

Hydroxy compounds

AS

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

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What you need to know

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

1. **Recall how alcohols are made** (reagents and conditions):

- (a) **electrophilic addition of steam** to an alkene: $\text{H}_2\text{O}(\text{g})$ with an H_3PO_4 catalyst;
- (b) an alkene with **cold, dilute, acidified** KMnO_4 , giving a **diol** (two OH groups);
- (c) **substitution of a halogenoalkane** with $\text{NaOH}(\text{aq})$ and heat;
- (d) **reduction of an aldehyde or ketone** with NaBH_4 or LiAlH_4 ;
- (e) **reduction of a carboxylic acid** with LiAlH_4 ;
- (f) **hydrolysis of an ester** by heating with dilute acid or dilute alkali.

2. **Describe the reactions of alcohols:**

- (a) **combustion** in oxygen;
- (b) **substitution to halogenoalkanes**, with $\text{HX}(\text{g})$; KCl and concentrated H_2SO_4 or H_3PO_4 ; PCl_3 and heat; PCl_5 ; or SOCl_2 ;
- (c) the reaction with **sodium**;
- (d) **oxidation** with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified KMnO_4 : to a carbonyl compound by **distillation**, to a carboxylic acid by **heating under reflux**. Primary alcohols give aldehydes, which can be oxidised further to carboxylic acids; secondary alcohols give ketones; tertiary alcohols are not oxidised;
- (e) **dehydration** to an alkene over heated Al_2O_3 or with a concentrated acid;
- (f) **ester formation** with a carboxylic acid and a concentrated H_2SO_4 catalyst (ethanol is the example).

3. (a) **Classify** alcohols as primary, secondary or tertiary, including molecules with more than one OH group;
(b) give **tests that tell them apart**, such as mild oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (orange to green).

4. **Deduce a $\text{CH}_3\text{CH}(\text{OH})-$ group** from the reaction with alkaline $\text{I}_2(\text{aq})$, which gives a yellow precipitate of tri-iodomethane, CHI_3 , and a carboxylate ion, RCO_2^- .

5. **Explain why alcohols are less acidic than water.**

Understand it

What an alcohol is

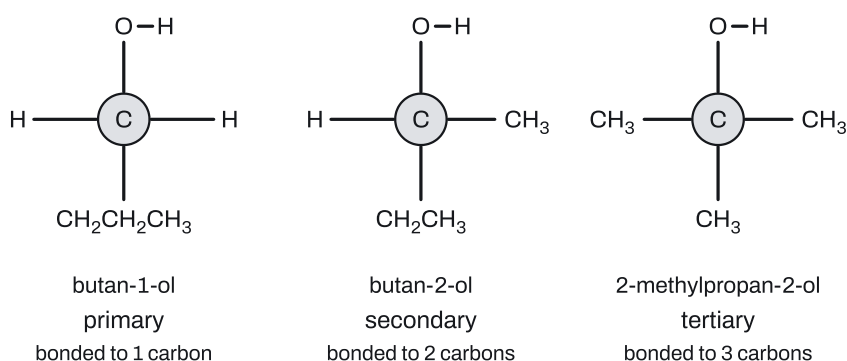
An **alcohol** contains an –OH group (a **hydroxy** group) bonded to a carbon that has only single bonds. The general formula of the simple alcohols is $C_nH_{2n+1}OH$. Name them from the alkane, ending in **-ol**, with the lowest number for the OH: $CH_3CH_2CH(OH)CH_3$ is butan-2-ol. Two OH groups make a **diol** (ethane-1,2-diol, $HOCH_2CH_2OH$); three make a triol.

The O–H bond is polar, so alcohols form **hydrogen bonds** with each other and with water. That is why they boil much higher than alkanes of similar size, and why the small ones mix with water.

Primary, secondary and tertiary

Classify an OH group by the carbon it sits on, the **carbinol carbon**. Count how many **other carbon atoms** are bonded to that carbon:

Class	Carbinol carbon bonded to	Carbinol carbon carries	Example
Primary (1°)	one other carbon (or none, in methanol)	two H (three in methanol)	butan-1-ol, $CH_3CH_2CH_2CH_2OH$
Secondary (2°)	two other carbons	one H	butan-2-ol, $CH_3CH_2CH(OH)CH_3$
Tertiary (3°)	three other carbons	no H	2-methylpropan-2-ol, $(CH_3)_3COH$



A branch does not change the class unless it is on the carbinol carbon: 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$, is primary. In a molecule with several OH groups, classify **each one separately**: butane-1,3-diol, $HOCH_2CH_2CH(OH)CH_3$, has one primary and one secondary OH.

The class matters most in oxidation, because oxidation removes a **hydrogen from the carbinol carbon**. Primary has two to lose, secondary one, tertiary none.

Making alcohols

Starting material	Reagent and conditions	Type of reaction	Example
Alkene	H ₂ O(g) (steam), H ₃ PO ₄ catalyst, high temperature and pressure	electrophilic addition	$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$
Alkene	cold, dilute, acidified KMnO ₄	oxidation (addition of two OH)	$\text{CH}_2=\text{CH}_2 + [\text{O}] + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{CH}_2\text{OH}$
Halogenoalkane	NaOH(aq), heat under reflux	nucleophilic substitution	$\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$
Aldehyde	NaBH ₄ or LiAlH ₄	reduction	$\text{CH}_3\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{OH}$
Ketone	NaBH ₄ or LiAlH ₄	reduction	$\text{CH}_3\text{COCH}_3 + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
Carboxylic acid	LiAlH ₄ (in dry ether)	reduction	$\text{CH}_3\text{COOH} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$
Ester	dilute acid, heat under reflux	hydrolysis	$\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}$
Ester	dilute alkali, e.g. NaOH(aq), heat under reflux	hydrolysis	$\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{CH}_3\text{CH}_2\text{OH}$

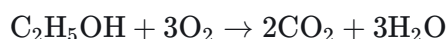
Points worth knowing:

- **Steam on an unsymmetrical alkene** gives two alcohols. Propene gives mainly propan-2-ol (the OH goes to the carbon that makes the more stable, secondary carbocation) and some propan-1-ol.
- **The KMnO₄ reaction** turns purple to colourless. It must be **cold and dilute**: hot, concentrated KMnO₄ breaks the C=C bond instead (Hydrocarbons).

- **Which reduces what.** NaBH_4 reduces aldehydes and ketones only. LiAlH_4 is stronger and also reduces carboxylic acids. So an aldehyde gives a primary alcohol, a ketone a secondary alcohol and a carboxylic acid a primary alcohol with the **same number of carbons**.
- **[H] equations.** [H] stands for one hydrogen atom from the reducing agent. $\text{C}=\text{O}$ to $\text{CH}-\text{OH}$ needs 2[H]. COOH to CH_2OH needs 4[H] and also makes H_2O . Add them up for each group in the molecule.
- **Alkaline hydrolysis** gives the **salt** of the acid (sodium ethanoate), not the acid itself.

Combustion

Alcohols burn in plenty of oxygen to carbon dioxide and water, which is why ethanol is used as a fuel:



For any alcohol $\text{C}_n\text{H}_{2n+1}\text{OH}$, 1 mol needs $\frac{3n}{2}$ mol of O_2 and gives n mol of CO_2 and $n + 1$ mol of H_2O . Balance C, then H, then O last, remembering the O already in the alcohol.

Substitution: alcohols to halogenoalkanes

The $-\text{OH}$ is replaced by a halogen atom. For chloroalkanes:

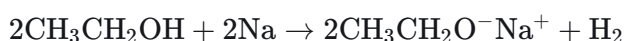
Reagent and conditions	Equation (R = alkyl group)	What you see
HCl(g) (or KCl with concentrated H_2SO_4 or H_3PO_4 , which makes HCl in the flask)	$\text{ROH} + \text{HCl} \rightarrow \text{RCl} + \text{H}_2\text{O}$	
PCl_3 , heat	$3\text{ROH} + \text{PCl}_3 \rightarrow 3\text{RCl} + \text{H}_3\text{PO}_3$	
PCl_5 , room temperature	$\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$	steamy (misty) fumes of HCl
SOCl_2 , room temperature	$\text{ROH} + \text{SOCl}_2 \rightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$	two acidic gases given off

Bromoalkanes are made the same way, for example with KBr and concentrated H_2SO_4 , or PBr_3 . **Every** OH group is replaced: propane-1,3-diol with excess PCl_5 gives 1,3-dichloropropane.

The PCl_5 reaction is a **test for an $-\text{OH}$ group**: steamy fumes that turn damp blue litmus red. The sample must be dry, because water also has an OH and reacts. Carboxylic acids ($-\text{COOH}$) give the fumes too, so the test shows an OH group, not that the compound is an alcohol. Aqueous KCl or dilute HCl on their own do **not** turn an alcohol into a chloroalkane.

Reaction with sodium

Sodium fizzes gently in an alcohol and slowly disappears. It gives hydrogen and a **sodium alkoxide**:



- **Observations:** effervescence (bubbles) and the sodium getting smaller; the gas "pops" with a lighted splint.

- **Sodium is the reducing agent:** it loses electrons ($\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$) and the H of the O–H is reduced to H_2 . The reaction is redox.
- **Counting OH groups.** Each OH gives $\frac{1}{2}$ mol of H_2 per mol of compound. A diol gives 1 mol of H_2 per mol, a triol $1\frac{1}{2}$ mol. Use $n = V \div 24.0 \text{ dm}^3$ for the gas at room conditions.
- Carboxylic acids react with sodium too. To tell an alcohol from an acid, use $\text{Na}_2\text{CO}_3(\text{aq})$: only the acid fizzes (gives CO_2).

Why alcohols are less acidic than water

Water and alcohols can both lose H^+ from an O–H bond, giving OH^- and RO^- . Sodium reacts **more slowly** with ethanol than with water, so ethanol gives up its H^+ less readily: it is a weaker acid.

The reason is the **alkyl group**. Alkyl groups are **electron-donating** (the **positive inductive effect**). The ethyl group pushes electron density towards the oxygen. This:

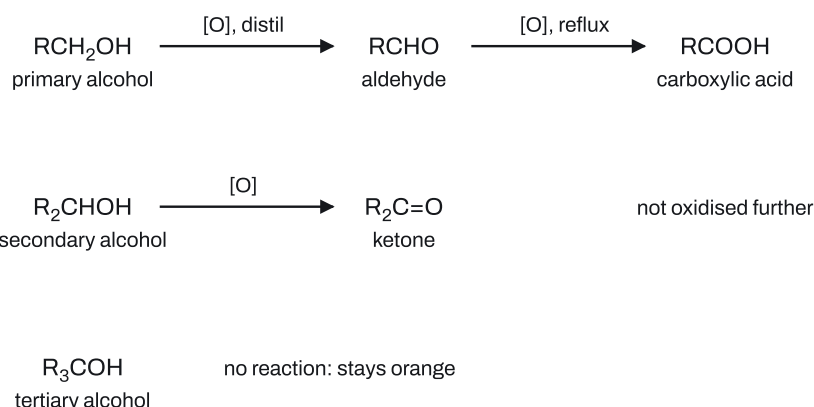
- strengthens the O–H bond, making the H^+ less likely to leave;
- concentrates the negative charge on the O of the ethoxide ion, making $\text{CH}_3\text{CH}_2\text{O}^-$ **less stable** than OH^- .

So the ethoxide ion is a **stronger base** than the hydroxide ion: it holds on to H^+ more strongly. Its charge sits on the one oxygen atom; it is not delocalised. Alcohols are so weakly acidic that they do not change the colour of litmus and do not react with carbonates.

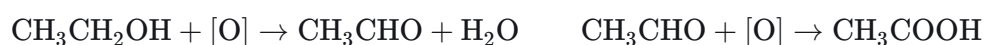
Oxidation

Acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 , is the usual oxidising agent. As it oxidises the alcohol, the orange $\text{Cr}_2\text{O}_7^{2-}$ is reduced to green Cr^{3+} : **orange to green**. Acidified KMnO_4 works too: **purple to colourless**. In equations, write $[\text{O}]$ for one oxygen atom from the oxidising agent.

Oxidation by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (orange to green)

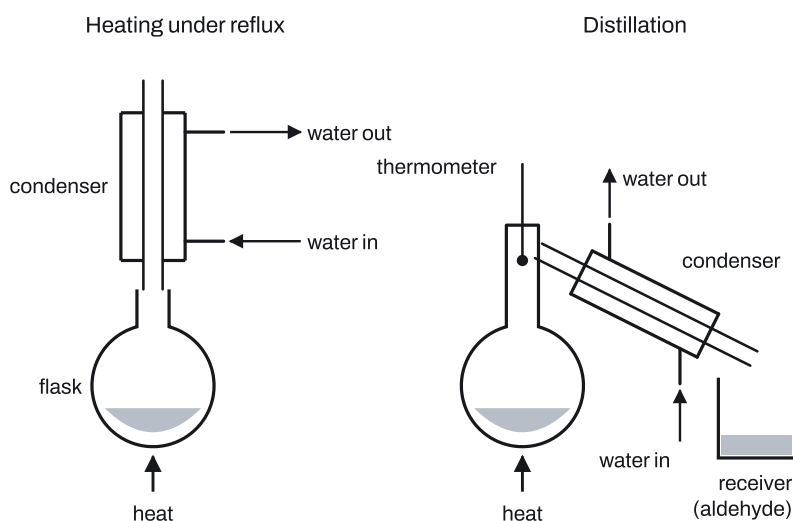


Primary alcohols are oxidised in two stages:



Overall to the acid: $\text{CH}_3\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$.

- **To stop at the aldehyde, distil it off as it forms.** Aldehydes boil lower than their alcohols (they have no O–H, so no hydrogen bonds between their molecules), so ethanal escapes from the warm mixture before it meets more oxidising agent. Use an excess of alcohol.
- **To get the carboxylic acid, heat under reflux** with an excess of oxidising agent. The vapour condenses and runs back into the flask, so the aldehyde stays in contact with the oxidising agent until it is fully oxidised, and nothing volatile escapes.



Secondary alcohols give **ketones**, which are not oxidised further:

$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$ (propanone). Reflux or distillation gives the same product.

Tertiary alcohols are **not oxidised**. The carbinol carbon has no H to lose, so the dichromate **stays orange**.

Molecules with more than one group. Treat each group on its own:

- every primary OH becomes COOH under reflux, and every secondary OH becomes C=O; a tertiary OH stays;
- an aldehyde group (CHO) already in the molecule is oxidised to COOH too;
- a C=C bond is **not** touched by acidified $\text{K}_2\text{Cr}_2\text{O}_7$. Hot, concentrated acidified KMnO_4 is harsher: it oxidises the OH groups **and** breaks C=C bonds. So pent-3-en-1-ol, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$, refluxed with excess dichromate gives $\text{CH}_3\text{CH}=\text{CHCH}_2\text{COOH}$, but with hot concentrated KMnO_4 it gives CH_3COOH and $\text{HOOCCH}_2\text{COOH}$.

Telling alcohols apart

Test	Primary	Secondary	Tertiary
Warm with acidified $\text{K}_2\text{Cr}_2\text{O}_7$	orange → green	orange → green	stays orange
Product after distilling	aldehyde	ketone	none
Warm with alkaline $\text{I}_2(\text{aq})$	yellow precipitate only for ethanol	yellow precipitate only if $\text{CH}_3\text{CH}(\text{OH})-$	no precipitate

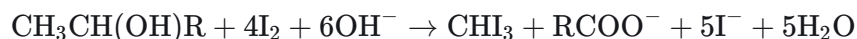
To tell a primary from a secondary alcohol, oxidise it and test the product: an aldehyde is oxidised further (for example by Fehling's or Tollens' reagent, which you will meet in Carbonyl compounds), a ketone is not; after reflux, only the acid from a primary alcohol fizzes with Na_2CO_3 .

The tri-iodomethane (iodoform) test

Warm the alcohol with iodine and sodium hydroxide solution (alkaline $\text{I}_2(\text{aq})$). A **pale yellow precipitate** of **tri-iodomethane**, CHI_3 (antiseptic smell), shows the group



that is, a carbinol carbon carrying an H and a CH_3 group. The CH_3 becomes CHI_3 , and the rest of the molecule leaves as a **carboxylate ion with one carbon fewer** than the alcohol:



Alcohol	R	Products
ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	H	CHI_3 + methanoate, HCOO^-
propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	CH_3	CHI_3 + ethanoate, CH_3COO^-
butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	CH_2CH_3	CHI_3 + propanoate, $\text{CH}_3\text{CH}_2\text{COO}^-$

Positive: ethanol, and secondary alcohols with a CH_3 on the carbinol carbon (propan-2-ol, butan-2-ol, pentan-2-ol, 3-methylbutan-2-ol). **Negative:** every other primary alcohol (the carbinol carbon has two H, no CH_3), secondary alcohols such as pentan-3-ol, and all tertiary alcohols. Ethanal and methyl ketones, $\text{CH}_3\text{CO}-$, also give the precipitate, because the iodine first oxidises $\text{CH}_3\text{CH}(\text{OH})-$ to $\text{CH}_3\text{CO}-$.

Dehydration to alkenes

Removing a water molecule from an alcohol gives an alkene. Either pass the alcohol vapour over **heated aluminium oxide**, Al_2O_3 , or heat the alcohol with **concentrated** H_2SO_4 or H_3PO_4 (the acid is a catalyst):



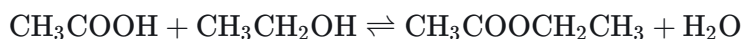
This is an **elimination** (dehydration). The OH leaves from the carbinol carbon and an H leaves from a **neighbouring** carbon, and the $\text{C}=\text{C}$ forms between them. It works in the same way as elimination from a halogenoalkane, so count the products the same way:

1. Find every neighbouring carbon that carries at least one H. Each different one gives a different alkene.
2. Check each alkene for **cis/trans isomers**: both $\text{C}=\text{C}$ carbons must carry two different groups.

Butan-2-ol has two different neighbours: losing H from C1 gives but-1-ene; losing H from C3 gives but-2-ene, which has cis and trans forms. That is **3** alkenes. Butan-1-ol has one neighbour, so it gives only but-1-ene. An alcohol whose carbinol carbon has no neighbouring C-H, such as 2,2-dimethylpropan-1-ol, cannot be dehydrated to an alkene.

Esters

An alcohol and a carboxylic acid, heated with a few drops of **concentrated** H_2SO_4 as a **catalyst**, give an **ester** and water:



This is **esterification**, a **condensation** reaction (two molecules join and lose water). It is reversible, so the yield is below 100%. Name the ester **alcohol part first**, then the acid part ending in **-oate**: ethanol and ethanoic acid give **ethyl ethanoate**; methanol and propanoic acid give methyl propanoate. The sulfuric acid is in the same phase as the reactants: a **homogeneous** catalyst.

Key facts and formulas

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

Formula or fact	Status
Relative atomic masses: C 12.0, H 1.0, O 16.0, Na 23.0, Cl 35.5	Given
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions	Given
Primary: carbinol C bonded to 1 other C; secondary: 2; tertiary: 3	Learn it
Primary $\xrightarrow{[\text{O}]}$ aldehyde (distil) $\xrightarrow{[\text{O}]}$ carboxylic acid (reflux); secondary $\rightarrow$ ketone; tertiary: no reaction	Learn it
Acidified $\text{K}_2\text{Cr}_2\text{O}_7$: orange $\rightarrow$ green; acidified KMnO_4 : purple $\rightarrow$ colourless	Learn it
$\text{RCH}_2\text{OH} + 2[\text{O}] \rightarrow \text{RCOOH} + \text{H}_2\text{O}$; $\text{RCH}_2\text{OH} + [\text{O}] \rightarrow \text{RCHO} + \text{H}_2\text{O}$	Learn it
$\text{C}=\text{O} \rightarrow \text{CH}-\text{OH}$: $2[\text{H}]$ (NaBH_4 or LiAlH_4); $\text{COOH} \rightarrow \text{CH}_2\text{OH}$: $4[\text{H}] + \text{H}_2\text{O}$ (LiAlH_4 only)	Learn it
$2\text{ROH} + 2\text{Na} \rightarrow 2\text{RO}^-\text{Na}^+ + \text{H}_2$: $\frac{1}{2}$ mol H_2 per OH	Learn it
$\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$; $\text{ROH} + \text{SOCl}_2 \rightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$; $3\text{ROH} + \text{PCl}_3 \rightarrow 3\text{RCl} + \text{H}_3\text{PO}_3$	Learn it
$\text{C}_n\text{H}_{2n+1}\text{OH} + \frac{3n}{2}\text{O}_2 \rightarrow n\text{CO}_2 + (n+1)\text{H}_2\text{O}$	Learn it
Dehydration: heated Al_2O_3 , or conc. H_2SO_4 or H_3PO_4 and heat	Learn it
Esterification: acid + alcohol $\rightleftharpoons$ ester + H_2O , conc. H_2SO_4 catalyst, heat	Learn it

Formula or fact	Status
$\text{CH}_3\text{CH}(\text{OH})\text{R} + \text{alkaline I}_2 \rightarrow \text{CHI}_3 \text{ (yellow precipitate)} + \text{RCOO}^-$	Learn it
Alcohols are less acidic than water: the alkyl group is electron-donating	Learn it
Percentage yield = $\frac{\text{actual amount}}{\text{theoretical amount}} \times 100$	Learn it

How to do it

We have tagged 91 questions on this topic from 2021–2025 (77 different, since some papers share questions). 46 of them mix more than one type, so the counts add up to more than 91.

Question type	Questions
Predict oxidation products, conditions and observations	44
Use the tri-iodomethane test	20
Deduce a structure from test results, or choose a test	17
Convert an alcohol to a halogenoalkane	16
Reaction with sodium	16
Dehydrate an alcohol to alkenes	15
Make an alcohol: reagents, conditions and [H] equations	14
Classify alcohols as primary, secondary or tertiary	8
Form an ester	6
Write or use a combustion equation	4
Explain why alcohols are less acidic than water	4

1. Predict oxidation products, conditions and observations (44 questions)

- Find every group that can be oxidised** and classify each OH: primary, secondary or tertiary. Note any CHO and C=C too.
- Read the conditions.** Distillation (or "mild", "limited oxidising agent") stops a primary OH at CHO. Heating under reflux with an excess of oxidising agent takes it to COOH, and turns any CHO into COOH as well.
- Write the product:** primary $\rightarrow$ CHO or COOH; secondary $\rightarrow$ C=O; tertiary unchanged; C=C unchanged by $\text{K}_2\text{Cr}_2\text{O}_7$.
- Observation:** orange to green if anything was oxidised; stays orange if nothing was.
- Equation:** count the [O] as 1 for each $\text{OH} \rightarrow \text{C=O}$ or $\text{CHO} \rightarrow \text{COOH}$ step, and 2 for each primary $\text{OH} \rightarrow \text{COOH}$. Each $\text{OH} \rightarrow \text{C=O}$ step also makes one H_2O .

Variations you will meet:

- **"Reagents and conditions"** for the acid: "acidified potassium dichromate(VI), heat under reflux". For the aldehyde: "acidified potassium dichromate(VI), warm, distil off the product as it forms".
- **Molecular formula of the product.** Each primary $\text{OH} \rightarrow \text{COOH}$ swaps H_2 for O; each $\text{OH} \rightarrow \text{C=O}$ loses H_2 . So butane-1,3-diol, $\text{C}_4\text{H}_{10}\text{O}_2$, refluxed with excess dichromate gives $\text{CH}_3\text{COCH}_2\text{COOH}$, $\text{C}_4\text{H}_6\text{O}_3$, using $3[\text{O}]$.
- **Work backwards from the equation.** Match **both** the $[\text{O}]$ count and the H_2O count: $\text{CH}_2\text{OH} \rightarrow \text{COOH}$ uses $2[\text{O}]$ and makes $1 \text{H}_2\text{O}$; any $\text{OH} \rightarrow \text{C=O}$ uses $1[\text{O}]$ and makes $1 \text{H}_2\text{O}$; $\text{CHO} \rightarrow \text{COOH}$ uses $1[\text{O}]$ and makes no H_2O . So " $\text{X} + 3[\text{O}] \rightarrow \text{Y} + \text{H}_2\text{O}$ " fits a CH_2OH and a CHO both becoming COOH ($2 + 1 = 3[\text{O}]$, $1 + 0 = 1 \text{H}_2\text{O}$), or one $\text{OH} \rightarrow \text{C=O}$ plus two $\text{CHO} \rightarrow \text{COOH}$. A primary $\text{OH} \rightarrow \text{COOH}$ plus a secondary $\text{OH} \rightarrow \text{C=O}$ also uses $3[\text{O}]$ but makes $2 \text{H}_2\text{O}$, so it does not fit. Test each option by counting both.
- **Hot concentrated acidified KMnO_4** also splits C=C bonds; $\text{K}_2\text{Cr}_2\text{O}_7$ doesn't.
- **Boiling points.** An aldehyde or ketone boils **lower** than its alcohol (no hydrogen bonding between its molecules); a carboxylic acid boils **higher** (it hydrogen-bonds strongly). So a product with a lower boiling point after reflux comes from a secondary alcohol (a ketone).
- **Percentage composition or mass.** Work out the product's formula, then its M_r . For a yield, 1 mol of alcohol gives 1 mol of product (Example 1).
- **Redox language.** The alcohol is oxidised; the dichromate is the oxidising agent and is reduced (Cr from +6 to +3).

2. Use the tri-iodomethane test (20 questions)

1. **Look at the carbinol carbon.** Does it carry an H **and** a CH_3 group? (Ethanol counts: its carbinol carbon is CH_2 next to CH_3 .) If yes, the test is positive.
2. **Observation:** pale yellow precipitate.
3. **Products:** CHI_3 and RCOO^- , where R is everything on the carbinol carbon except the CH_3 , the H and the OH. The carboxylate has **one carbon fewer** than the alcohol.

Variations you will meet:

- **Counting positive isomers.** List every alcohol with the formula, keep those with $\text{CH}_3\text{CH}(\text{OH})-$, then add stereoisomers if asked: the carbinol carbon of $\text{CH}_3\text{CH}(\text{OH})\text{R}$ is **chiral** whenever R is not CH_3 or H, so it counts twice. For $\text{C}_4\text{H}_{10}\text{O}$: only butan-2-ol is positive, and it has 2 optical isomers.
- **Combined with oxidation.** "X is oxidised to Y, which gives a yellow precipitate": Y is a methyl ketone or ethanal, so X is ethanol or a $\text{CH}_3\text{CH}(\text{OH})-$ alcohol. A methyl ketone also gives an orange precipitate with 2,4-DNPH (Carbonyl compounds).
- **Distinguish two isomers.** If only one has $\text{CH}_3\text{CH}(\text{OH})-$, alkaline I_2 is the test: it is often the only reagent in the options that gives different results.

3. Deduce a structure from test results, or choose a test (17 questions)

1. **Read each result as a fact:**

Result	Means
Acidified $K_2Cr_2O_7$ stays orange	no primary or secondary OH, no CHO (tertiary alcohol, ketone, ether, acid or alkane)
Orange $\rightarrow$ green	primary or secondary OH, or CHO
Yellow precipitate with alkaline I_2	$CH_3CH(OH)-$ (or CH_3CO-)
Fizzes with Na, not with Na_2CO_3	OH but no COOH
Fizzes with Na_2CO_3	COOH
Steamy fumes with PCl_5	OH (alcohol or acid)
Decolourises bromine water	$C=C$

2. **Draw every isomer** with the formula, then cross out those that fail a result.

3. **Answer what is asked:** a name, a structural formula or a displayed formula.

Choosing a test for a pair: find a group one has and the other lacks, give the reagent, the positive result, and which compound shows it. Use a **different reagent** for each pair if the question says so. Examples: tertiary vs primary alcohol, acidified $K_2Cr_2O_7$; butan-2-ol vs butan-1-ol, alkaline I_2 ; alcohol vs carboxylic acid, Na_2CO_3 ; alcohol vs ether, sodium.

4. Convert an alcohol to a halogenoalkane (16 questions)

- Reagent:** PCl_5 or $SOCl_2$ (room temperature), PCl_3 with heat, $HCl(g)$, or KCl with concentrated H_2SO_4 .
For bromoalkanes, KBr with concentrated H_2SO_4 .
- Type of reaction:** substitution (the OH is replaced).
- Product:** put the halogen exactly where each OH was; name it (propane-1,2-diol and excess PCl_5 give 1,2-dichloropropane).
- Equation:** use the table in "Understand it". Inorganic products: $POCl_3 + HCl$ (PCl_5), $SO_2 + HCl$ ($SOCl_2$), H_3PO_3 (PCl_3).

Variations you will meet: "which reagents give an acidic gas quickly?" (PCl_5 and $SOCl_2$, both HCl); "what can be deduced from misty fumes with PCl_5 ?" (only that there is an OH group, alcohol **or** acid); a step in a longer route, followed by KCN or $NaOH$ (Halogen compounds).

5. Reaction with sodium (16 questions)

- Equation:** $2ROH + 2Na \rightarrow 2RONa + H_2$; name the product (sodium ethoxide, sodium propan-2-oxide...).
- Observations:** fizzing (bubbles of a colourless gas), sodium disappears.
- Gas:** hydrogen. **Role of Na:** reducing agent (it donates electrons).

Variations you will meet:

- **Count OH groups from moles of H_2 :** number of OH = $2 \times \frac{\text{mol } H_2}{\text{mol compound}}$. 0.0020 mol of a compound giving 48.0 cm^3 (0.0020 mol) of H_2 has 2 OH (or COOH) groups.
- **Every OH and COOH reacts** in a molecule with both: citric-acid-like molecules lose the H from each.
- **Na fizzes but Na_2CO_3 does not** → alcohol, not acid.

6. Dehydrate an alcohol to alkenes (15 questions)

1. **Reagent and conditions:** heated Al_2O_3 , or concentrated H_2SO_4 (or H_3PO_4) and heat. The acid is a catalyst.
2. **Type:** elimination (dehydration).
3. **Products:** mark the carbinol carbon and each neighbouring carbon with an H. One alkene per different neighbour.
4. **Stereoisomers:** check each alkene for cis/trans and add them in.

Variations you will meet:

- **"How many isomeric alkenes?"** with structural and stereoisomerism: follow steps 3 and 4 and add up (Example 4).
- **Ring alcohols.** The C=C can form on either side of the carbinol carbon in the ring, and towards a side chain if that carbon has an H there. A C=C inside a small ring has no cis/trans pair (the ring holds it cis), but check whether a ring carbon in the product is chiral.
- **Work back from the products.** "Only two products (including stereoisomers)" means one neighbour giving a cis/trans pair, or two neighbours with no cis/trans.
- M_r of the alkene is the alcohol's M_r minus 18.0.

7. Make an alcohol: reagents, conditions and [H] equations (14 questions)

1. **Identify the starting group:** alkene, halogenoalkane, aldehyde, ketone, carboxylic acid or ester.
2. **Give the reagent and conditions from the table** in "Understand it": steam and H_3PO_4 ; cold dilute acidified $KMnO_4$; $NaOH(aq)$ and heat; $NaBH_4$ or $LiAlH_4$; $LiAlH_4$ for acids; dilute acid or alkali and heat for esters.
3. **Balance [H] equations:** 2[H] per C=O, 4[H] and one H_2O per COOH.

Variations you will meet:

- **A diacid** such as $HOOCCH_2COOH$ needs 8[H] and gives $2H_2O$:
 $HOOCCH_2COOH + 8[H] \rightarrow HOCH_2CH_2CH_2OH + 2H_2O$.
- **Role of $LiAlH_4$ or $NaBH_4$:** reducing agent. $NaBH_4$ is the wrong choice for a COOH group.
- **Two alcohols from one alkene** with steam: draw both (propene gives propan-1-ol and propan-2-ol).
- **Name the alkene** that gives a diol: the two OH groups sit on the two old C=C carbons.

8. Classify alcohols as primary, secondary or tertiary (8 questions)

1. **Circle each carbinol carbon.**
2. **Count the carbons bonded to it:** 1 (or 0) primary, 2 secondary, 3 tertiary. In a ring, the two ring neighbours count.
3. **Count each class** in a molecule with many OH groups.

Counting isomers by class. Draw the carbon skeletons, then place the OH on each different carbon. For $C_4H_{10}O$: butan-1-ol and 2-methylpropan-1-ol (primary), butan-2-ol (secondary), 2-methylpropan-2-ol (tertiary): **2, 1 and 1**. For $C_5H_{12}O$ there are 8 alcohols: 4 primary, 3 secondary and 1 tertiary.

9. Form an ester (6 questions)

1. **Reagents and conditions:** the carboxylic acid and the alcohol, a few drops of concentrated H_2SO_4 , heat.
2. **Type:** condensation (esterification). The other product is water.
3. **Structure:** join the acid's $C=O$ carbon to the alcohol's O: $RCOOR'$. Name it alcohol part first (ethyl, methyl...), then acid part (-oate).
4. **Role of H_2SO_4 :** catalyst (homogeneous).

10. Write or use a combustion equation (4 questions)

1. Write the formula as $C_xH_yO_z$.
2. O_2 needed per mol = $x + \frac{y}{4} - \frac{z}{2}$. Products: $x CO_2$ and $\frac{y}{2} H_2O$.
3. Double everything if you want whole numbers.

Working back: "1 mol needs 4.5 mol of O_2 " fits C_3H_8O ($3 + 2 - \frac{1}{2}$), a propanol or methoxyethane; other clues (such as oxidation) then pick one.

11. Explain why alcohols are less acidic than water (4 questions)

1. **Mark 1:** the alkyl group is electron-donating (positive inductive effect).
2. **Mark 2:** so it strengthens the O–H bond / makes the H^+ less likely to be lost, and the alkoxide ion is less stable (its charge is more concentrated).

Variations you will meet: "the ethoxide ion is a stronger base than the hydroxide ion" (true); "sodium reacts faster with ethanol than with water" (false); "the charge on ethoxide is delocalised" (false).

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

Propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, is oxidised using acidified potassium dichromate(VI).

- (a) State the colour change of the reaction mixture. **[1]**
- (b) Describe how the conditions must differ to make propanal rather than propanoic acid. Explain your answer. **[3]**
- (c) Write equations, using $[\text{O}]$, for the formation of propanal and of propanoic acid. **[2]**
- (d) 3.00 g of propan-1-ol gives 2.22 g of propanoic acid. Calculate the percentage yield. **[3]**
- (e) 2-methylpropan-2-ol is warmed with the same reagent. State and explain what you would see. **[2]**

(a) Orange to green. **B1**

(b) For propanal: warm the alcohol with the oxidising agent and **distil the propanal off as it forms**. **B1** For propanoic acid: **heat under reflux** with an **excess** of the oxidising agent. **B1** Propanal is volatile, so distilling removes it before it is oxidised further; under reflux it condenses back into the flask and is oxidised to the acid. **B1**

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$ **B1**

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O}$ **B1**

(d) M_r of $\text{C}_3\text{H}_8\text{O} = 3(12.0) + 8(1.0) + 16.0 = 60.0$; amount = $3.00 \div 60.0 = 0.0500$ mol. **M1**

1 mol of alcohol gives 1 mol of acid. M_r of $\text{C}_3\text{H}_6\text{O}_2 = 74.0$, so the theoretical mass is $0.0500 \times 74.0 = 3.70$ g. **M1**

$$\text{percentage yield} = \frac{2.22}{3.70} \times 100 = 60.0\%$$

A1

(e) It stays orange: no reaction. **B1** It is a tertiary alcohol: the carbon bonded to the OH has no hydrogen atom to lose. **B1**

Example 2

Four alcohols, **A**, **B**, **C** and **D**, all have the molecular formula $C_5H_{12}O$.

- **A** does not change the colour of warm acidified $K_2Cr_2O_7$.
- **B** and **C** each turn it green; their products after heating under reflux do not react with $Na_2CO_3(aq)$.
- **B** gives a yellow precipitate with warm alkaline $I_2(aq)$ and has an unbranched chain; **C** gives no precipitate.
- **D** turns the dichromate green; its product after reflux fizzes with $Na_2CO_3(aq)$. **D** has a chiral carbon atom.

(a) Identify **A**, **B**, **C** and **D**. [4]

(b) Give the formulas of the two products of the reaction of **B** with alkaline $I_2(aq)$. [2]

(c) Write an equation for the reaction of **D** with sodium, and state what you would see. [2]

(a)

- **A** is tertiary: the only tertiary $C_5H_{12}O$ alcohol is **2-methylbutan-2-ol**, $CH_3CH_2C(OH)(CH_3)_2$. **B1**
- **B** and **C** give ketones (no acid formed), so they are secondary. **B** has $CH_3CH(OH)-$ and no branch: **pentan-2-ol**, $CH_3CH(OH)CH_2CH_2CH_3$. **B1**
- **C** is secondary with no $CH_3CH(OH)-$: **pentan-3-ol**, $CH_3CH_2CH(OH)CH_2CH_3$. **B1**
- **D** gives an acid, so it is primary. Of the four primary alcohols, only **2-methylbutan-1-ol**, $HOCH_2CH(CH_3)CH_2CH_3$, has a chiral carbon (C2 carries H, CH_3 , C_2H_5 and CH_2OH). **B1**

(b) CHI_3 **B1** and the butanoate ion, $CH_3CH_2CH_2COO^-$ (four carbons, one fewer than B). **B1**

(c) $2CH_3CH_2CH(CH_3)CH_2OH + 2Na \rightarrow 2CH_3CH_2CH(CH_3)CH_2O^-Na^+ + H_2$ **B1** Effervescence (bubbles of gas) and the sodium disappears. **B1**

Example 3

Butane-1,3-diol, $HOCH_2CH_2CH(OH)CH_3$, is used in food flavourings.

(a) Classify each of its alcohol groups. [1]

(b) 0.450 g of butane-1,3-diol reacts with an excess of sodium. Calculate the volume of hydrogen produced, in cm^3 , at room conditions. [3]

(c) Name the organic product when butane-1,3-diol reacts with an excess of PCl_5 , and state what you would see. [2]

(d) Butane-1,3-diol is heated under reflux with an excess of acidified $K_2Cr_2O_7$. Give the structural formula of the organic product and write the equation using $[O]$. [2]

(e) Butane-1,3-diol can be made from CH_3COCH_2COOH . Identify the reducing agent and write the equation using $[H]$. [3]

(a) The OH on C1 is primary; the OH on C3 is secondary. **B1**

(b) M_r of $C_4H_{10}O_2 = 4(12.0) + 10(1.0) + 2(16.0) = 90.0$; amount = $0.450 \div 90.0 = 0.00500$ mol. **M1**

Two OH groups give 1 mol of H_2 per mol of diol, so 0.00500 mol of H_2 . **M1**

Volume = $0.00500 \times 24.0 = 0.120 \text{ dm}^3 = 120 \text{ cm}^3$. **A1**

(c) 1,3-dichlorobutane, $ClCH_2CH_2CHClCH_3$. **B1** Steamy (misty) fumes of HCl. **B1**

(d) The primary OH becomes COOH and the secondary OH becomes C=O: CH_3COCH_2COOH . **B1**

$HOCH_2CH_2CH(OH)CH_3 + 3[O] \rightarrow CH_3COCH_2COOH + 2H_2O$ **B1**

(e) $LiAlH_4$: $NaBH_4$ cannot reduce the COOH group. **B1**

The ketone needs 2[H] and the acid 4[H] plus one H_2O : **M1**



A1

Example 4

2-methylpentan-3-ol, $CH_3CH_2CH(OH)CH(CH_3)_2$, is heated with concentrated phosphoric acid.

(a) State the type of reaction and the role of the phosphoric acid. **[2]**

(b) Structural isomerism and stereoisomerism should be considered. How many alkenes can form? Explain your answer. **[3]**

(c) 2-methylpentan-3-ol can be made from a ketone. Name the ketone and give a suitable reagent. **[2]**

(d) Explain why 2-methylpentan-3-ol reacts more slowly with sodium than water does. **[2]**

(a) Elimination (dehydration). **B1** The acid is a catalyst. **B1**

(b) Both neighbours of the carbinol carbon (C2 and C4, counting from the ethyl end) carry H. **M1**

- Losing H from the CH_2 gives $CH_3CH=CHCH(CH_3)_2$, 4-methylpent-2-ene. Each C=C carbon carries H and a different group, so it has cis and trans forms: 2.
- Losing H from the CH gives $CH_3CH_2CH=C(CH_3)_2$, 2-methylpent-2-ene. One C=C carbon carries two CH_3 groups, so no cis/trans: 1. **A1**

Total: $2 + 1 = 3$ alkenes. **A1**

(c) 2-methylpentan-3-one, $CH_3CH_2COCH(CH_3)_2$ **B1**, with $NaBH_4$ (or $LiAlH_4$). **B1**

(d) The alkyl groups are electron-donating (positive inductive effect). **B1** This strengthens the O–H bond, so the alcohol loses H^+ less readily than water: it is a weaker acid. **B1**

Common mistakes

- **Mixing up reflux and distillation.** Examiner reports often see "heat under reflux" given for making an aldehyde. Reflux keeps everything in the flask, so it gives the **acid**; distil to stop at the aldehyde. Reports also note that many candidates cannot draw a reflux condenser: it stands **vertically** on the flask, with water in at the bottom.
- **Forgetting one of the groups.** In molecules with an OH and a CHO, or two OH groups, both are oxidised under reflux. Reports note answers that oxidised only one.
- **Oxidising a tertiary alcohol.** It has no H on the carbinol carbon: no reaction, stays orange.
- **Unbalanced [O] and [H] equations.** Primary alcohol to acid is $2[\text{O}]$ and one H_2O ; acid to alcohol is $4[\text{H}]$ and one H_2O . Reports mention missing $2[\text{H}]$ and missing water.
- **Using NaBH_4 for a carboxylic acid.** Only LiAlH_4 reduces COOH . Write its formula carefully: LiAlH_4 . Hybrid or made-up reducing agents score nothing.
- **Leaving out hydrogen in the sodium reaction**, or forgetting that an OH group reacts with Na as well as a COOH .
- **The wrong carboxylate in the iodoform test.** The ion has **one carbon fewer** than the alcohol: butan-2-ol gives propanoate, not butanoate. Reports also note candidates forgetting that the iodine must be **alkaline** (add NaOH).
- **Missing cis/trans isomers** when counting alkenes from dehydration, or counting the same alkene twice.
- **Displayed formulas with " $-\text{OH}$ ".** In a displayed formula every bond is drawn, including the O–H bond, and CH_3 must be shown with its three C–H bonds.
- **Calling the acid in esterification or dehydration a reactant or an oxidising agent.** It is a catalyst.
- **Saying ethanol is more acidic than water**, or that ethoxide's charge is delocalised. The alkyl group pushes electrons **towards** O, so the reverse is true.

How to get the marks

- **"Reagents and conditions"** needs both: "acidified potassium dichromate(VI) **and** heat under reflux", "steam **with** H_3PO_4 catalyst", " $\text{NaOH}(\text{aq})$ **and** heat". Acidified means say the acid (H_2SO_4 or H^+).
- **"Observation"** is what you see: "orange to green", "yellow precipitate", "effervescence", "steamy fumes". Not " Cr^{3+} forms" or "hydrogen is produced".
- **"Type of reaction"**: oxidation, reduction, substitution, elimination (dehydration), condensation (esterification), hydrolysis, electrophilic addition, redox.
- **Equations with [O] or [H]** must balance, including the water. Draw organic formulas unambiguously: $\text{CH}_3\text{CH}_2\text{COOH}$, not $\text{C}_3\text{H}_6\text{O}_2$.
- **"Deduce" or "Identify"** from test results: give the name or structure asked for. One clear answer; listing two alternatives when only one fits can lose the mark.
- **"Explain" acidity** needs the cause (electron-donating alkyl group) and the effect on the O–H bond or the ion.
- **Multiple-choice counting questions** that say "structural and stereoisomerism should be considered" want cis/trans and optical isomers included.

- **Calculations:** show M_r , moles and the mole ratio; give 3 significant figures unless told otherwise.

Quick check

1. Name the organic product, if any, when each alcohol is treated as stated: (a) butan-1-ol, acidified $K_2Cr_2O_7$, product distilled off; (b) butan-1-ol, excess acidified $K_2Cr_2O_7$, heated under reflux; (c) butan-2-ol, acidified $K_2Cr_2O_7$, reflux; (d) 2-methylpropan-2-ol, acidified $K_2Cr_2O_7$, reflux.
2. Which of these give a yellow precipitate with warm alkaline $I_2(aq)$: ethanol, propan-1-ol, butan-2-ol, 2-methylpropan-2-ol, pentan-3-ol? Give the organic ion formed in each positive test.
3. Propane-1,2,3-triol, $HOCH_2CH(OH)CH_2OH$ (M_r 92.0). (a) Classify its OH groups. (b) What volume of hydrogen, in cm^3 at room conditions, forms when 0.920 g reacts with excess sodium? (c) Name the product with excess PCl_5 .
4. (a) Give the reagents and conditions, and write the equation, for making ethyl propanoate from an alcohol and a carboxylic acid. (b) Give the reagent and conditions to make propan-1-ol from 1-bromopropane, and ethane-1,2-diol from ethene.
5. 1 mol of an alcohol $C_nH_{2n+1}OH$ needs 7.5 mol of oxygen for complete combustion. It gives a yellow precipitate with alkaline iodine and has an unbranched chain. Find n , identify the alcohol and write a balanced equation for its combustion.

Answers

- (a) Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$. (b) Butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$. (c) Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$.
(d) No reaction: it is tertiary, so the solution stays orange.
- Ethanol (gives methanoate, HCOO^-) and butan-2-ol (gives propanoate, $\text{CH}_3\text{CH}_2\text{COO}^-$). Propan-1-ol has no CH_3 on its carbinol carbon; pentan-3-ol has ethyl groups, not CH_3 ; 2-methylpropan-2-ol has no H on its carbinol carbon.
- (a) Two primary (C1 and C3) and one secondary (C2). (b) $0.920 \div 92.0 = 0.0100$ mol; three OH give $1.5 \times 0.0100 = 0.0150$ mol of H_2 ; $0.0150 \times 24.0 = 0.360 \text{ dm}^3 = 360 \text{ cm}^3$. (c) 1,2,3-trichloropropane.
- (a) Ethanol and propanoic acid, heated with a few drops of concentrated H_2SO_4 (catalyst):
 $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$. (b) NaOH(aq) , heat under reflux; cold, dilute, acidified KMnO_4 .
- $\frac{3n}{2} = 7.5$, so $n = 5$. Unbranched with $\text{CH}_3\text{CH(OH)-}$: pentan-2-ol, $\text{CH}_3\text{CH(OH)CH}_2\text{CH}_2\text{CH}_3$.
 $2\text{C}_5\text{H}_{11}\text{OH} + 15\text{O}_2 \rightarrow 10\text{CO}_2 + 12\text{H}_2\text{O}$.

Past questions to try

- 9701/22/M/J/25 Q4**: reducing an acid with $[\text{H}]$, a substitution with SOCl_2 , sodium, then identifying three butanols from test results.
- 9701/12/O/N/24 Q32**: the alkenes formed when butan-2-ol is dehydrated.
- 9701/23/O/N/22 Q4**: choosing a different reagent to tell apart each pair of compounds.
- 9701/12/O/N/22 Q34**: counting the alkenes from a tertiary alcohol, stereoisomers included.