

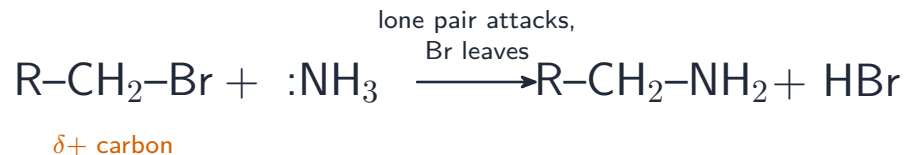
Exercise walk-through

19.2

Nitriles and hydroxynitriles

A-Level Chemistry

Making a primary amine



An **amine** has an —NH_2 group.
Heat a **halogenoalkane**
with NH_3 in ethanol.

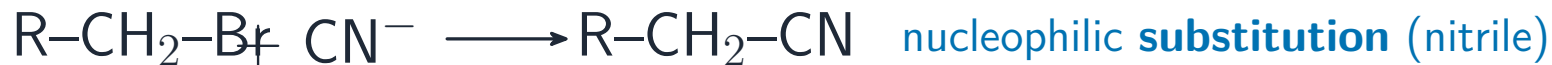
The lone pair on N attacks the $\delta+$ carbon and pushes out the halogen – a **nucleophilic substitution**. Use **excess** NH_3 .

Two ways cyanide adds a carbon

■ $\text{KCN} + \text{halogenoalkane} \rightarrow \text{a nitrile}$ (substitution)

■ $\text{HCN} + \text{carbonyl} \rightarrow \text{a hydroxynitrile}$ (addition)

Both **add one carbon** to the chain.

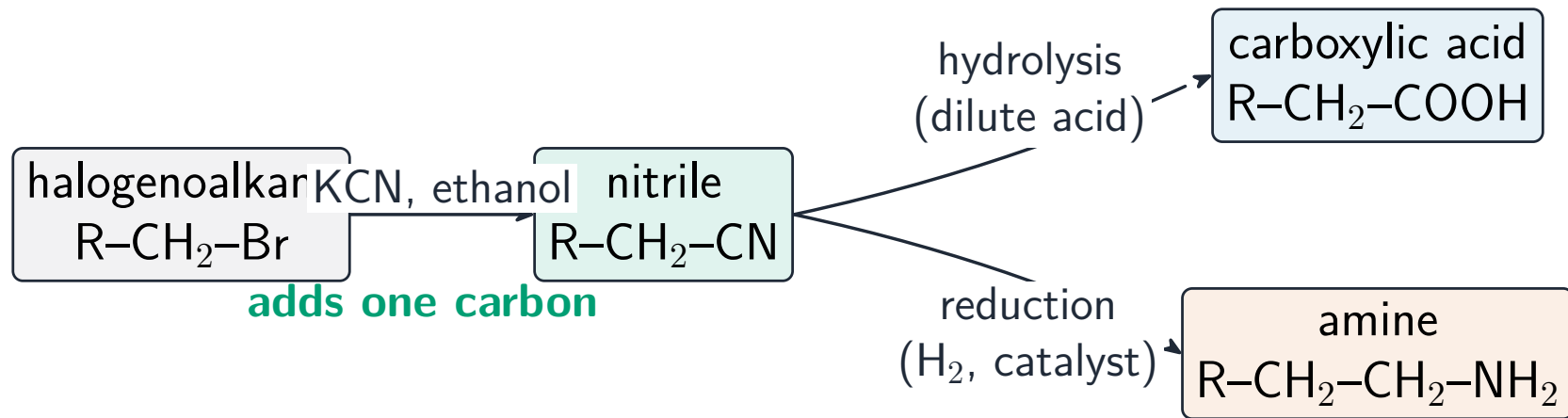


Nitrile routes

A **nitrile** is a useful hub:

- **hydrolysis** → a **carboxylic acid**
- **reduction** → an amine (a longer chain)

Nitrile routes, in detail



A **nitrile** is a useful hub – it leads two ways:

hydrolysis → a **carboxylic acid** .

reduction → an amine, one carbon longer than you started.

The two things a nitrile can become

hydrolysis

with dilute acid and heat, $\text{RCN} \rightarrow \text{RCOOH}$ – a **carboxylic acid** with the same number of carbons

reduction

with hydrogen and a catalyst (or LiAlH_4), $\text{RCN} \rightarrow \text{RCH}_2\text{NH}_2$ – an **amine**

why it matters

both routes **keep** the extra carbon the cyanide added

nucleophilic addition

how the cyanide got there: CN^- adds to an **aldehyde** or **ketone** to give a hydroxynitrile

hydrogen cyanide

the source of CN^- , used with KCN in ethanol

Count the carbons first. Bromoethane has 2 and propanoic acid has 3, so the route must add one – which is exactly what the cyanide step does.

Exercises 2.1·3.1

2.1 State the reagents and conditions to make a nitrile from a halogenoalkane. [2]

2.2 State what functional group a nitrile is changed into by hydrolysis. [1]

3.1 The reaction of KCN with a halogenoalkane is useful in synthesis because it: [1]

☐

- A** removes a carbon
- B** adds one carbon to the chain
- C** forms a double bond
- D** makes an ester

Exercises 2.1·3.1

2.1 State the reagents and conditions to make a nitrile from a halogenoalkane. [2]

2.1

- potassium cyanide (KCN) in ethanol; and heat

2.2 State what functional group a nitrile is changed into by hydrolysis. [1]

2.2

- a carboxylic acid ($-\text{COOH}$)

3.1 The reaction of KCN with a halogenoalkane is useful in synthesis because it: [1]

☐

A removes a carbon

B adds one carbon to the chain

C forms a double bond

D makes an ester

3.1 B

- KCN adds one carbon to the chain (forming the nitrile)

Exercise 3.2

3.2 Hydrolysis of ethanenitrile, CH_3CN , with dilute acid gives:

[1]

☐

A ethanol

B ethanoic acid

C ethylamine

D ethanal

Exercise 3.2

3.2 Hydrolysis of ethanenitrile, CH_3CN , with dilute acid gives:

[1]

☐

A ethanol

B ethanoic acid

C ethylamine

D ethanal

3.2 B

- Hydrolysis of a nitrile gives the carboxylic acid (ethanoic acid)

Exercises 3.3-3.4

3.3 (a) Write the equation for the reaction of bromoethane with KCN. [1]

(b) Describe how the nitrile product can be converted into a carboxylic acid. [2]

3.4 State the reagent and condition to make a hydroxynitrile from propanone (a ketone), and name the mechanism. [2]

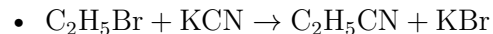
Exercises 3.3·3.4

3.3 (a) Write the equation for the reaction of bromoethane with KCN. [1]

(b) Describe how the nitrile product can be converted into a carboxylic acid. [2]

3.3

(a)



(b)

- warm the nitrile with dilute acid (or dilute alkali then acidify); the $-\text{CN}$ group is hydrolysed to $-\text{COOH}$

3.4 State the reagent and condition to make a hydroxynitrile from propanone (a ketone), and name the mechanism. [2]

3.4

- HCN with a KCN catalyst (and heat); nucleophilic addition