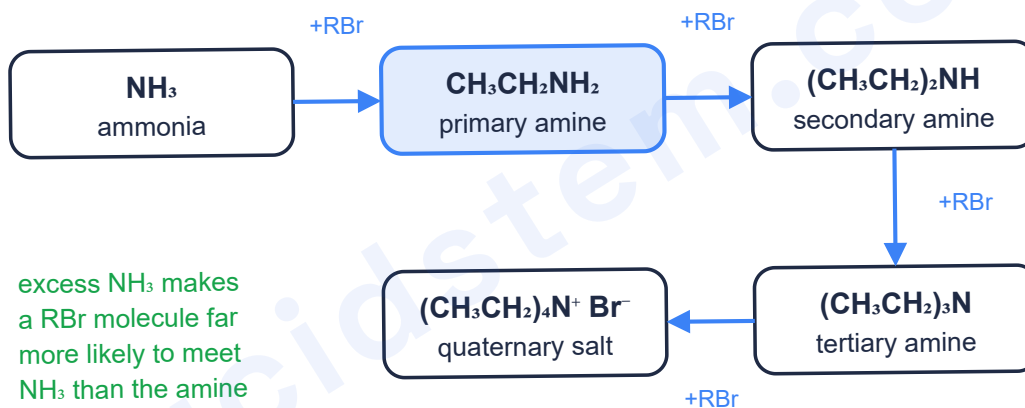


Fig. 1: making ethylamine, and the further substitution that excess ammonia holds back

Excess ammonia, sealed tube, lone pair.

- ✓ **Make:** $RX + \text{excess } NH_3$ in ethanol, heat under pressure.
- ✓ **2 mol NH_3 :** one substitutes, one removes H^+ .
- ✓ **Further substitution:** secondary, tertiary, quaternary salt.
- ✓ **Base:** $RNH_2 + HCl \rightarrow RNH_3^+Cl^-$; stronger than NH_3 .

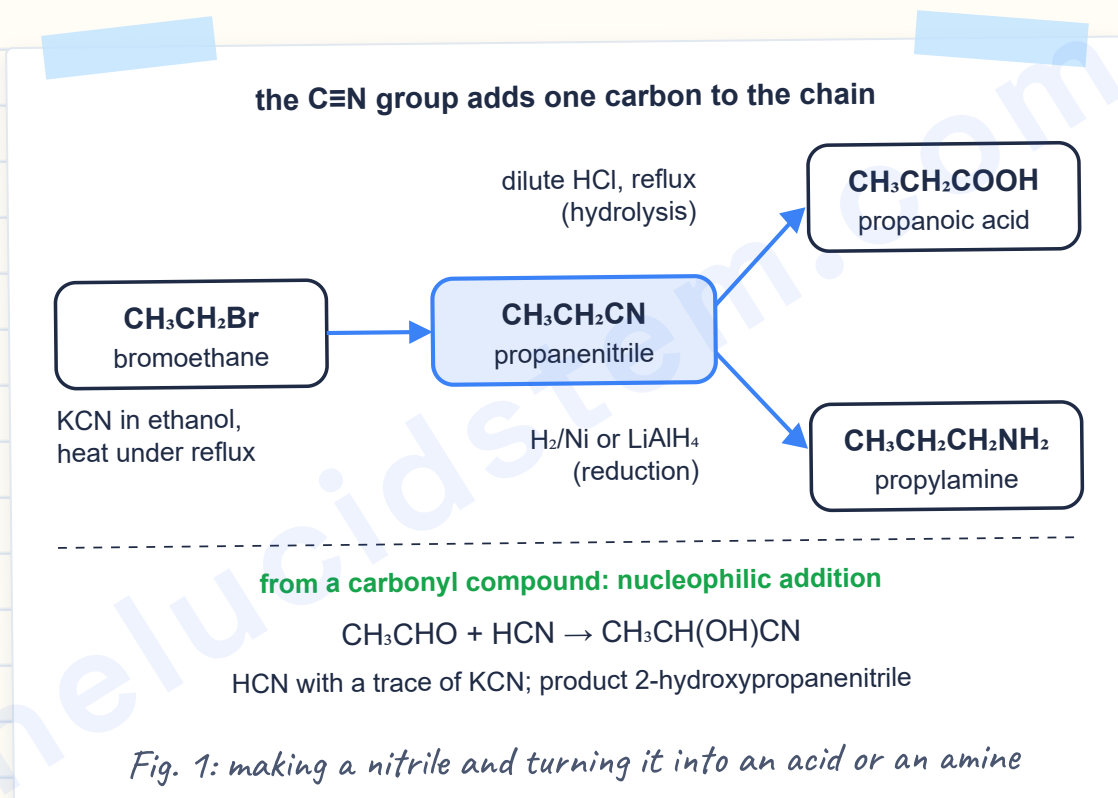
Watch out!

Use **excess ammonia**, not excess halogenoalkane, to get the primary amine; excess halogenoalkane pushes the substitution on to secondary and tertiary amines and the quaternary salt. Two moles of NH_3 are used per mole of halogenoalkane, because the second one takes the H^+ . Amines are **stronger** bases than ammonia, not weaker: the alkyl group pushes electron density **onto** the nitrogen. The salt with HCl is ionic, $CH_3CH_2NH_3^+Cl^-$; nothing is substituted on the carbon chain.

2 Nitriles and hydroxynitriles

Syllabus 19.2

A **nitrile** contains the $\text{-C}\equiv\text{N}$ group, and its carbon counts in the name: $\text{CH}_3\text{CH}_2\text{CN}$ is **propanenitrile**. Heating a halogenoalkane under reflux with **KCN in ethanol** substitutes CN^- for the halogen, adding **one carbon** to the chain. Aldehydes and ketones react with **HCN and a trace of KCN** by **nucleophilic addition** to give **2-hydroxynitriles**, such as $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ from ethanal. Nitriles are **hydrolysed** by heating under reflux with dilute acid to **carboxylic acids**, and **reduced** by H_2/Ni or LiAlH_4 to **primary amines**. These steps let you build a longer carbon chain and then turn it into the functional group you need.



KCN in ethanol, HCN with KCN, hydrolyse or reduce.

- ✓ **RX + KCN** in ethanol, reflux: nitrile, one more carbon.
- ✓ **C=O + HCN/KCN:** 2-hydroxynitrile by nucleophilic addition.
- ✓ **Hydrolysis:** dilute acid, reflux, gives RCOOH.
- ✓ **Reduction:** H₂/Ni or LiAlH₄ gives RCH₂NH₂.

Watch out!

A nitrile is named by counting the C of the C≡N group: CH₃CH₂CN is **propanenitrile**, not ethanenitrile. KCN must be in **ethanol**; in water you get an alcohol. HCN adds to C=O by **nucleophilic** addition, not electrophilic addition as for alkenes. Reducing a nitrile gives an amine with the **same** number of carbons as the nitrile, CH₂NH₂ at the end; hydrolysis turns the CN carbon into COOH and releases the nitrogen as NH₄⁺.