# Nitrogen compounds

Making primary amines from halogenoalkanes, and making and hydrolysing nitriles and hydroxynitriles.

## 19.1 Primary amines

A **primary amine** has the functional group **–**$NH_2$ on an alkyl group (ethylamine, $CH_3CH_2NH_2$).

### Preparation of amines

**Halogenoalkane with ammonia:** heat the halogenoalkane with a **concentrated solution of ammonia in ethanol under pressure** (in a sealed tube). Ammonia is the nucleophile.

$$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$$

A large **excess of ammonia** is used, because the amine formed is also a nucleophile and can react further to give secondary and tertiary amines and a quaternary salt. The second $NH_3$ removes the $H^+$ from the intermediate ammonium salt (that is why two moles appear in the equation).

Amines are **weak bases**, because the lone pair on N can accept a proton.

### Ammonia has two roles in amine preparation

Ammonia initially donates its lone pair to the partially positive halogenoalkane carbon while the C–X pair moves to X. Nitrogen acquires four bonds, producing a positively charged alkylammonium species. Another ammonia molecule removes a proton, forming the neutral amine and ammonium halide. Thus one ammonia acts as nucleophile and the other as base.

**Worked example:** bromoethane first gives $C_2H_5NH_3^+$ and bromide. Proton transfer gives $C_2H_5NH_2$ and $NH_4^+$. The organic carbon count stays two. The two-ammonia equation accounts both for introducing nitrogen and for removing the extra proton; using one equivalent without another base would not describe the same neutral products.

An excess of ammonia favours its encounter with halogenoalkane over reaction of the newly formed amine. Further alkylation is still possible because the amine is itself a nucleophile. Excess ammonia improves selectivity; it does not guarantee one perfectly pure product. This is a synthetic limitation to mention when evaluating a route.

> **TRY IT**
>
> Why is protonation of ethylamine not the same as converting it into a secondary amine?

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**Answer:** Protonation adds H to nitrogen but leaves only one carbon group attached. A secondary amine requires two carbon-containing groups directly bonded to N.

### Classification occurs at nitrogen

Primary amines have one carbon group bonded to nitrogen. This differs from classifying alcohols or halogenoalkanes by carbon neighbours of the functionalised carbon. Propan-2-amine remains a primary amine: N is attached to one isopropyl group and two hydrogens, even though the carbon attached to N has two carbon neighbours.

The lone pair accepts a proton, accounting for weak basicity: $RNH_2 + H^+ \rightarrow RNH_3^+$. A salt can therefore form with an acid without any carbon substitution. Use brackets and charges consistently; $RNH_3^+$ is not a neutral molecule with an extra hydrogen simply added.

> **TRY IT**
>
> Classify $(CH_3)_2NH$ and $(CH_3)_2CHNH_2$.

**Answer:** The first is secondary because two methyl groups attach to nitrogen. The second is primary because only one carbon-containing group attaches to nitrogen.

## 19.2 Nitriles and hydroxynitriles

A **nitrile** has the functional group **–C≡N**. Nitriles are named by adding **-nitrile** to the alkane name including the carbon of the C≡N: $CH_3CH_2CN$ is propanenitrile.

### Preparation of nitriles and hydroxynitriles

- **Nitriles** from a halogenoalkane: heat with **KCN in ethanol** (nucleophilic substitution):

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$

This **adds one carbon** to the chain, so it is useful in synthesis.

- **Hydroxynitriles** from an aldehyde or ketone: **HCN with KCN as catalyst** (nucleophilic addition), as in the chapter on carbonyl compounds.

### Hydrolysis to carboxylic acids

Heat under reflux with **dilute acid**, or with **dilute alkali** followed by **acidification**, to give a carboxylic acid:

$$CH_3CH_2CN + 2H_2O + HCl \rightarrow CH_3CH_2COOH + NH_4Cl$$

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A hydroxynitrile hydrolyses to a **hydroxy acid**, for example 2-hydroxypropanenitrile gives 2-hydroxypropanoic acid (lactic acid).

> **Route to lengthen a carbon chain: halogenoalkane → nitrile (KCN, ethanol, heat) → carboxylic acid (dilute acid, reflux) — or reduce the nitrile to an amine with $LiAlH_4$ (A Level).**

> TRY IT
>
> Starting from bromoethane, give a two-step route to propanoic acid.

Step 1: KCN in ethanol, heat, giving propanenitrile. Step 2: heat under reflux with dilute HCl, giving propanoic acid.

## Count the carbon in the nitrile group

$CH_3CN$ is ethanenitrile, with two carbons. Cyanide substitution creates a C–C bond and adds one carbon to the organic skeleton. Draw the nitrile as C≡N attached through **carbon**, rather than replacing the halogen with N alone. The nitrile carbon later becomes the carboxyl carbon on hydrolysis.

**Worked route:** 1-bromopropane plus cyanide gives $CH_3CH_2CH_2CN$, butanenitrile. Hydrolysis gives $CH_3CH_2CH_2COOH$, butanoic acid. The hydrolysis stage does not add a fifth carbon; it changes the existing nitrile carbon into a new functional group.

> TRY IT
>
> Which halogenoalkane could produce pentanenitrile by straightforward cyanide substitution?

**Answer:** A suitable 1-halogenobutane, such as 1-bromobutane. Four starting carbons plus cyanide's carbon give five. A five-carbon starting halogenoalkane would give a six-carbon nitrile.

## Acidic and alkaline hydrolysis have different ionic products

In acid, nitrile hydrolysis gives carboxylic acid and ammonium. In alkali, it gives carboxylate and ammonia. Reflux supplies prolonged heating without losing volatile materials. If the free acid is required after alkaline hydrolysis, acidification is a distinct necessary work-up step.

For alkaline hydrolysis:

$$CH_3CN + H_2O + OH^- \rightarrow CH_3COO^- + NH_3$$

For acid, the two-water/proton equation instead gives $NH_4^+$. Check atoms and charge in either expression. The organic conversion is similar, but writing a free acid as the major product in excess hydroxide is

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inconsistent.

**Worked calculation:** 0.0200 mol nitrile can give 0.0200 mol acid group on complete hydrolysis. If the acid's molar mass is 88.0 g $mol^{-1}$, the theoretical mass is 1.76 g. The number of waters consumed is not the number of acid molecules produced.

## Hydroxynitriles link carbonyls to hydroxy acids

HCN addition introduces CN and OH at the original carbonyl carbon. Nitrile hydrolysis then turns CN into COOH while retaining the OH group. Ethanal gives $CH_3CH(OH)CN$ followed by $CH_3CH(OH)COOH$. The product has one more carbon than ethanal and two distinct oxygen-containing functions.

A new stereogenic centre may arise because the formerly planar carbonyl carbon now bears four groups. Ethanal-derived hydroxynitrile has H, methyl, OH and CN, so achiral reaction conditions give a racemic mixture. Propanone-derived product has two methyl groups and lacks that chiral centre. Check actual substituents before predicting optical isomerism.

> **TRY IT**
>
> State a route from ethanal to 2-hydroxypropanoic acid, identifying the first reaction type.

**Answer:** Nucleophilic addition of HCN with a cyanide source gives 2-hydroxypropanenitrile. Heated acidic hydrolysis, or alkaline hydrolysis followed by acidification, gives the hydroxy acid. The cyanide supplies the extra carbon.

**Chapter check:** account for deprotonation after ammonia attack, classify at nitrogen and follow the nitrile carbon through each stage. Further amine chemistry follows in **A Level nitrogen compounds**.

### References and further reading

Scope follows section 19 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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