

Cambridge AS & A Level · Chemistry 9701 · Notes

Organic synthesis AS

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What you need to know

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

1. **Take a molecule with several functional groups and:**

- (a) **identify its functional groups** from how it reacts: the tests and reactions you met in the AS topics on hydrocarbons, halogen compounds, hydroxy compounds, carbonyl compounds, carboxylic acids and esters, and nitrogen compounds;
- (b) **predict its properties and reactions**: which reagents it reacts with, what each one does to it, and what the product is.

2. **Devise a synthetic route** of two or more steps from a starting compound to a target, using only the reactions in the AS syllabus, with the reagents and conditions for each step.

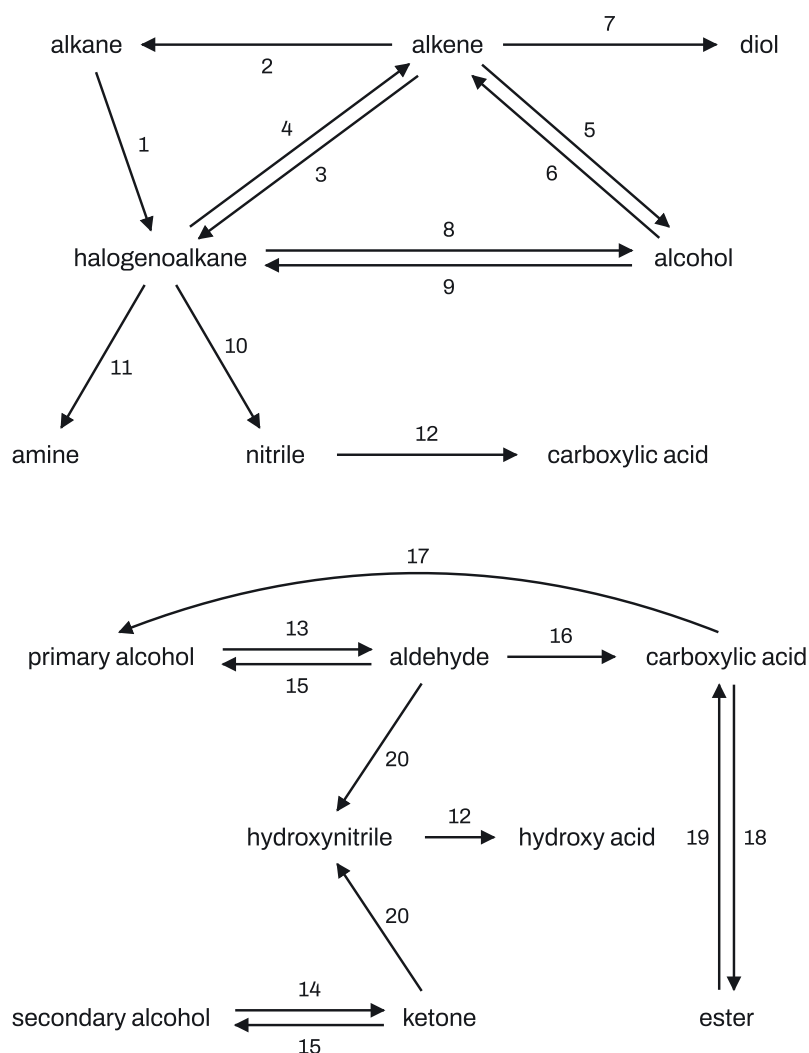
3. **Analyse a given route**: name the type of reaction in each step, give the reagents and conditions it needs, and suggest possible by-products.

This topic has no new reactions. It is about **using** the AS reactions together. Routes that use benzene, phenol, acyl chlorides, amides or amino acids belong to A Level organic synthesis.

Understand it

The reaction map

Every AS reaction turns one functional group into another. Put them together and you get a map. A synthesis is a path through it: each arrow is one step, and each step needs its own reagents and conditions.



The numbers match this table. Learn it: the exam gives you none of it.

#	Change	Reagents and conditions	Type of reaction
1	alkane → halogenoalkane	Cl ₂ or Br ₂ , ultraviolet light	free-radical substitution
2	alkene → alkane	H ₂ (g), Pt or Ni catalyst, heat	addition (hydrogenation)
3	alkene → halogenoalkane	HX(g) at room temperature, or X ₂ (gives a dihalide)	electrophilic addition
4	halogenoalkane → alkene	NaOH in ethanol , heat	elimination
5	alkene → alcohol	steam, H ₂ O(g), with H ₃ PO ₄ catalyst	electrophilic addition
6	alcohol → alkene	heated Al ₂ O ₃ , or heat with concentrated H ₂ SO ₄ or H ₃ PO ₄	dehydration (elimination)
7	alkene → diol	cold, dilute , acidified KMnO ₄	oxidation
8	halogenoalkane → alcohol	NaOH**(aq)***, heat	nucleophilic substitution (hydrolysis)
9	alcohol → halogenoalkane	HX(g); or KCl (KBr) with concentrated H ₂ SO ₄ or H ₃ PO ₄ ; or PCl ₃ and heat; or PCl ₅ ; or SOCl ₂	substitution

#	Change	Reagents and conditions	Type of reaction
10	halogenoalkane → nitrile	KCN in ethanol , heat	nucleophilic substitution
11	halogenoalkane → amine	NH ₃ in ethanol, heat under pressure	nucleophilic substitution
12	nitrile → carboxylic acid	dilute acid and heat (or dilute alkali and heat, then acidify)	hydrolysis
13	primary alcohol → aldehyde	acidified K ₂ Cr ₂ O ₇ (or acidified KMnO ₄), heat and distil	oxidation
14	secondary alcohol → ketone	acidified K ₂ Cr ₂ O ₇ (or acidified KMnO ₄), heat and distil	oxidation
15	aldehyde or ketone → alcohol	NaBH ₄ or LiAlH ₄	reduction
16	primary alcohol or aldehyde → carboxylic acid	acidified K ₂ Cr ₂ O ₇ (or acidified KMnO ₄), heat under reflux	oxidation
17	carboxylic acid → primary alcohol	LiAlH ₄	reduction
18	carboxylic acid + alcohol → ester	concentrated H ₂ SO ₄ catalyst, heat	condensation (esterification)
19	ester → carboxylic acid + alcohol	dilute acid, or dilute alkali, and heat (then acidify)	hydrolysis
20	aldehyde or ketone → hydroxynitrile	HCN with KCN catalyst, heat	nucleophilic addition

Two more that you need: **hot, concentrated**, acidified KMnO₄ splits an alkene at its C=C (a = CH₂ end becomes CO₂ and water, a = CHR end becomes RCOOH, and a = CRR' end becomes a ketone), and **cracking** (heat with Al₂O₃) breaks a long alkane into a shorter alkane and an alkene.

Tests that identify functional groups

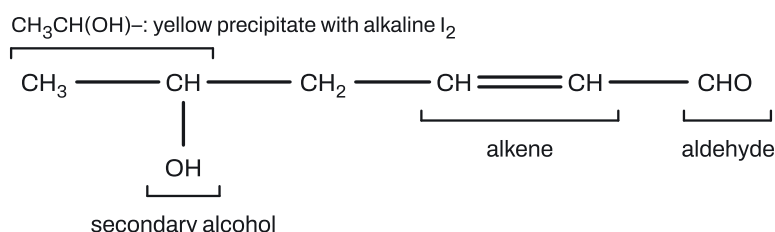
Reagent	Positive result	Shows
bromine water, Br ₂ (aq)	orange → colourless	C=C
2,4-DNPH	orange (yellow-orange or red) precipitate	C=O of an aldehyde or ketone
Tollens' reagent, warm	silver mirror	aldehyde only
Fehling's reagent, warm	blue solution → brick-red precipitate	aldehyde only
acidified K ₂ Cr ₂ O ₇ , warm	orange → green	primary or secondary alcohol, or aldehyde
alkaline I ₂ (aq), warm	yellow precipitate of CHI ₃	CH ₃ CO– or CH ₃ CH(OH)–
Na ₂ CO ₃ (aq)	effervescence of CO ₂	carboxylic acid, COOH

Reagent	Positive result	Shows
sodium metal	effervescence of H_2	any O–H: alcohol and carboxylic acid
$AgNO_3(aq)$ in ethanol, warm	white (Cl), cream (Br) or yellow (I) precipitate	halogenoalkane

A test is only useful if the result is **different** for the two things you are telling apart. Tertiary alcohols, ketones, carboxylic acids and alkenes all leave acidified $K_2Cr_2O_7$ orange.

A molecule with several groups

In a molecule with several functional groups, **each group reacts as it would on its own**. Work through the groups one at a time and ask, for each reagent, "does this group react with it?"



For 5-hydroxyhex-2-enal, $CH_3CH(OH)CH_2CH=CHCHO$:

Reagent	Result	Because of
$Br_2(aq)$	decolourised	$C=C$
2,4-DNPH	orange precipitate	CHO
Tollens' reagent	silver mirror	CHO
alkaline $I_2(aq)$	yellow precipitate	$CH_3CH(OH)-$
sodium	fizzes	O–H of the alcohol
$Na_2CO_3(aq)$	no visible change	there is no COOH
$NaBH_4$	gives $CH_3CH(OH)CH_2CH=CHCH_2OH$	reduces the CHO only
excess acidified $K_2Cr_2O_7$, reflux	gives $CH_3COCH_2CH=CHCOOH$	oxidises the CHO and the secondary alcohol

The skill is knowing **which groups each reagent touches**:

Reagent	Reacts with	Leaves alone
$NaBH_4$	aldehyde and ketone $C=O$	COOH, ester, $C=C$
$LiAlH_4$	aldehyde and ketone $C=O$, and COOH	$C=C$

Reagent	Reacts with	Leaves alone
H ₂ , Ni, heat	C=C	(at AS, use it only for C=C)
acidified K ₂ Cr ₂ O ₇	primary and secondary alcohols, aldehydes	tertiary alcohols, ketones, COOH, C=C
acidified KMnO ₄	the same groups, and C=C (cold and dilute: diol; hot and concentrated: split)	tertiary alcohols, ketones, COOH
Tollens' or Fehling's reagent	aldehyde only	everything else
Na	every O–H (alcohol and acid)	C=O, C=C, C–X
Na ₂ CO ₃	COOH only	alcohols
NaOH(aq), heat	COOH (neutralised), esters and C–X (hydrolysed)	C=C, alcohols

So to oxidise an alcohol in a molecule that also has a C=C, choose dichromate, not manganate(VII). To oxidise an aldehyde but keep a primary or secondary alcohol, use Tollens' or Fehling's reagent and then acidify. To reduce a C=O but keep a COOH, use NaBH₄, not LiAlH₄.

Why alcohols don't fizz with carbonate. A carboxylic acid is a much stronger acid than an alcohol: its anion, RCOO[–], spreads the negative charge over two oxygen atoms, so it gives up H⁺ easily. An alcohol is an even weaker acid than water, so it only reacts with something as reactive as sodium metal. Each COOH reacts with carbonate in the usual acid way, so a diacid uses one carbonate per molecule:



Counting with [O] and [H]

Equations for organic redox use [O] for an oxygen atom from the oxidising agent and [H] for a hydrogen atom from the reducing agent. Per group:

Change	Equation for one group
CH ₂ OH → CHO or CH(OH) → C=O	+ [O], gives H ₂ O
CHO → COOH	+ [O]
CH ₂ OH → COOH	+ 2[O], gives H ₂ O
CHO → CH ₂ OH or C=O → CH(OH)	+ 2[H]
COOH → CH ₂ OH	+ 4[H], gives H ₂ O

Add up over every group that reacts. For example, pentanedioic acid with excess LiAlH₄: two COOH groups, so $\text{HOOC}(\text{CH}_2)_3\text{COOH} + 8[\text{H}] \rightarrow \text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{OH} + 2\text{H}_2\text{O}$.

With sodium, **each O–H gives one H atom**, so 1 mol of a compound with *n* O–H groups gives $\frac{n}{2}$ mol of H₂.

Changing the carbon chain

Count the carbons in the start and the target first. Only two AS reactions make a new C–C bond, and each adds **one** carbon as C≡N:

- **KCN in ethanol** with a **halogenoalkane** (the CN replaces the halogen): $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9\text{CN}$, then hydrolysis gives pentanoic acid.
- **HCN with KCN catalyst** with an **aldehyde or ketone** (the CN and an OH go on the same carbon): butanone gives 2-hydroxy-2-methylbutanenitrile, then hydrolysis gives a **2-hydroxy acid**.

The two look alike, but they act on different groups and have different mechanisms. The nitrile then goes to COOH by hydrolysis (12).

Carbons are **lost** only when hot concentrated KMnO_4 splits a C=C, or in cracking.

Moving a group along the chain

No AS reaction moves an OH or a halogen directly. Instead, **eliminate to make a C=C, then add across it**. The addition follows **Markovnikov's rule**: the H goes to the C=C carbon that already has more H atoms, because this gives the more stable (more substituted) carbocation. So pentan-1-ol becomes pentan-2-ol:



Using HBr(g) in the second step instead gives 2-bromopentane. The same idea turns one halogen into two: eliminate, then add X_2 .

By-products

"Suggest a by-product" can mean an inorganic or an organic one.

- **Inorganic**: water from dehydration, oxidation and esterification; POCl_3 and HCl from PCl_5 (a vigorous reaction with every O–H, giving misty fumes of HCl); SO_2 and HCl from SOCl_2 ; H_3PO_3 from PCl_3 ; NaBr from NaOH and a bromoalkane; NH_4^+ (for example NH_4Cl) from acid hydrolysis of a nitrile; HX from free-radical substitution.
- **Organic**: the **minor** product of adding HX or water to an unsymmetrical alkene; other alkenes from elimination (a positional isomer, or cis and trans forms); an alkene formed by elimination while you wanted substitution; di- and tri-substituted products (and longer alkanes, from termination) in free-radical substitution.

Key facts and formulas

"Given" means it is in the 9701 Data Booklet. "Learn it" means you must remember it. Nothing about reagents or conditions is given.

Formula or fact	Status
Relative atomic masses: C 12.0, H 1.0, O 16.0	Given

Formula or fact	Status
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions	Given
The 20 reactions in the table above, with their reagents, conditions and types	Learn it
The tests and their positive results	Learn it
Which groups each reagent touches (NaBH_4 vs LiAlH_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ vs KMnO_4 , Na vs Na_2CO_3)	Learn it
New C–C bond: KCN in ethanol (halogenoalkane) or HCN/KCN (aldehyde or ketone), one carbon each	Learn it
Markovnikov: H adds to the C=C carbon with more H atoms	Learn it
Hot concentrated KMnO_4 : $=\text{CH}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$, $=\text{CHR} \rightarrow \text{RCOOH}$, $=\text{CRR}' \rightarrow \text{RCOR}'$	Learn it
[O] and [H] per group: $\text{COOH} \rightarrow \text{CH}_2\text{OH}$ needs 4[H] and gives H_2O	Learn it
Sodium: 1 mol of O–H groups gives $\frac{1}{2} \text{ mol H}_2$	Learn it

How to do it

We have tagged 30 questions on this topic from 2021–2025 (26 different, since some papers share questions). 5 of them mix more than one type, so the counts add up to more than 30.

Question type	Questions
Reagents and conditions for each step	17
Predict the reactions of a molecule with several groups	8
Identify the products of a sequence	6
Name the type of reaction in each step	6
Devise a route yourself	1

1. Reagents and conditions for each step (17 questions)

- Write the structure at every stage.** If an intermediate isn't given, compare the start and the product of the two steps and work out what must be in between.
- Say what changes in each step:** which group becomes which, and whether the carbon count changes.
- Find the arrow on the reaction map** and give its reagents.
- Write the reagent and the conditions:** the state (aqueous or in ethanol, gas), the catalyst, heat, and reflux or distil. "NaOH" alone is not enough.

Variations you will meet:

- A missing intermediate.** Moving a group or adding a second halogen needs elimination then addition. For example, 1-chlorobutane to 1,2-dibromobutane: NaOH in ethanol and heat (but-1-ene), then Br_2 at room temperature.

- **Changing the chain length.** One more carbon means KCN in ethanol (from a halogenoalkane) or HCN/KCN (from a carbonyl compound), then hydrolysis with dilute acid and heat.
- **Choose the pair that works** from four rows. Test each row step by step: does the first reagent really give the intermediate, and does the second give the target? Common traps: NaBH_4 cannot reduce a COOH ; aqueous NaOH gives an alcohol, not an alkene; Cl_2 adds two Cl atoms across a $\text{C}=\text{C}$ where HCl adds one; HBr adds by Markovnikov's rule, so check where the Br ends up.
- **More than one way to the same product.** A tertiary chloroalkane such as 2-chloro-2-methylbutane can come from 2-methylbut-2-ene with HCl(g) at room temperature (Markovnikov), from 2-methylbutan-2-ol with SOCl_2 or PCl_5 , or, as one of several products, from 2-methylbutane with Cl_2 in UV light. Check every listed route rather than stopping at the first that works.
- **Choosing a selective reagent** for a molecule with two groups (see type 2): for example Tollens' reagent to oxidise only an aldehyde.
- **Two portions of one starting material** that are joined at the end, usually as an ester: one portion is turned into the alcohol, the other into the acid, then concentrated H_2SO_4 and heat.

2. Predict the reactions of a molecule with several groups (8 questions)

1. **Find every group.** Classify each alcohol as primary, secondary or tertiary, and look for $\text{CH}_3\text{CO}-$ and $\text{CH}_3\text{CH(OH)}-$.
2. **Take each reagent in turn** and use the "reacts with / leaves alone" table. Change only the groups that react and copy the rest of the molecule unchanged.
3. **Count if asked:** O-H groups for sodium, COOH groups for carbonate, and $[\text{O}]$ or $[\text{H}]$ for a redox equation.

Variations you will meet:

- **Tests on pairs of compounds.** Pick a reagent that gives a positive result with one and not the other, and say which one it is and what you see. Write "no visible change" for a negative result, not "nothing".
- **Two reagents one after the other.** Do the first change completely, then apply the second reagent to the **new** molecule. Hydrolysing an ester (or a cyclic ester) with warm dilute acid makes a new OH **and** a new COOH ; cold dilute KMnO_4 then turns **each** $\text{C}=\text{C}$ into two more OH groups. Count them all.
- **How many H atoms react with sodium**, or how much H_2 : one per O-H, including the OH inside each COOH .
- **Which reagents turned X into these products?** Check each reagent against every group: acidified dichromate is wrong if a product still has a primary or secondary alcohol that it would have oxidised; sodium is not a reducing agent for $\text{C}=\text{O}$.
- **Tests before and after a reaction**, for example after heating with excess acidified KMnO_4 : aldehydes have become acids (no more Fehling's), secondary alcohols have become ketones (now positive with 2,4-DNPH), and any $\text{C}=\text{C}$ has been split.

3. Identify the products of a sequence (6 questions)

1. **Draw the product of each step** before moving on. Keep the carbon skeleton in view and count carbons at every step.
2. **For additions to an unsymmetrical alkene, use Markovnikov's rule** to get the major product.

3. **Name the final product** from its structure: longest chain containing the main group, lowest numbers.

Variations you will meet:

- **Working backwards.** If a compound gives a diacid and two alcohol molecules on hydrolysis, it is a diester: join each COOH to an alcohol OH and remove water. If one step made Y, ask which group in X could give Y's group with a single reagent.
- **Oxidising and reducing in turn**, for example acid $\rightarrow$ primary alcohol (LiAlH_4) $\rightarrow$ alkene (dehydration) $\rightarrow$ a **different** alcohol (steam adds by Markovnikov's rule, so the OH lands on the middle carbon).
- **Chain-lengthening sequences:** HBr to a branched alkene, then KCN, then hydrolysis. The COOH carbon is the new one, on the carbon that carried the Br.
- **Hot concentrated KMnO_4 on a larger molecule:** split at every C=C and use the end rules.

4. Name the type of reaction in each step (6 questions)

Compare the molecule before and after the step:

What happened	Type
atoms added across a C=C (or C=O), nothing lost	addition
one atom or group swapped for another	substitution
a small molecule (HX, H_2O) removed to make a C=C	elimination (dehydration if it is water)
a molecule split by water	hydrolysis
two molecules joined, water lost	condensation
O gained or H lost	oxidation
H gained or O lost	reduction

If the question asks for the mechanism type, add the attacking species: **electrophilic** addition (alkenes with HX, X_2 , steam), **nucleophilic** substitution (halogenoalkanes with OH^- , CN^- , NH_3), **nucleophilic** addition (HCN to C=O), **free-radical** substitution (alkanes with halogens and UV).

Variations you will meet:

- **Hydrogenation** is an addition and also a reduction; turning C=O into CH(OH) is a reduction.
- **Losing two H atoms to form a C=C** (with no H_2O or HX lost) counts as **oxidation**, not elimination.
- **Cold dilute KMnO_4** making a diol is oxidation, not addition, in these answers.
- **Ester hydrolysis** is hydrolysis; forming the ester is condensation (esterification).

5. Devise a route yourself (1 question)

1. **Compare start and target:** carbon count, groups, and their positions.
2. **Work backwards from the target.** Ask "what makes this group?" from the table, then "what makes that?", until you reach the starting compound.

3. **Write every step** as: reagent and conditions → the organic product (name or structure). Examiners want the product of **each** step, not just the last one.
4. **Check each step doesn't damage another group** in the molecule.

For an ester from one starting compound, split it: make the alcohol from one portion and the acid from another, then join them.

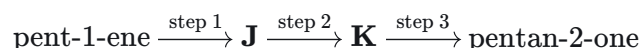
Worked examples

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

Pent-1-ene is converted into pentan-2-one in three steps.



- (a) Identify **J**, a bromoalkane, and **K**. **[2]**
 - (b) Give the reagents and conditions for each step. **[3]**
 - (c) Name the type of reaction in each step. **[3]**
 - (d) Suggest one organic by-product of step 1 and one of step 2. **[2]**
 - (e) Suggest a single step that could replace steps 1 and 2. **[1]**
- (a)** Pentan-2-one has its C=O on carbon 2, so the Br and then the OH must be on carbon 2. **J** is 2-bromopentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_3$ **B1**; **K** is pentan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)CH}_3$. **B1**
- (b)** Step 1: HBr(g) at room temperature. **B1** Step 2: NaOH(aq) , heat under reflux. **B1** Step 3: acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat and distil. **B1**
- (c)** Step 1: electrophilic addition. **B1** Step 2: nucleophilic substitution. **B1** Step 3: oxidation. **B1**
- (d)** Step 1: 1-bromopentane, the minor product (H adds to C2 instead of C1, through the less stable primary carbocation). **B1** Step 2: pent-1-ene or pent-2-ene, from elimination of HBr. **B1**
- (e)** Steam with H_3PO_4 catalyst, which adds water by Markovnikov's rule to give pentan-2-ol directly. **B1**

Example 2

Compound **L**, $\text{CH}_2=\text{CHCH(OH)CH}_2\text{COOH}$, is 3-hydroxypent-4-enoic acid.

- (a) For each of the three functional groups in **L**, give a reagent that reacts with it and the observation. **[3]**
- (b) 0.580 g of **L** reacts with an excess of sodium. Calculate the volume of hydrogen made at room conditions. **[3]**
- (c) Give the structure of the organic product when **L** reacts with: (i) LiAlH_4 ; (ii) H_2 and Ni with heat; (iii) an excess of hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$ under reflux. **[3]**
- (d) The product of (c)(i) does not react with $\text{Na}_2\text{CO}_3(\text{aq})$. Explain why. **[1]**
- (a)** $\text{C}=\text{C}$: bromine water turns from orange to colourless. **B1** COOH : $\text{Na}_2\text{CO}_3(\text{aq})$ gives effervescence. **B1**
Secondary alcohol: acidified $\text{K}_2\text{Cr}_2\text{O}_7$ turns from orange to green (there is no aldehyde to confuse this). **B1**
- (b)** $M_r(\text{C}_5\text{H}_8\text{O}_3) = 5(12.0) + 8(1.0) + 3(16.0) = 116.0$, so $n(\text{L}) = 0.580 \div 116.0 = 0.00500 \text{ mol}$. **M1**
- L** has two O–H groups (the alcohol and the acid), so 1 mol of **L** gives 1 mol of H_2 : $n(\text{H}_2) = 0.00500 \text{ mol}$. **M1**
- Volume = $0.00500 \times 24.0 = 0.120 \text{ dm}^3$, that is 120 cm^3 . **A1**
- (c)** (i) Only the COOH is reduced: $\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$, pent-4-ene-1,3-diol. **B1** (ii) Only the $\text{C}=\text{C}$ adds H_2 : $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{COOH}$. **B1** (iii) Only the secondary alcohol is oxidised; dichromate leaves the $\text{C}=\text{C}$: $\text{CH}_2=\text{CHCOCH}_2\text{COOH}$. **B1**
- (d)** It has no COOH . Alcohols are much weaker acids than carboxylic acids (weaker even than water), so they cannot release CO_2 from a carbonate. **B1**

Example 3

Devise a three-step synthesis of 2-hydroxy-2-methylbutanoic acid, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{COOH}$, from butan-2-ol. For each step, give the reagents and conditions, the organic product and the type of reaction. **[6]**

Then explain why KCN in ethanol cannot be used in the step that adds a carbon. **[1]**

Plan: butan-2-ol has 4 carbons and the target has 5, so one step must add a carbon as CN. The target has OH and COOH on the **same** carbon, which is the pattern from HCN adding to a $\text{C}=\text{O}$, then hydrolysis. So the route goes through butanone.

Step 1: acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat and distil, gives butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$: oxidation. **B1 B1**

Step 2: HCN with KCN catalyst, heat, gives 2-hydroxy-2-methylbutanenitrile, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CN}$: nucleophilic addition. **B1 B1**

Step 3: dilute HCl, heat under reflux, gives the target acid (and NH_4Cl): hydrolysis. **B1 B1**

KCN in ethanol substitutes the halogen in a **halogenoalkane**; butanone has no halogen. Adding to a $\text{C}=\text{O}$ needs HCN, with KCN only as the catalyst. **B1**

Example 4

Propyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$, is to be made using 1-bromopropane as the only organic starting material.

(a) Describe a synthesis in four steps. Give the reagents and conditions, and the organic product, for each step.

[6]

(b) Write an equation for the last step and calculate the M_r of propyl butanoate. [2]

(c) A student uses NaOH in ethanol for the step that should make the alcohol. Name the organic product and the type of reaction. [2]

(d) Give a test that tells butanoic acid apart from butanenitrile. [1]

(a) The ester splits into propan-1-ol (3 carbons) and butanoic acid (4 carbons). The alcohol keeps the chain; the acid needs one more carbon, so it goes through a nitrile.

Step 1 (first portion): NaOH(aq), heat under reflux, gives propan-1-ol. **B1**

Step 2 (second portion): KCN in ethanol, heat, gives butanenitrile, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$. **B1 B1**

Step 3: dilute HCl, heat under reflux, gives butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$. **B1 B1**

Step 4: butanoic acid and propan-1-ol, concentrated H_2SO_4 catalyst, heat. **B1**

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

$M_r(\text{C}_7\text{H}_{14}\text{O}_2) = 7(12.0) + 14(1.0) + 2(16.0) = 130.0$ **B1**

(c) Propene, $\text{CH}_3\text{CH}=\text{CH}_2$ **B1**, by elimination of HBr. **B1**

(d) Add $\text{Na}_2\text{CO}_3(\text{aq})$: butanoic acid gives effervescence of CO_2 ; butanenitrile gives no visible change. **B1**

Common mistakes

- **Mixing up the two cyanide reactions.** KCN in ethanol substitutes a halogen; HCN with KCN catalyst adds to a C=O. Examiners report that candidates regularly swap the reagents and conditions for these two steps.
- **Leaving out conditions.** "Heat" is often missing, and aqueous and ethanolic NaOH give different products. "Ethanolic" is not "ethanoic". In a devised route, examiners also want the organic product of each step, not just the reagents.
- **Forgetting a second group reacts.** Refluxing with acidified dichromate oxidises **every** primary and secondary alcohol and every aldehyde in the molecule, not just the one you are thinking about. A common wrong answer oxidises an aldehyde with dichromate while an alcohol elsewhere is meant to survive.
- **Not counting new OH groups.** Hydrolysing an ester gives an OH **and** a COOH, and cold dilute KMnO_4 gives two OH per C=C. Only a small share of candidates counted all of them in a question about sodium, and many forget that the alcohol OH reacts with sodium as well as the acid.
- **Forgetting that HBr substitutes an OH.** Warming an alcohol with excess HBr puts a Br where the OH was; it is not only an alkene reagent.
- **Using NaBH_4 for a carboxylic acid.** Only LiAlH_4 reduces COOH. Write its formula correctly: LiAlH_4 .
- **Unbalanced [O] and [H] equations.** Water is usually missing on the right, or $[\text{H}^+]$ or O_2 appears. Count atoms: $\text{COOH} \rightarrow \text{CH}_2\text{OH}$ uses 4[H] and makes H_2O .

- **Calling the wrong type.** Oxidation and reduction get swapped, and dehydration is often written as "hydrolysis". Use the before-and-after table.
- **Wrong names for reagents.** If you name an organic reagent rather than drawing it, the name must be exact, for example 3-methylbutan-1-ol, not 3-methylbutanol.

How to get the marks

- **"Reagents and conditions"** needs both: the reagent (with "acidified", "aqueous", "in ethanol", "concentrated" or "dilute" as needed) **and** the condition (heat, reflux or distil, catalyst, UV light, room temperature, pressure). One without the other usually loses the mark.
- **"State the reagent"** needs only the substance, but give it exactly. Formulas are safer than names.
- **"Identify the type of reaction"**: give the word the mark scheme uses: addition, substitution, elimination (or dehydration), hydrolysis, condensation, oxidation or reduction. Add electrophilic, nucleophilic or free-radical if the mechanism is asked for.
- **"Devise a route"**: one line per step with reagent, conditions and the organic product named or drawn. Marks are for each correct step, so a route with one weak step still scores for the others.
- **"Suggest"** means there may be more than one right answer, such as either by-product alkene; give one clearly.
- **Test tables**: name the reagent, the observation (colour **change** or precipitate, with its colour) and which compound gives it. Use a different reagent for each pair if the question says so.
- **Equations with [O] and [H]**: balance the organic part and add water where an O leaves the molecule.
- **Multiple choice**: draw the structure after every step and check each option against it; don't guess from the names.

Quick check

1. Give the reagents and conditions, and the type of reaction, for each step: 1-chlorobutane → butan-1-ol → butanal.
2. For 3-hydroxybutanal, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$, predict what you would see with (a) Tollens' reagent, (b) alkaline $\text{I}_2(\text{aq})$, (c) $\text{Na}_2\text{CO}_3(\text{aq})$.
3. Give a two-step route, with reagents and conditions, for each: (a) 1-iodobutane → pentanoic acid; (b) propanal → 2-hydroxybutanoic acid.
4. 2.12 g of butane-1,2,4-triol, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$ ($M_r = 106.0$), reacts with excess sodium. Calculate the volume of hydrogen at room conditions.
5. An alkene, C_7H_{14} , is heated with hot concentrated acidified KMnO_4 . The only organic products are butanone and propanoic acid. Identify the alkene.

Answers

- Step 1: NaOH(aq), heat under reflux; nucleophilic substitution. Step 2: acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat and **distil** off the butanal as it forms (so it is not oxidised further to butanoic acid); oxidation.
- (a) Silver mirror (it has a CHO). (b) Yellow precipitate of CHI_3 (it has $\text{CH}_3\text{CH}(\text{OH})-$). (c) No visible change (no COOH).
- (a) KCN in ethanol, heat, gives pentanenitrile, $\text{C}_4\text{H}_9\text{CN}$; then dilute acid, heat under reflux, gives pentanoic acid. (b) HCN with KCN catalyst, heat, gives 2-hydroxybutanenitrile, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$; then dilute acid, heat under reflux, gives $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}$.
- $n = 2.12 \div 106.0 = 0.0200$ mol. Three O–H groups, so $n(\text{H}_2) = 0.0200 \times \frac{3}{2} = 0.0300$ mol, and the volume is $0.0300 \times 24.0 = 0.720 \text{ dm}^3 = 720 \text{ cm}^3$.
- Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$, comes from a $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=$ end; propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, from a $=\text{CHCH}_2\text{CH}_3$ end. Joining them gives $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_3$, 3-methylhex-3-ene ($4 + 3 = 7$ carbons).

Past questions to try

- 9701/22/O/N/23 Q4**: part (b), two three-step routes to the same acid, with reagents for every step.
- 9701/22/O/N/22 Q3**: part (d), devise a route to an ester from a single starting compound.
- 9701/13/M/J/23 Q35**: following HBr, KCN and hydrolysis on a branched alkene.
- 9701/13/O/N/22 Q29**: counting O–H groups after hydrolysis and cold KMnO_4 .