

Cambridge AS & A Level · Chemistry 9701 · Notes

Carboxylic acids and derivatives AS

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Read first: [An introduction to AS Level organic chemistry](#), [Halogen compounds](#), [Hydroxy 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 three ways to make a carboxylic acid:**

- (a) **oxidising a primary alcohol or an aldehyde** with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$, heating under **reflux**;
- (b) **hydrolysing a nitrile** with dilute acid, or with dilute alkali and then acidifying;
- (c) **hydrolysing an ester** with dilute acid, or with dilute alkali, and heat, then acidifying.

2. **Describe five reactions of carboxylic acids:**

- (a) with **reactive metals** (a redox reaction), giving a salt and hydrogen gas;
- (b) with **alkalis** (neutralisation), giving a salt and water;
- (c) with **carbonates** (an acid–base reaction), giving a salt, water and carbon dioxide;
- (d) with **alcohols**, using concentrated H_2SO_4 as a catalyst, giving an **ester** (esterification);
- (e) **reduction by $LiAlH_4$** to a **primary alcohol**.

3. **Recall how esters are made:** a condensation reaction between an alcohol and a carboxylic acid, with concentrated H_2SO_4 as the catalyst.

4. **Describe the hydrolysis of esters**, both by dilute acid and by dilute alkali, with heat.

Acyl chlorides, the acidity of chlorine-substituted acids and the oxidation of methanoic and ethanedioic acids come later, in the A Level topic.

Understand it

The carboxyl group

A carboxylic acid contains the **carboxyl group**, $-COOH$ (also written $-CO_2H$): a carbon with a $C=O$ and an $O-H$ on it. It is always at the end of a chain, so its carbon is C1 and needs no number. Name the acid from the longest chain **including** that carbon, ending **-oic acid**:

Acid	Formula	Carbons
methanoic acid	HCOOH	1
ethanoic acid	CH ₃ COOH	2
propanoic acid	CH ₃ CH ₂ COOH	3
butanoic acid	CH ₃ CH ₂ CH ₂ COOH	4
2-methylpropanoic acid	(CH ₃) ₂ CHCOOH	4
propanedioic acid (a dicarboxylic acid)	HOOCCH ₂ COOH	3

Saturated acids with one COOH have the general formula C_nH_{2n}O₂. The O–H lets the molecules **hydrogen-bond** to each other, so acids boil higher than alcohols of similar *M_r*, and the small ones mix with water.

Why they are acids. In water the O–H bond breaks and the acid gives away H⁺, leaving a **carboxylate ion**:

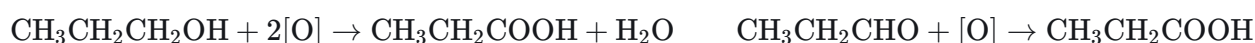


Only a small fraction of the molecules do this, so carboxylic acids are **weak acids**. Water is therefore enough to make a solution that contains ethanoate ions. The negative ion's name ends in **-oate**: ethanoate, propanoate. Its salts are sodium ethanoate, CH₃COONa (or CH₃COO[−]Na⁺), magnesium ethanoate, (CH₃COO)₂Mg, and so on.

Carboxylic acids are much stronger acids than alcohols. An alcohol's O–H hardly gives up H⁺ at all: alcohols do **not** react with carbonates or with NaOH(aq). Both an alcohol O–H and an acid O–H **do** react with sodium metal.

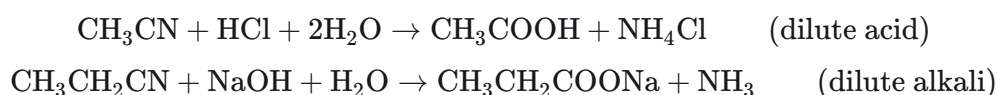
Making carboxylic acids

(a) Oxidising a primary alcohol or an aldehyde. Heat under **reflux** with an excess of acidified potassium dichromate(VI), K₂Cr₂O₇ and dilute H₂SO₄ (orange turns green), or acidified KMnO₄. Reflux keeps the aldehyde formed first in the flask until it is oxidised all the way. [O] is an oxygen atom from the oxidising agent:



The acid keeps the **same number of carbons**. A diol with two primary OH groups gives a dicarboxylic acid: HOCH₂CH₂CH₂CH₂OH + 4[O] → HOOCCH₂CH₂COOH + 2H₂O. Secondary and tertiary alcohols do not give carboxylic acids.

(b) Hydrolysing a nitrile. A nitrile, R–C≡N, is heated under reflux with dilute acid or dilute alkali. The CN carbon becomes the COOH carbon, and the nitrogen ends up as ammonium ions or ammonia:



In alkali you get the **salt** and ammonia gas; adding dilute acid afterwards turns the salt into the acid. Nitriles are made from halogenoalkanes with **KCN in ethanol, heated** (Halogen compounds). That step adds a carbon, so bromoethane → propanenitrile → **propanoic** acid: the acid has **one more carbon** than the halogenoalkane.

(c) **Hydrolysing an ester**, covered below. It gives the acid (or its salt) and an alcohol.

Reactions as an acid

The COOH group reacts with metals, alkalis and carbonates just as a mineral acid does, only more slowly. Each COOH gives one carboxylate; a metal ion with a 2+ charge needs two of them.

Reacts with	Type	Example	What you see
reactive metal (Na, Mg, Ca, Zn)	redox	$2\text{CH}_3\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{COO})_2\text{Mg} + \text{H}_2$	fizzing (H_2); metal dissolves
sodium	redox	$\text{CH}_3\text{COOH} + \text{Na} \rightarrow \text{CH}_3\text{COONa} + \frac{1}{2}\text{H}_2$	fizzing
alkali (NaOH, KOH)	neutralisation	$\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$	no visible change (no gas)
carbonate or hydrogencarbonate	acid-base	$2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$	fizzing (CO_2)
		$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$	

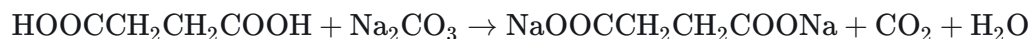
With a metal, the metal is **oxidised** (it loses electrons) and the H^+ of the acid is **reduced** to H_2 . With alkalis and carbonates nothing changes oxidation number.

Carboxylic acids are stronger acids than carbonic acid, so they release CO_2 from carbonates. **Fizzing with $\text{Na}_2\text{CO}_3(\text{aq})$ or $\text{NaHCO}_3(\text{aq})$ is the test for a $-\text{COOH}$ group**: alcohols are far weaker acids and do not do it.

Molecules with several groups. Count the groups before you balance:

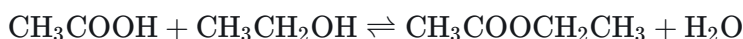
- **Na** reacts with **every O–H**, whether it is in a COOH or an alcohol OH. Each O–H gives $\frac{1}{2}\text{H}_2$ and one O^- .
- **NaOH, Na_2CO_3 , NaHCO_3 and Mg** react with the **COOH groups only**.

So for 3-hydroxybutanoic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOH}$: sodium makes $\text{CH}_3\text{CH}(\text{O}^-)\text{CH}_2\text{COO}^-$ (charge 2–) and gives 1 mol of H_2 per mole; NaOH makes $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COO}^-$ (charge 1–). A diacid with excess Na_2CO_3 turns both ends into $\text{COO}^- \text{Na}^+$:



Esterification

Heat a carboxylic acid with an alcohol and a few drops of **concentrated H_2SO_4** (the **catalyst**). The OH of the acid and the H of the alcohol's OH leave as water, and the two pieces join through an oxygen: the **ester link**, $-\text{COO}-$.



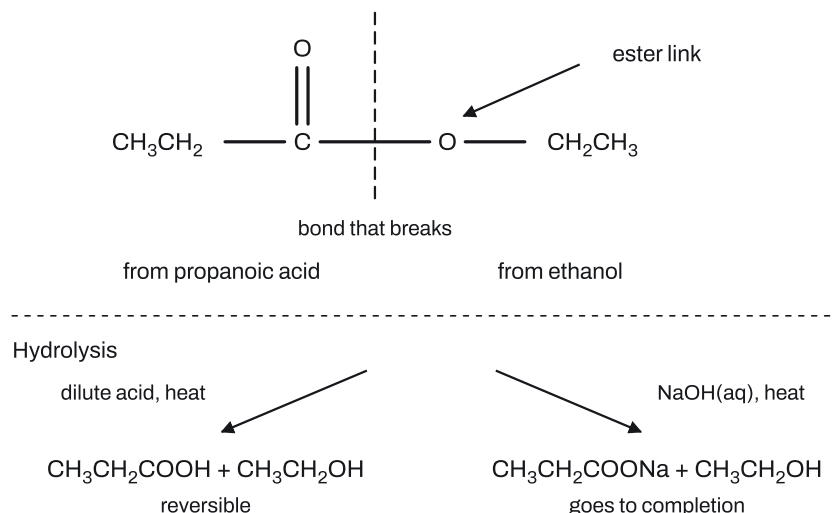
Two molecules join and a small molecule (water) is lost, so this is a **condensation** reaction (also called esterification). It is **reversible** and reaches equilibrium, so the yield is never 100%. Esters have fruity smells; they are used as flavourings, perfumes and solvents.

Naming an ester: alcohol part first, acid part second. The alcohol gives an **alkyl** word (methyl, ethyl, propyl, butyl); the acid gives an **-oate** word.

Acid	Alcohol	Ester	Formula
ethanoic acid	ethanol	ethyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$
ethanoic acid	propan-1-ol	propyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$
propanoic acid	methanol	methyl propanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_3$
methanoic acid	ethanol	ethyl methanoate	$\text{HCOOCH}_2\text{CH}_3$
butanoic acid	ethanol	ethyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$

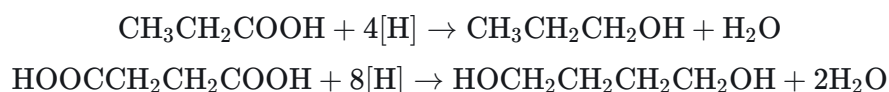
The **formula** is written the other way round, acid part first: in $\text{CH}_3\text{CH}_2\text{COOCH}_3$ the $\text{CH}_3\text{CH}_2\text{CO}$ piece (3 carbons) came from propanoic acid and the OCH_3 from methanol. The acid piece is the one whose carbon carries the $\text{C}=\text{O}$. Sometimes the formula is written alcohol part first, such as $\text{CH}_3\text{OCOCH}_2\text{CH}_3$ (the same ester): always find the $\text{C}=\text{O}$ carbon and read from there.

Ethyl propanoate



Reduction with LiAlH_4

Lithium tetrahydridoaluminate, LiAlH_4 , in dry ether, is a strong enough **reducing agent** to reduce COOH to CH_2OH . The product is a **primary alcohol with the same carbon chain**. Each COOH needs $4[\text{H}]$ and gives one water:



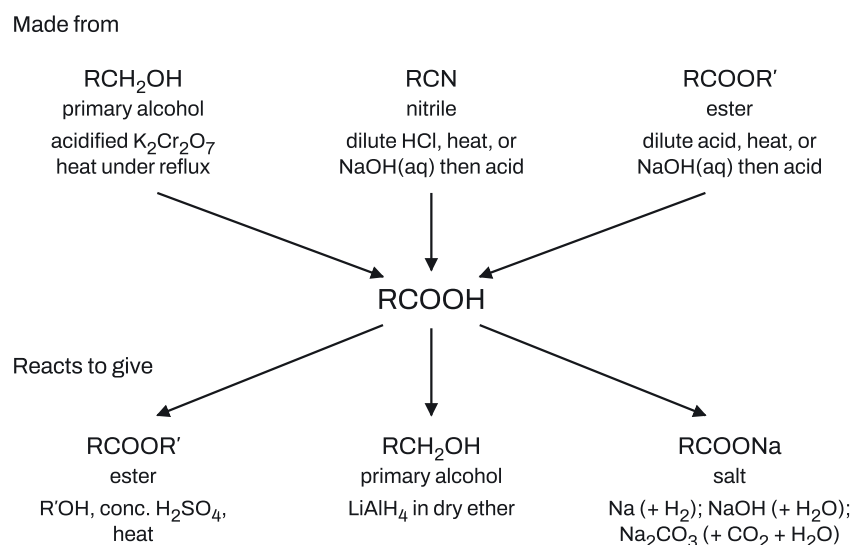
NaBH_4 is **not** strong enough: it reduces aldehydes and ketones only (Carbonyl compounds). So "reduced by LiAlH_4 but not by NaBH_4 " points to a carboxylic acid. The aldehyde is formed on the way, but with LiAlH_4 it is reduced straight on, so the final product is the alcohol.

Hydrolysis of esters

Hydrolysis is esterification run backwards: water splits the ester link, the C–O bond between the C=O carbon and the oxygen breaks, and you get back the acid and the alcohol. Heating with water alone is far too slow, so an acid or an alkali is used.

- **Dilute acid** (for example $\text{H}_2\text{SO}_4(\text{aq})$ or $\text{HCl}(\text{aq})$), heat under reflux. The acid is only a catalyst. The products are the **carboxylic acid and the alcohol**. The reaction is **reversible**, so some ester is always left: $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}$
- **Dilute alkali** ($\text{NaOH}(\text{aq})$), heat under reflux. The products are the **carboxylate salt and the alcohol**. The acid formed is at once neutralised by the alkali, so the reaction **goes to completion**, which is why alkali is the usual choice: $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{CH}_3\text{CH}_2\text{OH}$ Adding dilute acid afterwards turns the salt into the carboxylic acid.

The alcohol always comes out as the **alcohol**, never as an alkoxide ion (RO^-); only the acid part becomes an ion in alkali. An ester made from a **diol or a diacid** has two ester links; hydrolysis breaks both, using two water molecules (or 2 NaOH).



Key facts and formulas

"Given" means it is printed in the 9701 Data Booklet. "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, Mg 24.3	Given

Formula or fact	Status
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions, $22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p.	Given
$\text{RCH}_2\text{OH} + 2[\text{O}] \rightarrow \text{RCOOH} + \text{H}_2\text{O}$ (acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat under reflux)	Learn it
$\text{RCN} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}$; $\text{RCN} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{RCOONa} + \text{NH}_3$	Learn it
$2\text{RCOOH} + \text{Mg} \rightarrow (\text{RCOO})_2\text{Mg} + \text{H}_2$; $\text{RCOOH} + \text{Na} \rightarrow \text{RCOONa} + \frac{1}{2}\text{H}_2$	Learn it
$\text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}$	Learn it
$2\text{RCOOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2$	Learn it
$\text{RCOOH} + \text{R}'\text{OH} \rightleftharpoons \text{RCOOR}' + \text{H}_2\text{O}$ (concentrated H_2SO_4 catalyst, heat)	Learn it
$\text{RCOOH} + 4[\text{H}] \rightarrow \text{RCH}_2\text{OH} + \text{H}_2\text{O}$ (LiAlH_4 only, not NaBH_4)	Learn it
$\text{RCOOR}' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{R}'\text{OH}$ (dilute acid, heat)	Learn it
$\text{RCOOR}' + \text{NaOH} \rightarrow \text{RCOONa} + \text{R}'\text{OH}$ (dilute alkali, heat; goes to completion)	Learn it
Na reacts with every O–H (COOH and alcohol OH): $\frac{1}{2}\text{H}_2$ each; NaOH, carbonates and Mg react with COOH only	Learn it
$\text{moles} = \frac{\text{mass}}{M_r}$; gas volume = moles $\times 24.0 \text{ dm}^3$	Learn it

How to do it

We have tagged 100 questions on this topic from 2021–2025 (86 different, since some papers share questions). 18 of them mix more than one type, so the counts add up to more than 100.

Question type	Questions
Predict the products of ester hydrolysis, or the ester from its products	31
Esterification: reactants, name, equation and conditions	28
Reduce a carboxylic acid with LiAlH_4	16
Write equations for acids with metals, carbonates and alkalis	16
Choose or describe a route to a carboxylic acid	14

Question type	Questions
Calculate moles, gas volumes and Mr	12
Use tests to identify a carboxylic acid	8

1. Predict the products of ester hydrolysis, or the ester from its products (31 questions)

1. **Find the ester link**, -COO- : the carbon with the C=O and the O next to it.
2. **Cut the single C–O bond** between the C=O carbon and that oxygen.
3. **The side with the C=O becomes the acid**: add OH to it to get RCOOH . **The other side becomes the alcohol**: add H to the oxygen to get R'OH .
4. **Check the conditions**. Dilute acid: carboxylic acid + alcohol. NaOH(aq) or KOH(aq) : **salt** (RCOO^-Na^+) + alcohol. The alcohol is never an ion.

For example, $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$ with NaOH(aq) gives CH_3COONa (sodium ethanoate) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (propan-1-ol).

Variations you will meet:

- **Formulas written alcohol first**. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCOCH}_3$ is read from the C=O carbon: OCOCH_3 is the ethanoate part, so the products are ethanoic acid and propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$.
- **Work backwards** from the products: join the acid and alcohol, removing water. A given alcohol and acid tell you the ester, and a named alcohol from hydrolysis tells you which ester of a set.
- **Esters with two ester links** (from a diol or a diacid): break **both** links, and draw every product. $\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{COOCH}_3$ gives butanedioic acid and **two** methanol. Drawing one: write the acid part with both COO groups first, then put an alkyl group on each O.
- **Cyclic esters** (the ester link in a ring): hydrolysis opens the ring and gives **one** molecule carrying both an OH and a COOH (or COO^- in alkali).
- **Several esters at once** (a mixture, or a fat): list the acid from each; acidifying at the end turns every salt into its acid.
- **Follow-up questions**: the alcohol's class (primary, secondary, tertiary) from its carbon; reducing the acid product with LiAlH_4 ; the M_r or percentage by mass of a product. A percentage of oxygen can identify the ester: an ester with one COO group has two O, so $M_r = \frac{32.0}{\%O} \times 100$.
- **Which method goes to completion?** Alkaline hydrolysis; acid hydrolysis is reversible.
- **Which product reduces to the other?** LiAlH_4 turns RCOOH into RCH_2OH , so the alcohol half must be the acid's chain with CH_2OH in place of COOH: propyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$, works; propyl ethanoate does not.

2. Esterification: reactants, name, equation and conditions (28 questions)

1. **Reagents and conditions**: carboxylic acid + alcohol, a few drops of **concentrated** H_2SO_4 (catalyst), heat (under reflux).

2. **Equation:** join the acid's C=O carbon to the alcohol's O, and write H₂O as the other product. Use structural formulas and the $\rightleftharpoons$ sign.
3. **Name:** alkyl word from the alcohol, then -oate from the acid (propyl ethanoate).
4. **Type of reaction:** condensation (esterification).

Variations you will meet:

- **Which acid and alcohol make this ester?** Cut it as in type 1. For CH₃CH₂COOCH₂CH₃: propanoic acid and ethanol, **not** ethanoic acid and propan-1-ol.
- **Counting esters of a molecular formula.** Split the carbons between the acid part and the alcohol part in every way, and count the different chains on each side. For C₄H₈O₂: methanoic acid with propan-1-ol or propan-2-ol (2), ethanoic acid with ethanol (1), propanoic acid with methanol (1): **4** esters. If the question allows only primary alcohols, drop the ones from secondary alcohols.
- **Esters from a molecule with both OH and COOH.** Two such molecules can join head to tail; if the OH and COOH are far enough apart in one molecule, they react with each other and form a **cyclic ester** (a ring containing –COO–), losing one H₂O.
- **Diesters.** A diol reacts with two acid molecules (or a diacid with two alcohol molecules), losing two H₂O.
- **Masses and M_r .** One mole of acid gives one mole of ester and one mole of water per ester link.
Percentage yield = $\frac{\text{actual mass}}{\text{theoretical mass}} \times 100$.
- **Two steps in one question**, for example "butanoic acid with LiAlH₄ gives P; P with ethanoic acid gives Q": P is butan-1-ol, Q is butyl ethanoate, CH₃COOCH₂CH₂CH₂CH₃.
- **Following the reaction by infrared** (Analytical techniques). Watch the **C=O** absorption: it moves from the carboxyl range, 1670–1740 cm^{–1}, to the ester range, 1710–1750 cm^{–1}. C–O is no help, because the acid has one too. O–H is usually no help either: the alcohol and the water formed also absorb there. O–H disappearing is only usable when no alcohol or water O–H is left, as when a hydroxy acid forms a cyclic ester: the acid's broad O–H (2500–3000 cm^{–1}) and alcohol O–H (3200–3600 cm^{–1}) are both gone from the ester's spectrum. Try [9701/22/O/N/23 Q3](#) and [9701/22/M/J/23 Q5](#).

3. Reduce a carboxylic acid with LiAlH₄ (16 questions)

1. **Reagent:** LiAlH₄ (in dry ether). Its role: **reducing agent**; the reaction: **reduction**.
2. **Product:** turn every COOH into CH₂OH. Keep every other part of the molecule. Aldehyde and ketone C=O groups are reduced too (to CH₂OH and CH(OH)); C=C bonds are not.
3. **Equation:** 4[H] and one H₂O for each COOH, plus 2[H] for each aldehyde or ketone C=O.

Variations you will meet:

- **"Reduced by LiAlH₄ but not by NaBH₄"** means a carboxylic acid (or an ester). Use any formula clue to pick the acid: an acid with empirical formula CH₂O has two O atoms, so it is C₂H₄O₂, ethanoic acid.
- **Diacids and hydroxy acids:** every COOH is reduced.
HOCH₂COOH + 4[H] → HOCH₂CH₂OH + H₂O. Count the carbons to check the product.
- **Molecular formula of the product:** each COOH → CH₂OH removes one O and adds two H.
- **The product is not an aldehyde.** With LiAlH₄ the reduction goes all the way to the alcohol.

- **Which reaction gives a primary alcohol?** LiAlH_4 with a carboxylic acid, or NaBH_4 with an aldehyde; a ketone gives a secondary alcohol.

4. Write equations for acids with metals, carbonates and alkalis (16 questions)

1. **Count the COOH groups** (and, for sodium, the alcohol OH groups too).
2. **Write the salt:** each reacting O–H becomes O^-Na^+ (or O^- with half an Mg^{2+}).
3. **Add the other products:** metal $\rightarrow \text{H}_2$; alkali $\rightarrow \text{H}_2\text{O}$; carbonate $\rightarrow \text{H}_2\text{O} + \text{CO}_2$.
4. **Balance**, using $\frac{1}{2}\text{H}_2$ or doubling as needed. Two acid molecules per Mg, Ca or Na_2CO_3 .

Variations you will meet:

- **Checking given equations** (multiple choice): look for the right salt formula ($(\text{CH}_3\text{COO})_2\text{Mg}$, not CH_3COOMg), the right gas (H_2 from metals, CO_2 from carbonates, **none** from alkalis) and balanced atoms.
- **Excess reagent with a diacid:** every COOH reacts, so excess NaOH turns $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ into $\text{NaOOCCH}_2\text{CH}_2\text{COONa}$. Other groups are untouched: propenoic acid, $\text{CH}_2=\text{CHCOOH}$, gives $\text{CH}_2=\text{CHCOONa}$ and keeps its $\text{C}=\text{C}$.
- **Which reagent gives no gas?** NaOH (neutralisation). **Which is redox?** The metal reaction.
- **Which gives ethanoate ions?** Water (the acid partly ionises), NaOH, carbonates and metals; LiAlH_4 does not (it gives ethanol).
- **"Why does the alcohol not react with Na_2CO_3 ?"** The alcohol is a much weaker acid than the carboxylic acid (too weak to release CO_2 from a carbonate).
- **The charge on the organic ion:** count the O–H groups that react. With excess Na every O–H loses H^+ ; with NaOH only the COOH groups.

5. Choose or describe a route to a carboxylic acid (14 questions)

1. **Count carbons** in the start and the target.
2. **Same number of carbons:**
 - from a primary alcohol or aldehyde: acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (or KMnO_4), **heat under reflux**;
 - from a nitrile: dilute HCl (or H_2SO_4), heat; or NaOH(aq), heat, then acidify;
 - from an ester: dilute acid, or NaOH(aq), heat, then acidify.
3. **One more carbon:** halogenoalkane $\rightarrow$ nitrile with **KCN in ethanol, heat**, then hydrolyse the nitrile.
4. **Write the equation if asked.** Nitrile with acid: $\text{RCN} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NH}_4\text{Cl}$ (the nitrogen ends up as **ammonium**). With alkali: $\text{RCN} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{RCOONa} + \text{NH}_3$. Type: **hydrolysis**.

Variations you will meet:

- **Earlier steps you may be asked for:**
 - alcohol $\rightarrow$ chloroalkane: PCl_5 , or SOCl_2 , or PCl_3 and heat, or HCl(g) (or NaCl with concentrated H_2SO_4); a substitution;
 - chloroalkane $\rightarrow$ alcohol: NaOH(aq), heat; a substitution (hydrolysis);

- diol → diacid: acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat under reflux; an **oxidation**.
- **Which compounds give a named acid?** Count carbons: propanoic acid (3 C) comes from propanenitrile, propan-1-ol, propanal or a propanoate ester, and from a two-carbon halogenoalkane (bromoethane) via the nitrile.
- **Why KCN in ethanol, not HCN?** HCN with KCN adds to aldehydes and ketones (Carbonyl compounds); a halogenoalkane needs CN^- as a nucleophile in ethanol for substitution.

6. Calculate moles, gas volumes and Mr (12 questions)

- Moles of the organic compound:** $n = \text{mass} \div M_r$.
- Count what reacts** per molecule: COOH groups for Mg, carbonates and NaOH; all O–H groups (COOH + OH) for Na.
- Moles of gas:**
 - Na: $\frac{1}{2}$ mol H_2 per O–H;
 - Mg: $\frac{1}{2}$ mol H_2 per COOH;
 - Na_2CO_3 : $\frac{1}{2}$ mol CO_2 per COOH; NaHCO_3 : 1 mol CO_2 per COOH.
- Volume** = $n \times 24.0 \text{ dm}^3$ at room conditions (use 22.4 only if the question says s.t.p.). $1 \text{ dm}^3 = 1000 \text{ cm}^3$.

Variations you will meet:

- **Put reactions in order of gas volume:** work out the moles of gas per mole of compound for each; NaOH gives none.
- **Find M_r from a gas volume:** gas moles → moles of acid (2 acid per H_2 with Mg) → $M_r = \text{mass} \div \text{moles}$. Use the molar volume the question states.
- **Volume of NaOH to neutralise:** moles of NaOH = moles of acid × number of COOH; volume = moles ÷ concentration.
- **How many OH groups?** Moles of H_2 from Na per mole of compound, times 2, gives the number of O–H groups. Show the working.
- **M_r of a salt:** replace each reacting H by Na (+22.0 each) or two of them by one Mg.

7. Use tests to identify a carboxylic acid (8 questions)

Test	Carboxylic acid	Alcohol	Ester	Aldehyde / ketone
$\text{Na}_2\text{CO}_3(\text{aq})$ or $\text{NaHCO}_3(\text{aq})$	effervescence , CO_2	no change	no change	no change
Na(s)	effervescence, H_2	effervescence, H_2	no change	no change
acidified $\text{K}_2\text{Cr}_2\text{O}_7$, warm	stays orange	orange → green (1°, 2°)	stays orange	green for aldehydes only
2,4-DNPH	no precipitate	no precipitate	no precipitate	orange precipitate

1. **Read each result as a fact** from the table; test the gas if asked (CO_2 gives a white precipitate with limewater; H_2 pops with a lighted splint).
2. **Match every result** against each candidate structure, and give one answer.

Variations you will meet:

- **Telling three acids apart**, such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{COCH}_2\text{COOH}$: all fizz with Na_2CO_3 , so use the **other** group. Acidified dichromate turns green only with the secondary OH; 2,4-DNPH gives a precipitate only with the ketone.
- **Methanoic acid**, HCOOH , has an H on its $\text{C}=\text{O}$ carbon, like an aldehyde. When a question tells you it is oxidised like an aldehyde, expect the aldehyde results: a red-brown precipitate with Fehling's reagent and a silver mirror with Tollens' reagent.

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

Propanoic acid reacts with ethanol to form an ester, **E**.

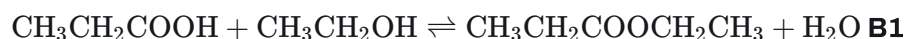
(a) Give the reagent and conditions needed, write an equation using structural formulas, and name the type of reaction. **[4]**

(b) Name **E**. **[1]**

(c) 3.70 g of propanoic acid gave 3.57 g of **E**. Calculate the percentage yield. **[3]**

(d) **E** is heated under reflux with $\text{NaOH}(\text{aq})$. Name both products and explain why alkaline hydrolysis is preferred to acid hydrolysis. **[3]**

(a) A few drops of concentrated H_2SO_4 **B1**, heat. **B1**



Condensation (esterification). **B1**

(b) Ethyl propanoate. **B1**

(c) $M_r(\text{C}_3\text{H}_6\text{O}_2) = 3(12.0) + 6(1.0) + 2(16.0) = 74.0$, so moles of acid = $3.70 \div 74.0 = 0.0500$ mol. **M1**

$M_r(\text{C}_5\text{H}_{10}\text{O}_2) = 102.0$, so the theoretical mass is $0.0500 \times 102.0 = 5.10 \text{ g}$. **M1**

$$\text{percentage yield} = \frac{3.57}{5.10} \times 100 = 70.0\%$$

A1

(d) Sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$ **B1**, and ethanol. **B1** In alkali the acid is removed as its salt as soon as it forms, so the reaction goes to completion; acid hydrolysis is reversible and leaves some ester. **B1**

Example 2

2,3-dihydroxypropanoic acid, $\text{HOCH}_2\text{CH}(\text{OH})\text{COOH}$, is a solid. Separate 0.530 g samples react completely with an excess of each reagent below. Gas volumes are at room conditions.

(a) Calculate the volume of gas produced with sodium. **[3]**

(b) Write an equation for the reaction with Na_2CO_3 , and calculate the volume of gas produced. **[3]**

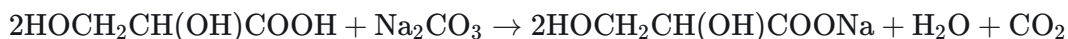
(c) Calculate the volume of $0.100 \text{ mol dm}^{-3}$ $\text{NaOH}(\text{aq})$ that reacts with one sample. **[2]**

(a) $M_r(\text{C}_3\text{H}_6\text{O}_4) = 36.0 + 6.0 + 64.0 = 106.0$, so $n = 0.530 \div 106.0 = 0.00500 \text{ mol}$. **M1**

Sodium reacts with all **three** O–H groups (two OH and one COOH), giving $\frac{3}{2}$ mol of H_2 per mole: $0.00500 \times 1.5 = 0.00750 \text{ mol H}_2$. **M1**

Volume = $0.00750 \times 24.0 = 0.180 \text{ dm}^3$, that is 180 cm^3 . **A1**

(b) Only the COOH group reacts:



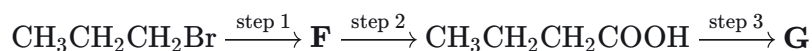
B1

$n(\text{CO}_2) = 0.00500 \div 2 = 0.00250 \text{ mol}$ **M1**, volume = $0.00250 \times 24.0 = 0.0600 \text{ dm}^3 = 60.0 \text{ cm}^3$. **A1**

(c) One COOH, so $n(\text{NaOH}) = 0.00500 \text{ mol}$. **M1** Volume = $0.00500 \div 0.100 = 0.0500 \text{ dm}^3 = 50.0 \text{ cm}^3$. **A1**

Example 3

Butyl butanoate, a fruity-smelling ester, is made from 1-bromopropane in this sequence:



Butanoic acid and **G** are then heated together with concentrated H_2SO_4 .

(a) Give the reagent and conditions for step 1, and name **F**. **[3]**

(b) In step 2, **F** is heated with dilute hydrochloric acid. Write an equation and name the type of reaction. **[2]**

(c) Step 3 uses LiAlH_4 . Write an equation using $[\text{H}]$, name **G**, and explain why NaBH_4 cannot be used. **[3]**

(d) Give the structural formula of butyl butanoate and calculate its M_r . **[2]**

(a) KCN in ethanol **B1**, heat. **B1** **F** is butanenitrile, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ (the CN adds a fourth carbon). **B1**

(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$ **B1**; hydrolysis. **B1**

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}$ **B1**. **G** is butan-1-ol. **B1** NaBH_4 is too weak a reducing agent to reduce a carboxylic acid; it reduces only aldehydes and ketones. **B1**

(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ **B1**, $\text{C}_8\text{H}_{16}\text{O}_2$: $M_r = 8(12.0) + 16(1.0) + 2(16.0) = 144.0$. **B1**

Example 4

Compound **P**, $\text{C}_9\text{H}_{16}\text{O}_4$, is a neutral liquid that does not react with sodium or with $\text{Na}_2\text{CO}_3(\text{aq})$. When **P** is heated with dilute sulfuric acid it gives two products:

- **Q**, $M_r = 60.0$, which fizzes with $\text{Na}_2\text{CO}_3(\text{aq})$;
- **R**, $\text{C}_5\text{H}_{12}\text{O}_2$, an unbranched compound that fizzes with sodium but not with $\text{Na}_2\text{CO}_3(\text{aq})$. Each carbon at the end of its chain carries an OH group.

(a) Identify **Q** and **R**, and draw the structural formula of **P**. [3]

(b) Write an equation for the hydrolysis of **P**. [1]

(c) **R** is heated under reflux with an excess of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to give **S**, $\text{C}_5\text{H}_8\text{O}_4$. State the colour change, name **S** and the type of reaction. [3]

(d) Write an equation for the reduction of **S** with an excess of LiAlH_4 . [2]

(e) Calculate the volume of gas, at room conditions, given when 1.32 g of **S** reacts with an excess of $\text{Na}_2\text{CO}_3(\text{aq})$. [3]

(a) **Q** is a carboxylic acid with $M_r = 60.0$: ethanoic acid, CH_3COOH . **B1** **R** reacts with Na but not carbonate, so it has alcohol OH groups only: pentane-1,5-diol, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$. **B1** **P** has an ester link at each end of **R**: $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOCCH}_3$. **B1** (Check: $5 + 2 \times 2 = 9$ carbons.)

(b) $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OOCCH}_3 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CH}_3\text{COOH} + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ **B1**

(c) Orange to green. **B1** **S** is pentanedioic acid, $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ **B1**; oxidation. **B1**

(d) $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH} + 8[\text{H}] \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2\text{H}_2\text{O}$ **M1** (organic product) **A1** (balanced).

(e) $M_r(\text{C}_5\text{H}_8\text{O}_4) = 60.0 + 8.0 + 64.0 = 132.0$, so $n = 1.32 \div 132.0 = 0.0100$ mol. **M1**

$\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow \text{NaOOCCH}_2\text{CH}_2\text{CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$: two COOH give one CO_2 , so 0.0100 mol CO_2 . **M1**

Volume = $0.0100 \times 24.0 = 0.240 \text{ dm}^3 = 240 \text{ cm}^3$. **A1**

Common mistakes

- **Giving the acid instead of the salt in alkaline hydrolysis.** With NaOH(aq) the product is RCOO^-Na^+ ; the carboxylic acid appears only after acidifying. And the alcohol stays an alcohol: never write RO^-Na^+ .
- **Splitting an ester the wrong way.** $\text{CH}_3\text{CH}_2\text{COOCH}_3$ comes from **propanoic acid and methanol**, not ethanoic acid and ethanol. Find the C=O carbon: it belongs to the acid.
- **Naming the ester back to front.** The alcohol's alkyl group comes first: propyl ethanoate, not ethyl propanoate, for $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$.
- **Drawing only one ester link.** Reports note that the ester group is often drawn correctly but the rest of the molecule is not. In a diester put an ester link on **each** OH or COOH, and count the carbons.
- **Nitrile hydrolysis equations.** Reports say many candidates gave the acid but not the ammonium ion, or left the equation unbalanced. With HCl the products are $\text{RCOOH} + \text{NH}_4\text{Cl}$, using **2** H_2O ; with NaOH they are $\text{RCOONa} + \text{NH}_3$.
- **KCN conditions.** Reports see HCN, or KCN with acid, for turning a halogenoalkane into a nitrile. That needs **KCN in ethanol, heat**; HCN with KCN is for aldehydes and ketones.
- **NaBH_4 for a carboxylic acid.** It cannot reduce COOH; only LiAlH_4 can. And the equation needs **4[H]** and H_2O per COOH.
- **Forgetting that Na reacts with alcohol OH groups too.** In gas-volume questions Na counts every O–H; carbonates, NaOH and Mg count only COOH.
- **The wrong molar volume.** Use 24.0 dm^3 at room conditions and 22.4 dm^3 only at s.t.p.; a report shows mixing them up led straight to a wrong answer.
- **Wrong stoichiometry with Mg and carbonates.** Two RCOOH per Mg or per CO_3^{2-} : $(\text{CH}_3\text{COO})_2\text{Mg}$, not CH_3COOMg .
- **Vague observations.** Write "effervescence" or "fizzing", not "gas released"; "no visible change", not "no observation". Name the group fully as "carboxylic acid" or –COOH, not just "carboxyl".

How to get the marks

- **"Reagents and conditions"** needs both: "ethanol and concentrated H_2SO_4 , heat"; " LiAlH_4 in dry ether"; "KCN in ethanol, heat"; "acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat under reflux"; "NaOH(aq), heat". Give reagents as full names or formulas: "concentrated H_2SO_4 ", not "acid".
- **"Type of reaction"**: esterification or condensation (acid + alcohol); hydrolysis (ester or nitrile with water, acid or alkali); reduction (LiAlH_4); oxidation (dichromate); neutralisation (alkali); redox (metal).
- **"Role of" a reagent**: LiAlH_4 is a reducing agent; concentrated H_2SO_4 is a catalyst; sodium is a reducing agent (it gives electrons).
- **Equations with structural formulas** score only if they are balanced and unambiguous: $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$, not $\text{C}_5\text{H}_{10}\text{O}_2$. For [H] equations, one mark is often for the organic product and one for the balancing.
- **"Draw the structure"** of an ester: the ester link must be clear, $-\text{C}(=\text{O})-\text{O}-$, with the right groups on each side. "Displayed formula" means every bond drawn, including each C–H.

- **"Suggest why"** answers need the chemical reason: "the alcohol is a weaker acid than the carboxylic acid", "the salt is formed so the reaction goes to completion".
- **Calculations:** show M_r , moles and the ratio from the equation; give 3 significant figures and units.
- **Multiple choice with numbered statements:** test each statement separately against the facts above.

Quick check

1. Give the name and structural formula of the ester formed from butanoic acid and methanol.
2. The ester $(\text{CH}_3)_2\text{CHOOCCCH}_2\text{CH}_3$ is heated under reflux with NaOH(aq) . Give the structural formula and name of each product.
3. Write equations for the reactions of propanoic acid with (a) magnesium, (b) sodium carbonate, (c) sodium hydroxide.
4. Calculate the volume of carbon dioxide, at room conditions, produced when 2.22 g of propanoic acid reacts with an excess of $\text{Na}_2\text{CO}_3(\text{aq})$.
5. Give the reagents and conditions to make propanoic acid (a) from propan-1-ol in one step, and (b) from bromoethane in two steps.

Answers

1. Methyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$.
2. Read from the $\text{C}=\text{O}$ carbon: $\text{OOCCH}_2\text{CH}_3$ is the propanoate part. Products: sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$, and propan-2-ol, $(\text{CH}_3)_2\text{CHOH}$.
3. (a) $2\text{CH}_3\text{CH}_2\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{CH}_2\text{COO})_2\text{Mg} + \text{H}_2$. (b) $2\text{CH}_3\text{CH}_2\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$. (c) $\text{CH}_3\text{CH}_2\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O}$.
4. $M_r = 74.0$, so $2.22 \div 74.0 = 0.0300$ mol of acid. Two acid molecules give one CO_2 : 0.0150 mol. Volume = $0.0150 \times 24.0 = 0.360 \text{ dm}^3 = 360 \text{ cm}^3$.
5. (a) Acidified potassium dichromate(VI), heat under reflux. (b) Step 1: KCN in ethanol, heat, giving propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$. Step 2: dilute HCl, heat (or NaOH(aq), heat, then acidify).

Past questions to try

- **9701/22/M/J/25 Q4**: reducing propanoic acid with LiAlH_4 , then a nitrile hydrolysed by NaOH(aq).
- **9701/12/F/M/25 Q26**: which compound LiAlH_4 reduces but NaBH_4 does not.
- **9701/12/O/N/23 Q38**: counting the esters of one molecular formula.
- **9701/12/M/J/25 Q27**: methanoic acid with Fehling's reagent.