Nitrogen compounds

A-Level Chemistry

Primary amines

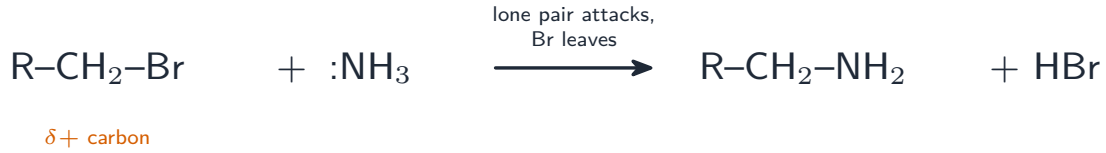
An **amine** 胺 has an $-NH_2$ group (the nitrogen replaces a hydrogen of ammonia).

Making a primary amine

Heat a **halogenoalkane** 卤代烷 with ammonia dissolved in ethanol, under pressure:

$$C_2H_5Br + NH_3 \rightarrow C_2H_5NH_2 + HBr$$

This is a **nucleophilic substitution** 亲核取代: the lone pair on the nitrogen of ammonia attacks the slightly positive carbon and pushes out the halogen. You use an excess of ammonia, or the amine made can react again.



Making a primary amine: ammonia's lone pair attacks the δ+ carbon and pushes out the halogen —a nucleophilic substitution

Nitriles and hydroxynitriles

Making a nitrile

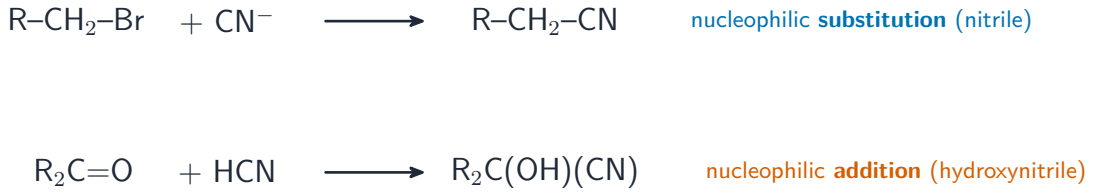
Heat a halogenoalkane with potassium cyanide (KCN) in ethanol:

$$C_2H_5Br + KCN \rightarrow C_2H_5CN + KBr$$

This is also a nucleophilic substitution, with the CN^- ion as the nucleophile. It is useful because it **adds one carbon** to the chain. The product is a **nitrile** 腈.

Making a hydroxynitrile

Add HCN (with KCN as catalyst, and heat) to an **aldehyde** 醛 or **ketone** 酮. The H and CN add across the C=O bond to give a **hydroxynitrile** 羟基腈. The reagent is **hydrogen cyanide** 氰化氢, and the mechanism is **nucleophilic addition** 亲核加成.



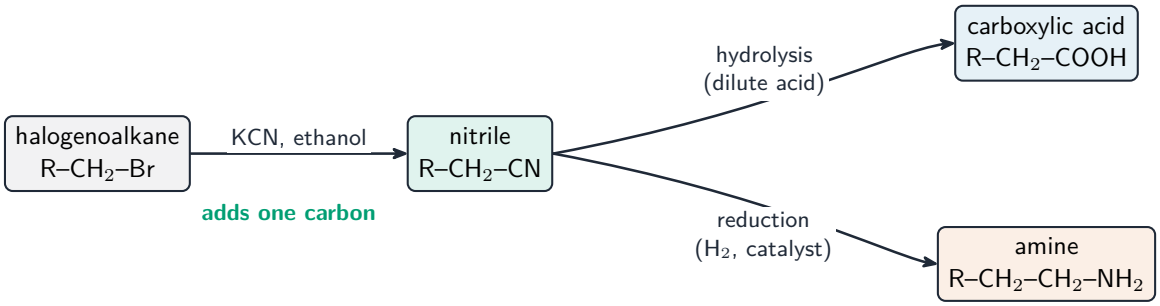
Two ways cyanide adds a carbon: KCN with a halogenoalkane substitutes to a nitrile; HCN with a carbonyl adds to a hydroxynitrile

Hydrolysis of nitriles

Warm a nitrile with dilute acid (or dilute alkali, then acidify). This **hydrolysis** 水解 turns the –CN group into a –COOH group, giving a **carboxylic acid** 羧酸:

$$CH_3CN + 2H_2O + HCl \rightarrow CH_3COOH + NH_4Cl$$

A nitrile can also be **reduced** by hydrogen and a catalyst to form an amine, which is the **reduction** 还原 route to a longer-chain amine.



Nitriles are a useful hub: KCN adds a carbon to make the nitrile, which then hydrolyses to a carboxylic acid or reduces to an amine

Reducing a nitrile gives an amine; amines and diacids link up to make polyamides such as nylon —the fibre first made famous in stockings

Worked example. Starting from bromoethane, make propanoic acid. Compare the carbons first: bromoethane has 2, propanoic acid has 3, so a carbon must be **added** - and the KCN step is the reaction that does it. Step 1: warm bromoethane with **ethanolic KCN**; nucleophilic substitution gives propanenitrile, CH_3CH_2CN, which now has 3 carbons because the CN carbon joins the chain. Step 2: reflux the nitrile with **dilute HCl**; hydrolysis gives propanoic acid. Count the carbons **before** you plan: whenever the target has exactly one more than the starting material, the nitrile route is almost always the intended answer, and remember the CN carbon is part of the new chain.

Exam tips

- **Amines are bases** (the N lone pair accepts H^+); aliphatic amines are stronger bases than ammonia.
- Making amines: **reduce a nitrile**, or react a halogenoalkane with excess ammonia.
- **KCN adds one carbon** (halogenoalkane → nitrile) —track the carbon count carefully in synthesis routes.
- State reagents and conditions precisely for each conversion.