

Nitrogen compounds

AS

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Read first: [An introduction to AS Level organic chemistry](#), [Halogen compounds](#), [Carbonyl compounds](#)

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What you need to know

By the end of this topic you should be able to:

1. **Recall how a primary amine is made:** heat a halogenoalkane with **ammonia dissolved in ethanol, under pressure** (in a sealed tube). For example, bromoethane gives ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$.
2. **Recall how a nitrile is made:** heat a halogenoalkane with **potassium cyanide, KCN, dissolved in ethanol**. For example, bromoethane gives propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$. The chain gains one carbon.
3. **Recall how a hydroxynitrile is made:** heat an aldehyde or a ketone with **HCN, with KCN as a catalyst**. For example, ethanal gives 2-hydroxypropanenitrile, $\text{CH}_3\text{CH}(\text{OH})\text{CN}$.
4. **Describe the hydrolysis of a nitrile** to a carboxylic acid: heat with **dilute acid**, or with **dilute alkali and then acidify**.

Sorting amines into primary, secondary and tertiary is not tested at AS Level. The reduction of nitriles, the basicity of amines, amides and amino acids are A Level; AS questions that use them tell you the reaction (types 5 and 7 below show how to handle them).

Understand it

The three nitrogen groups

Group	Formula	Example	Name
primary amine	$-\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine (ethanamine)
nitrile	$-\text{C}\equiv\text{N}$	$\text{CH}_3\text{CH}_2\text{CN}$	propanenitrile
hydroxynitrile	$-\text{OH}$ and $-\text{C}\equiv\text{N}$ on one molecule	$\text{CH}_3\text{CH}(\text{OH})\text{CN}$	2-hydroxypropanenitrile

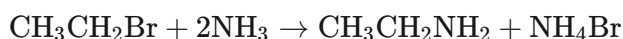
Naming. An amine is named from the alkyl group on the nitrogen: $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ is propylamine, also called propan-1-amine or 1-aminopropane. A nitrile is named from the whole chain **including the carbon of the CN group**, ending **-nitrile**: CH_3CN is ethanenitrile (2 carbons), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ is butanenitrile (4 carbons). The CN carbon is C1, so in 2-hydroxypropanenitrile the OH is on the carbon next to it. Keep the "e": propanenitrile.

In $R-C\equiv N$ the chain is joined to the **carbon** of the CN group, never to the nitrogen. The $C\equiv N$ triple bond has one σ and two π bonds, and the nitrogen keeps a lone pair.

Making an amine: halogenoalkane and ammonia

Ammonia has a lone pair on its nitrogen, so it is a **nucleophile**. It attacks the $\delta+$ carbon of the $C-X$ bond and the halide ion leaves, just like OH^- in Halogen compounds: a **nucleophilic substitution**.

Conditions: ammonia in ethanol, heated under pressure (a sealed tube). Ammonia is a gas, so heating it in an open flask or under reflux would drive it off; the sealed tube keeps it in the mixture. Use an **excess** of ammonia so that the amine made does not go on reacting with more halogenoalkane.



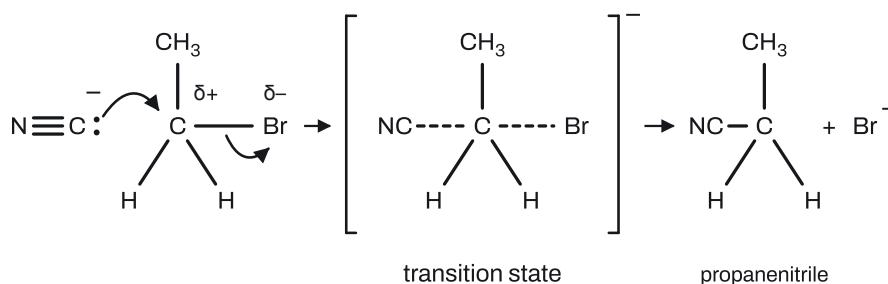
Why **two** NH_3 ? The first ammonia joins the carbon and ends up as $CH_3CH_2NH_3^+$, one H too many. A second ammonia takes that H^+ (an acid–base step), giving the amine and an ammonium ion. With one NH_3 you may see the salt written instead: $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+ Br^-$.

Ring products. If one molecule has two $C-X$ bonds, one nitrogen can bond to both carbons and close a ring, losing 2 HX : a 1,5-dibromo compound gives a six-membered ring (5 C and the N).

Making a nitrile: halogenoalkane and cyanide

The cyanide ion, $:C\equiv N^-$, has a lone pair and the negative charge **on the carbon**, so it attacks through its carbon. This is again **nucleophilic substitution**; for a primary halogenoalkane it happens in one step (S_N2):

S_N2 : cyanide ion and bromoethane



Conditions: KCN (or NaCN) dissolved in ethanol, heat under reflux.

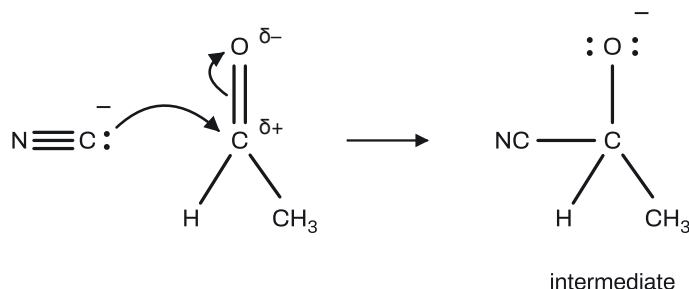


This is one of the two AS reactions (with HCN addition) that make a **new C–C bond**, so the chain gets **one carbon longer**: bromoethane (2 C) gives propanenitrile (3 C). A molecule with two $C-X$ bonds reacts at both, if the KCN is in excess: 1,3-dibromopropane gives $NCCH_2CH_2CH_2CN$, pentanedinitrile.

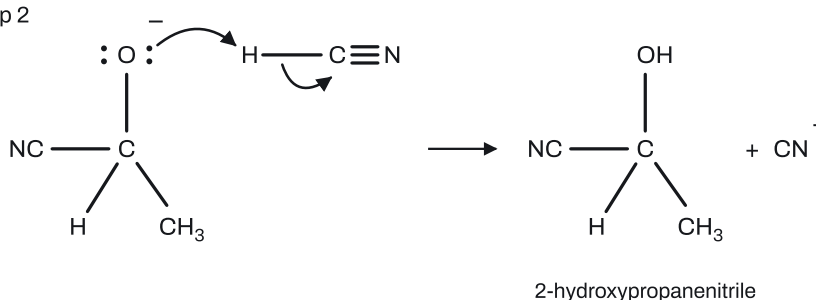
Making a hydroxynitrile: aldehyde or ketone and HCN

HCN adds across the C=O bond of an aldehyde or ketone. The reagents are **HCN with a little KCN as a catalyst**, and **heat**. KCN supplies the CN^- ions that start the reaction, and they are made again at the end, which is why a small amount works. This is **nucleophilic addition**:

Step 1



Step 2



The product has **one more carbon** than the carbonyl compound, with the OH and CN on the **same** carbon (the old C=O carbon).

Optical isomers. From ethanal, the central carbon of $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ carries four different groups (H, CH_3 , OH, CN), so it is **chiral** and the product exists as a pair of optical isomers. From propanone, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$ has two identical CH_3 groups on that carbon, so it is **not** chiral. Every aldehyde except methanal gives a chiral product; a ketone does only if its two groups are different.

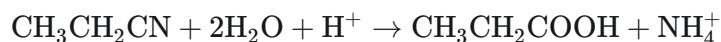
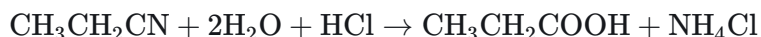
Two cyanide reactions, two sets of conditions. Examiners see these mixed up every year:

Starting compound	Reagent	Mechanism	Product
halogenoalkane	KCN in ethanol, heat	nucleophilic substitution	nitrile
aldehyde or ketone	HCN with KCN catalyst, heat	nucleophilic addition	hydroxynitrile

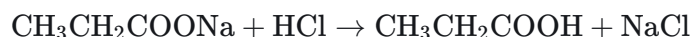
Hydrolysis of nitriles

Heating a nitrile with water alone is far too slow, so an acid or an alkali is used, **heated under reflux**. The CN carbon becomes the COOH carbon (**same number of carbons** as the nitrile), and the nitrogen leaves as ammonium ions or ammonia.

With **dilute acid** (HCl(aq) or $\text{H}_2\text{SO}_4\text{(aq)}$) you get the carboxylic acid and an **ammonium salt**:

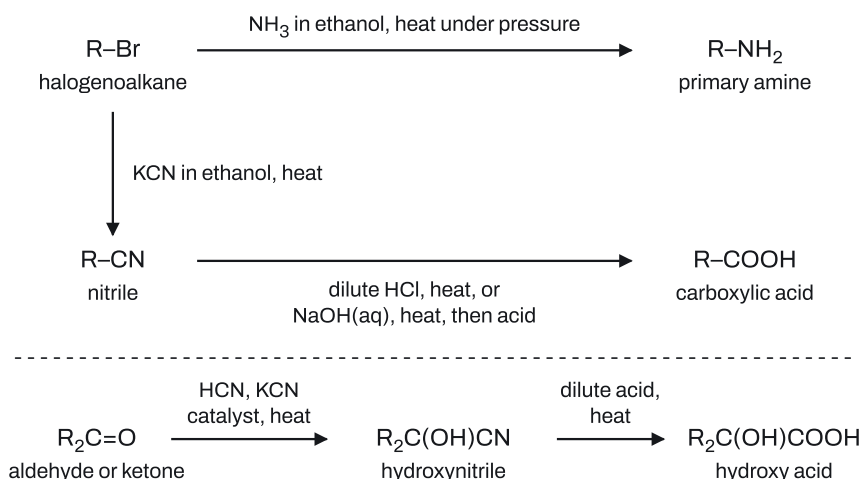


With **dilute alkali** (NaOH(aq)) you get the **sodium salt** and **ammonia gas**; adding dilute acid afterwards turns the salt into the acid:



Count the waters: **two** H_2O with acid, **one** with alkali. Any other group stays as it was: a hydroxynitrile gives a **hydroxy acid**, so $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ gives 2-hydroxypropanoic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. A dinitrile gives a diacid and two ammonium ions.

Putting the routes together



The favourite exam route is **halogenoalkane** $\rightarrow$ **nitrile** $\rightarrow$ **carboxylic acid**, which gives an acid with **one more carbon** than the halogenoalkane: 1-bromopropane $\rightarrow$ butanenitrile $\rightarrow$ butanoic acid. Compare the routes you already know: NaOH(aq) with 1-bromopropane gives propan-1-ol (same chain), and oxidising that gives propanoic acid (still three carbons).

Spotting nitrogen groups by infrared

In an infrared spectrum (the Data Booklet table is given in the question), **$\text{C}\equiv\text{N}$ absorbs at $2200\text{--}2250\text{ cm}^{-1}$** , a region where little else absorbs, so it is the easiest way to show a nitrile is present or has gone. N-H in amines absorbs at $3300\text{--}3500\text{ cm}^{-1}$. When a nitrile is hydrolysed, the $\text{C}\equiv\text{N}$ absorption disappears and the C=O ($1670\text{--}1740$) and broad O-H ($2500\text{--}3000$) of COOH appear. Name the **bond** (" $\text{C}\equiv\text{N}$ "), not just the group.

Key facts and formulas

"Given" means it is in the 9701 Data Booklet (or printed in the question). "Learn it" means you must remember it. Reagents, conditions and equations are never printed.

Formula or fact	Status
Relative atomic masses: C 12.0, H 1.0, N 14.0, O 16.0, Na 23.0, Cl 35.5, Br 79.9	Given
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions	Given
Infrared: $\text{C}\equiv\text{N}$ 2200–2250 cm^{-1} ; N-H 3300–3500 cm^{-1}	Given
$\text{RX} + 2\text{NH}_3 \rightarrow \text{RNH}_2 + \text{NH}_4\text{X}$ (ammonia in ethanol, heat under pressure)	Learn it
$\text{RX} + \text{KCN} \rightarrow \text{RCN} + \text{KX}$ (KCN in ethanol, heat; one more carbon)	Learn it
$\text{R}_2\text{C}=\text{O} + \text{HCN} \rightarrow \text{R}_2\text{C}(\text{OH})\text{CN}$ (HCN, KCN catalyst, heat)	Learn it
$\text{RCN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}$ (dilute acid, heat)	Learn it
$\text{RCN} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{RCOONa} + \text{NH}_3$ (dilute alkali, heat; then acidify)	Learn it
Mechanisms: NH_3 or CN^- with RX is nucleophilic substitution; HCN with $\text{C}=\text{O}$ is nucleophilic addition	Learn it
$\text{moles} = \frac{\text{mass}}{M_r}$; gas volume = moles $\times 24.0 \text{ dm}^3$; percentage yield = $\frac{\text{actual}}{\text{theoretical}} \times 100$	Learn it

How to do it

We have tagged 39 questions on this topic from 2021–2025 (35 different, since some papers share questions). 23 of them mix more than one type, so the counts add up to more than 39.

Question type	Questions
Hydrolyse a nitrile to a carboxylic acid	27
Make a nitrile from a halogenoalkane	20
Make an amine from a halogenoalkane and ammonia	6
Make a hydroxynitrile from an aldehyde or ketone	6
Reduce a nitrile to an amine (reaction given)	4
Calculate masses, yields and gas volumes	2

Question type	Questions
Amines as bases (reaction given)	2

1. Hydrolyse a nitrile to a carboxylic acid (27 questions)

1. **Find the CN group** and turn it into COOH. Keep every other part of the molecule, including any OH.
2. **Check the conditions:**
 - dilute acid (HCl or H₂SO₄), heat → **carboxylic acid + ammonium ion**;
 - NaOH(aq), heat → **sodium salt + ammonia**; add acid afterwards to get the carboxylic acid.
3. **Balance:** with HCl, $\text{RCN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}$; with H⁺, the product is NH₄⁺; with NaOH, $\text{RCN} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{RCOONa} + \text{NH}_3$.
4. **Name the reaction:** hydrolysis (acid or alkaline hydrolysis).

Variations you will meet:

- **Work backwards from the acid.** The nitrile has the **same** number of carbons as the acid: propanoic acid comes from propanenitrile, CH₃CH₂CN, not ethanenitrile. A compound of C, H and N that gives propanoic acid with HCl(aq) is propanenitrile.
- **Branched chains.** Count carbons from the CN carbon: (CH₃)₃CCN is 2,2-dimethylpropanenitrile, so it gives 2,2-dimethylpropanoic acid, (CH₃)₃CCOOH (dimethylpropanoic acid). 2-methylbutanenitrile gives 2-methylbutanoic acid.
- **A follow-on step.** LiAlH₄ reduces the acid to a **primary** alcohol, RCH₂OH (Carboxylic acids and derivatives), whatever the branching.
- **"Which mixture gives sodium propanoate?"** Only a reaction that makes the salt: propanenitrile with NaOH(aq). NaBH₄ reduces an aldehyde to an alcohol, and sodium with an alcohol gives an alkoxide, not a carboxylate.
- **The inorganic product.** With HCl it is NH₄Cl; with H₂SO₄ it is (NH₄)₂SO₄; with NaOH it is NH₃ gas. A dinitrile gives **two** of them.
- **Hydroxynitriles** give hydroxy acids: (CH₃)₂C(OH)CN from propanone gives (CH₃)₂C(OH)COOH. For the reagents, "HCl(aq) or H₂SO₄(aq), heat" scores.

2. Make a nitrile from a halogenoalkane (20 questions)

1. **Reagent and conditions: KCN (or NaCN) in ethanol, heat.** All three parts: the cyanide, the ethanol solvent and heat.
2. **Product:** replace the halogen with CN. The chain gets **one carbon longer**; name it from the new total.
3. **Type of reaction:** nucleophilic substitution (the nucleophile is CN⁻).
4. **Mechanism** if asked (S_N2, as in the diagram):
 - the dipole on C–X: δ+ on C, δ– on X;
 - a lone pair on the **carbon** of CN⁻ and a curly arrow from it to the δ+ carbon;
 - a curly arrow from the C–X bond to X;

- products: the nitrile and X^- .

Variations you will meet:

- **Two-step routes to an acid** with one more carbon: step 1 KCN in ethanol, heat (nucleophilic substitution); step 2 dilute acid, heat (hydrolysis). So 1-bromopropane $\rightarrow$ butanenitrile $\rightarrow$ butanoic acid, and chloroethane $\rightarrow$ propanenitrile $\rightarrow$ propanoic acid (or sodium propanoate with NaOH).
- **"Which reagent makes a nitrile?"** Only KCN in ethanol with a halogenoalkane. NH_3 gives an amine, HCN(aq) with a halogenoalkane does not work, HCN with a ketone gives a hydroxynitrile, and 2,4-DNPH gives an orange precipitate.
- **Making the halogenoalkane first** from an alcohol: $SOCl_2$, PCl_5 , PCl_3 and heat, $HCl(g)$, or KCl with concentrated H_2SO_4 (a substitution). So $CH_3OH \rightarrow CH_3Cl \rightarrow CH_3CN$.
- **Two halogens** (for example after adding Br_2 to an alkene): both are replaced, giving a dinitrile, then a diacid on hydrolysis.
- **Identify it by infrared:** the product has $C\equiv N$ at $2200-2250\text{ cm}^{-1}$.

3. Make an amine from a halogenoalkane and ammonia (6 questions)

1. **Reagent and conditions:** ammonia (NH_3) in ethanol, heated under pressure (sealed tube). Not "under reflux".
2. **Product:** replace the halogen with NH_2 . The chain length **does not change**.
3. **Equation:** $RX + 2NH_3 \rightarrow RNH_2 + NH_4X$.
4. **Type:** nucleophilic substitution (NH_3 is the nucleophile, using the lone pair on N).

Variations you will meet:

- **Tell it apart from the nitrile route.** With NH_3 , 1-bromopropane gives $CH_3CH_2CH_2NH_2$ (3 C); with KCN it gives butanenitrile (4 C).
- **Name the amine** from its alkyl group: propylamine, propan-1-amine or 1-aminopropane. "Propamine" is wrong, and so is an amide name.
- **A dibromo compound and ammonia** can make a ring: N bonds to both carbons that carried Br, losing 2 HBr. Count the ring: the N plus the carbons between and including the two C-Br carbons.
- **"What is the mechanism?"** of $C_2H_5I + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4I$: nucleophilic substitution.

4. Make a hydroxynitrile from an aldehyde or ketone (6 questions)

1. **Reagents and conditions:** HCN with KCN (catalyst), heat.
2. **Product:** the $C=O$ becomes $C(OH)$ and a CN joins the **same** carbon. One more carbon than the starting compound.
3. **Mechanism** (nucleophilic addition, as in the diagram):
 - dipole on $C=O$ (δ^+ C, δ^- O); lone pair on the C of CN^- ; curly arrow from it to the carbonyl C; curly arrow from the $C=O$ bond to O;
 - the **intermediate** with O^- (show its charge);

- curly arrow from a lone pair on O^- to the H of HCN and from the H–C bond to C, giving the product and CN^- again.

4. **Name the product:** count the chain from the CN carbon. Ethanal gives 2-hydroxypropanenitrile; propanone gives 2-hydroxy-2-methylpropanenitrile.

Variations you will meet:

- **Optical isomers.** Look at the new $\text{C}(\text{OH})(\text{CN})$ carbon: chiral only if its other two groups differ. Ethanal's product is chiral (H and CH_3); propanone's is not (two CH_3). "Explain why it does not show optical isomerism": the carbon is **not bonded to four different groups**.
- **Then hydrolyse** with $\text{H}_2\text{SO}_4(\text{aq})$ or $\text{HCl}(\text{aq})$ and heat, giving a 2-hydroxy acid: propanone $\rightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$.
- **Then dehydrate:** heating a hydroxynitrile with concentrated H_2SO_4 (or H_3PO_4 , or Al_2O_3) removes H_2O and makes a $\text{C}=\text{C}$, as for any alcohol: $\text{CH}_3\text{CH}(\text{OH})\text{CN} \rightarrow \text{CH}_2=\text{CHCN} + \text{H}_2\text{O}$.
- **Draw the two optical isomers** in 3D: the chiral carbon with two bonds in the plane, one wedge and one dashed; the second isomer is its mirror image.

5. Reduce a nitrile to an amine (reaction given) (4 questions)

The question tells you that a nitrile is reduced (by H_2 with a Ni or Pt catalyst, or by LiAlH_4). Use what it gives you:

1. **Product:** $\text{C}\equiv\text{N}$ becomes CH_2NH_2 , a primary amine with the **same** number of carbons as the nitrile. Propanenitrile gives propylamine.
2. **Equation:** each $\text{C}\equiv\text{N}$ needs **4 H atoms**: $\text{RCN} + 2\text{H}_2 \rightarrow \text{RCH}_2\text{NH}_2$, or $\text{RCN} + 4[\text{H}] \rightarrow \text{RCH}_2\text{NH}_2$.
3. **Role of LiAlH_4 (or H_2):** reducing agent; the reaction is a reduction.

Variations you will meet:

- **Moles of hydrogen:** 2 mol H_2 per mole of nitrile, so the gas volume is $2 \times n \times 24.0 \text{ dm}^3$.
- **Longer routes:** halogenoalkane $\rightarrow$ nitrile $\rightarrow$ amine gives an amine with **one more carbon** than the halogenoalkane, unlike the direct reaction with NH_3 .

6. Calculate masses, yields and gas volumes (2 questions)

1. **Write the equation** first and read the mole ratio from it (1 : 1 for nitrile to acid or salt; 1 : 2 for nitrile to H_2).
2. **Moles of the starting compound** = $\text{mass} \div M_r$.
3. **Moles of product** from the ratio, then $\times$ the percentage yield $\div 100$ if one is given.
4. **Mass** = $n \times M_r$ of the product; **gas volume** = $n \times 24.0 \text{ dm}^3$ ($\times 1000$ for cm^3).

Check which product the question means: nitrile + NaOH gives the **sodium salt** (CH_3COONa , $M_r = 82.0$), not the acid.

7. Amines as bases (reaction given) (2 questions)

Amines behave like ammonia: the lone pair on N accepts H^+ .

1. **Amine + acid → salt:** $\text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{NH}_3^+ \text{Cl}^-$ (methylammonium chloride), like $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$.
2. **Salt + NaOH → amine back:** $\text{CH}_3\text{NH}_3\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{NaCl} + \text{H}_2\text{O}$, like $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NH}_3 + \text{NaCl} + \text{H}_2\text{O}$.
3. **Which steps are Brønsted–Lowry acid–base?** Those where an H^+ **moves** from one species to another. A step where a lone pair attacks a carbon, or a $\text{C}=\text{O}$ reforms and pushes out Cl^- , is not; a step where Cl^- or an amine takes H^+ from $\text{N}^+ - \text{H}$ is.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

2-chlorobutane, $\text{CH}_3\text{CHClCH}_2\text{CH}_3$, is used to make two different nitrogen compounds.

- (a) State the reagent and conditions to convert 2-chlorobutane into $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$. Write an equation and name the type of reaction. **[4]**
- (b) 2-chlorobutane is heated with KCN in ethanol. Give the structural formula and name of the organic product, **J**. **[2]**
- (c) **J** is heated under reflux with $\text{NaOH}(\text{aq})$, and the mixture is then acidified. Write an equation for the reaction with $\text{NaOH}(\text{aq})$ and name the final organic product. **[2]**

(a) Ammonia in ethanol **B1**, heated under pressure (in a sealed tube). **B1**



Nucleophilic substitution. **B1**

(b) $\text{CH}_3\text{CH}(\text{CN})\text{CH}_2\text{CH}_3$ **B1**, 2-methylbutanenitrile (five carbons; the longest chain runs from the CN carbon through the CH_2CH_3 , leaving a methyl branch on C2). **B1**



After acidifying: 2-methylbutanoic acid, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$. **B1**

Example 2

Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$, reacts with HCN to form **K**, $\text{C}_5\text{H}_9\text{NO}$.

- (a) State the reagents and conditions, and name the mechanism. **[2]**
 - (b) Describe the mechanism (it follows the same steps as the ethanal diagram in "Understand it"). **[3]**
 - (c) Explain why **K** exists as two optical isomers, and why the product from propanone does not. **[2]**
 - (d) **K** is heated under reflux with dilute hydrochloric acid. Write an equation and name the organic product. **[2]**
 - (e) State one infrared absorption present in **K** but not in butanone, with the bond responsible. **[1]**
- (a)** HCN with KCN as a catalyst, heat. **B1** Nucleophilic addition. **B1**
- (b)** The C of CN^- uses its lone pair to attack the δ^+ carbonyl carbon, and the $\text{C}=\text{O}$ π electrons move onto the oxygen. **M1** This gives the intermediate $\text{CH}_3\text{C}(\text{O}^-)(\text{CN})\text{CH}_2\text{CH}_3$. **M1** The O^- takes H^+ from HCN, giving **K**, 2-hydroxy-2-methylbutanenitrile, $\text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_2\text{CH}_3$, and CN^- again. **A1**
- (c)** The central carbon of **K** is bonded to four different groups, CH_3 , CH_2CH_3 , OH and CN, so it is chiral. **B1** In $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$ that carbon carries two identical CH_3 groups, so it is not chiral. **B1**
- (d)** $\text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_2\text{CH}_3 + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{CH}_3 + \text{NH}_4\text{Cl}$ **B1**; 2-hydroxy-2-methylbutanoic acid. **B1**
- (e)** $2200\text{--}2250\text{ cm}^{-1}$, $\text{C}\equiv\text{N}$ (or $3200\text{--}3600\text{ cm}^{-1}$, O–H). **B1**

Example 3

7.85 g of 1-chloropropane is heated with KCN in ethanol. The yield of butanenitrile is 80.0%.

- (a) Calculate the mass of butanenitrile formed. **[3]**
 - (b) All of this butanenitrile is heated with an excess of $\text{NaOH}(\text{aq})$. Write an equation and calculate the volume of ammonia given off, at room conditions. **[3]**
 - (c) Butanenitrile can be reduced to butylamine by hydrogen with a nickel catalyst. Write an equation and calculate the volume of hydrogen, at room conditions, needed to reduce the butanenitrile from (a). **[3]**
- (a)** $M_r(\text{C}_3\text{H}_7\text{Cl}) = 3(12.0) + 7(1.0) + 35.5 = 78.5$, so $n = 7.85 \div 78.5 = 0.100\text{ mol}$. **M1**
- 1 : 1, with 80.0% yield: $0.100 \times 0.800 = 0.0800\text{ mol}$ of butanenitrile. **M1**
- $M_r(\text{C}_4\text{H}_7\text{N}) = 4(12.0) + 7(1.0) + 14.0 = 69.0$, so mass = $0.0800 \times 69.0 = 5.52\text{ g}$. **A1**
- (b)** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa} + \text{NH}_3$ **B1**

1 mol NH_3 per mol nitrile: 0.0800 mol. **M1** Volume = $0.0800 \times 24.0 = 1.92 \text{ dm}^3$. **A1**

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ **B1**

$n(\text{H}_2) = 2 \times 0.0800 = 0.160 \text{ mol}$ **M1**, volume = $0.160 \times 24.0 = 3.84 \text{ dm}^3$. **A1**

Example 4

1,3-dibromopropane, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$, is the starting material for two syntheses.

(a) It is heated with an excess of KCN in ethanol to give **L**. Give the structural formula of **L** and the number of carbon atoms in it. **[2]**

(b) **L** is heated under reflux with dilute hydrochloric acid. Write a balanced equation and name the organic product. **[2]**

(c) 1,3-dibromopropane is heated under pressure with an excess of ammonia in ethanol, giving **M**, $\text{C}_3\text{H}_{10}\text{N}_2$. Write an equation for this reaction. **[2]**

(d) **M** dissolves in an excess of $\text{HCl}(\text{aq})$ to form a salt. When the salt is warmed with $\text{NaOH}(\text{aq})$, **M** is re-formed. Explain these reactions and write an equation for the reaction with HCl . **[3]**

(a) Both bromines are replaced: **L** is $\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CN}$ **B1**, with 5 carbon atoms (pentanedinitrile). **B1**

(b) $\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CN} + 4\text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH} + 2\text{NH}_4\text{Cl}$ **B1**; pentanedioic acid. **B1**

(c) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + 4\text{NH}_3 \rightarrow \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + 2\text{NH}_4\text{Br}$ **M1** (organic product) **A1** (balanced).

(d) Each N in **M** has a lone pair that accepts H^+ , so **M** is a base, like ammonia. **B1**

$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + 2\text{HCl} \rightarrow \text{ClH}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{Cl}$ **B1**

OH^- is a stronger base; it takes H^+ back from each $-\text{NH}_3^+$, re-forming **M**, NaCl and water. **B1**

Common mistakes

- **Mixing up the two cyanide reactions.** Reports every year see HCN , or KCN with acid, for a halogenoalkane. Halogenoalkane $\rightarrow$ nitrile needs **KCN in ethanol, heat**; HCN with KCN catalyst is for aldehydes and ketones only. And many answers leave out the **ethanol**.
- **Wrong conditions for ammonia.** "Heat under reflux" is wrong: ammonia must be heated **under pressure** (sealed tube), **in ethanol**. Reports note that both conditions were rarely given together.
- **Joining the chain to the N of CN.** The nitrile carbon bonds to the chain: $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$. In a mechanism, draw the lone pair (and the minus) **on the carbon** of CN^- and start the curly arrow there; reports say the lone pair is often missing.

- **Incomplete hydrolysis equations.** Reports see the right acid but no ammonium ion, H^+ or HCl missing from the left, HCN as a product, or the equation not balanced. With acid:
$$\text{RCN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}.$$
- **Losing or miscounting carbons.** KCN adds one carbon; hydrolysis and ammonia do not. Propanoic acid comes from propanenitrile (3 C) or from bromoethane (2 C) via the nitrile.
- **Names.** Propanenitrile, not propionitrile, ethyl cyanide or "propannitrile"; propylamine or propan-1-amine, not "propamine" or an amide name.
- **The wrong H_2 ratio.** Reducing $\text{C}\equiv\text{N}$ to CH_2NH_2 takes **2** H_2 (4 [H]); reports say few candidates got this.
- **Drawing CN in the product** of a hydrolysis. Every CN becomes COOH (or COO^- in alkali).
- **Vague infrared answers.** Write the bond, " $\text{C}\equiv\text{N}$ at $2200\text{--}2250\text{ cm}^{-1}$ ", not just "nitrile".

How to get the marks

- **"Reagents and conditions"** needs every part: " KCN in ethanol, heat"; " NH_3 in ethanol, heat under pressure"; " HCN with KCN , heat"; "dilute HCl , heat under reflux" or " NaOH(aq) , heat, then acidify".
- **"Type of reaction" or "mechanism"**: nucleophilic substitution (halogenoalkane with CN^- or NH_3); nucleophilic addition (HCN with C=O); hydrolysis (nitrile with acid or alkali); reduction (nitrile with H_2 or LiAlH_4).
- **Mechanisms** score for each detail: dipoles, lone pairs (on the C of CN^-), curly arrows starting at a lone pair or a bond and ending at an atom, the charge on the intermediate, and the products including Br^- or CN^- .
- **Equations** must be balanced and use structural formulas unless the question gives a molecular formula. Check the waters and the ammonium or ammonia product.
- **"Draw the structure"**: make the CN , NH_2 or COOH group clear; "displayed" means every bond, including $\text{C}\equiv\text{N}$ as three lines.
- **"Explain why it does (not) show optical isomerism"**: talk about whether one carbon has **four different groups**.
- **Calculations**: show M_r , moles and the ratio; give 3 significant figures and units. Multiple-choice answers often sit on the wrong-ratio numbers, so check your ratio.

Quick check

1. Name the organic product and give the reagent and conditions when bromoethane is converted into (a) ethylamine, (b) propanenitrile.
2. Write an equation for the hydrolysis of 2-methylpropanenitrile, $(\text{CH}_3)_2\text{CHCN}$, by dilute hydrochloric acid.
3. Give the structural formula and name of the product when propanal reacts with HCN , and state whether it is chiral.
4. Calculate the mass of sodium propanoate formed when 2.75 g of propanenitrile is heated with an excess of NaOH(aq) .

5. Starting from a halogenoalkane, give the two steps (reagents and conditions) to make 3-methylbutanoic acid, $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$, and name the halogenoalkane and the intermediate.

Answers

1. (a) Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$: ammonia in ethanol, heat under pressure. (b) Propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$: KCN in ethanol, heat.
2. $(\text{CH}_3)_2\text{CHCN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow (\text{CH}_3)_2\text{CHCOOH} + \text{NH}_4\text{Cl}$ (2-methylpropanoic acid).
3. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$, 2-hydroxybutanenitrile. Its $\text{C}(\text{OH})(\text{CN})$ carbon carries H, CH_2CH_3 , OH and CN, four different groups, so it is chiral.
4. $M_r(\text{C}_3\text{H}_5\text{N}) = 55.0$, so $2.75 \div 55.0 = 0.0500$ mol. One mole of salt per mole:
 $M_r(\text{CH}_3\text{CH}_2\text{COONa}) = 96.0$, so the mass is $0.0500 \times 96.0 = 4.80$ g.
5. The acid has 5 carbons, so start from a 4-carbon halogenoalkane: 1-bromo-2-methylpropane, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$. Step 1: KCN in ethanol, heat, giving 3-methylbutanenitrile, $(\text{CH}_3)_2\text{CHCH}_2\text{CN}$. Step 2: dilute HCl, heat under reflux (or NaOH(aq), heat, then acidify).

Past questions to try

- **9701/22/M/J/22 Q5**: ammonia and cyanide with halogenoalkanes, the $\text{S}_{\text{N}}2$ mechanism and a hydrolysis equation.
- **9701/23/M/J/23 Q6**: the HCN mechanism, optical isomers of a hydroxynitrile, and reducing a nitrile with hydrogen.
- **9701/22/M/J/21 Q5**: a three-step route through a nitrile, with its infrared spectrum.
- **9701/12/M/J/22 Q32**: a ring made from ammonia and a dibromo compound.