



# Cambridge (CIE) A Level Chemistry



## Alcohols

### Contents

- \* Producing Alcohols
- \* Reactions of Alcohols
- \* Classifying & Testing for Alcohols
- \* Acidity of Alcohols



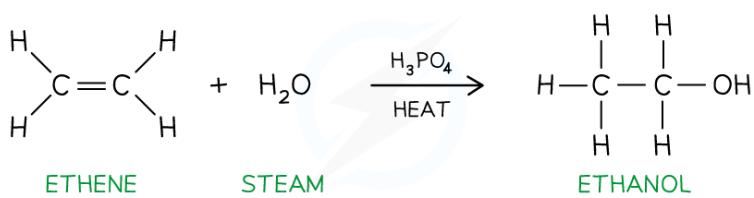
# Production of Alcohols

- Alcohols are compounds that contain at least one **hydroxy** (-OH) group
- The general formula of alcohols is  $C_nH_{2n+1}OH$
- Alcohols can be prepared by a wide range of chemical reactions

## Electrophilic addition of alkenes

- When hot steam is reacted with an alkene, using concentrated phosphoric(VI) acid ( $H_3PO_4$ ) as a catalyst, **electrophilic addition** takes place to form an **alcohol**

### The electrophilic addition of ethene using water

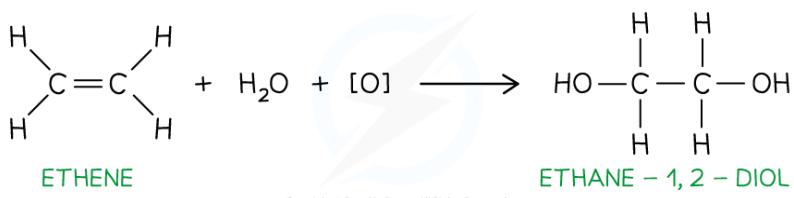


*Electrophilic addition of steam to alkenes forms alcohols*

## Oxidation of alkenes

- Cold, dilute  $KMnO_4$  is a **mild oxidising agent** and oxidises **alkenes**
- The C-C double bond is not fully broken and a diol is formed
  - A diol is a compound with two hydroxy, -OH, groups

### Oxidation of ethene using cold, dilute $KMnO_4$



*The oxidation of alkenes using cold, dilute  $KMnO_4$  forms a diol*

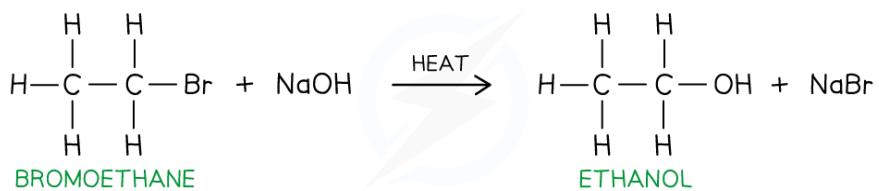
## Nucleophilic substitution of halogenoalkanes

- The halide atom in halogenoalkanes can be substituted when heated with aqueous  $NaOH$  in a **nucleophilic substitution** reaction

### Nucleophilic substitution of bromoethane using $NaOH$



## Your notes



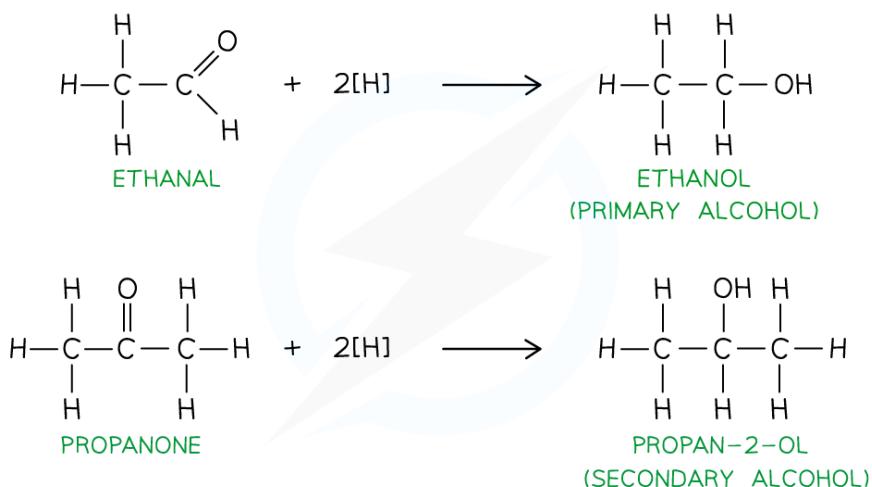
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The nucleophilic substitution of halogenoalkanes using NaOH forms an alcohol

# Reduction of aldehydes & ketones

- **Aldehydes** and **ketones** can be reduced by reducing agents such as  $\text{NaBH}_4$  or  $\text{LiAlH}_4$
  - Aldehydes are reduced to **primary alcohols**
    - The carbon attached to the hydroxy group is bonded to one other alkyl group
  - Ketones are reduced to **secondary alcohols**
    - The carbon attached to the hydroxy group is bonded to two other alkyl groups

# The reduction of ethanal and propanone

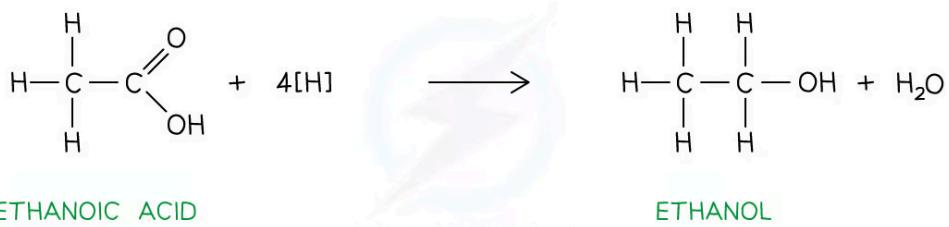


**The reduction of aldehydes and ketones forms primary and secondary alcohols respectively.**

## Reduction of carboxylic acids

- Similarly, carboxylic acids are reduced by  $\text{LiAlH}_4$  to primary alcohols
  - $\text{NaBH}_4$  is not used as it is not a strong enough reducing agent for this reaction

## The reduction of ethanoic acid



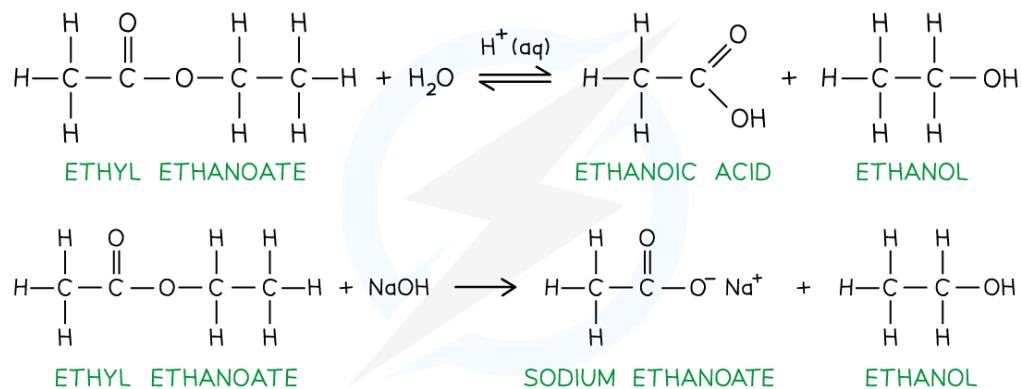
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**The reduction of carboxylic acids forms primary alcohols**

## Hydrolysis of ester

- Esters are made by a **condensation reaction** between an alcohol and a carboxylic acid
- When an ester is heated with dilute acid or alkali, **hydrolysis** will take place and the carboxylic acid and alcohol will be reformed

### Acidic and alkaline hydrolysis of ethyl ethanoate



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**The hydrolysis of esters forms alcohols**

## Alcohol production reactions table

Reaction Type	Reagents	Conditions	Product
Electrophilic addition	Alkene Steam	Heat H <sub>3</sub> PO <sub>4</sub> catalyst	Alcohol
Oxidation	Alkenes Cold, dilute KMnO <sub>4</sub>	Shaking of reagents	Diol
Nucleophilic substitution	Halogenoalkanes Aqueous NaOH	Heat	Alcohol

Reduction	Aldehydes / ketones	$\text{LiAlH}_4$ or $\text{NaBH}_4$	Primary / secondary alcohol
Reduction	Carboxylic acid	$\text{LiAlH}_4$	Primary alcohol
Hydrolysis	Esters	Dilute acid or alkali Heat	Alcohol



Your notes



### Examiner Tips and Tricks

The symbol [O] is used to represent oxygen provided by an oxidising agent

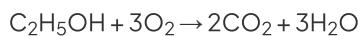


# Reactions of Alcohols

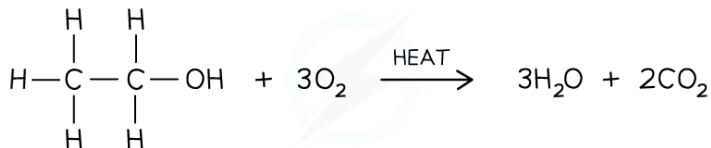
- Alcohols are reactive molecules which undergo a wide range of reactions

## Combustion of alcohols

- Alcohols react with oxygen in the air when ignited and undergo **complete combustion** to form carbon dioxide and water



### The complete combustion of ethanol



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Complete combustion of alcohols produces carbon dioxide and water

## Substitution of alcohols

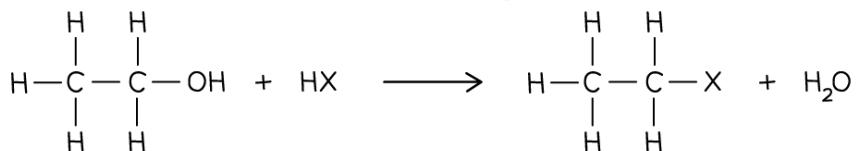
- In the **substitution** of alcohols, a hydroxy group (-OH) is replaced by a halogen to form an **halogenoalkane**
- The substitution of the alcohol group for a halogen can be achieved by reacting the alcohol with:
  - HX** (rather than using HBr, KBr is reacted with  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  to make HBr that will then react with the alcohol)
  - PCl<sub>3</sub>** and heat
  - PCl<sub>5</sub>** at room temperature
  - SOCl<sub>2</sub>**

## Substitution of alcohols



Your notes

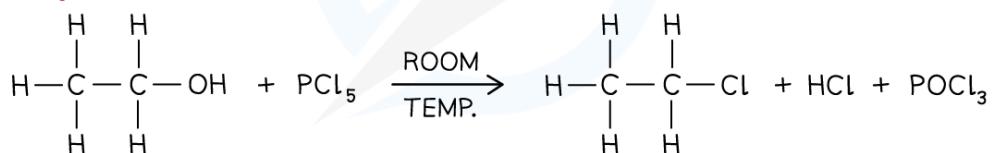
◦ HX (OR KBr WITH  $H_2SO_4$  OR  $H_3PO_4$ )



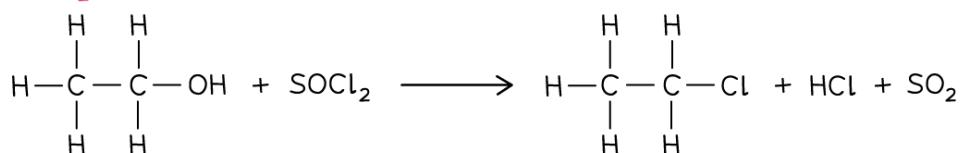
◦  $\text{PCl}_3$  + HEAT



◦  $\text{PCl}_5$



◦  $\text{SOCl}_2$



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The substitution of alcohols produces halogenoalkanes

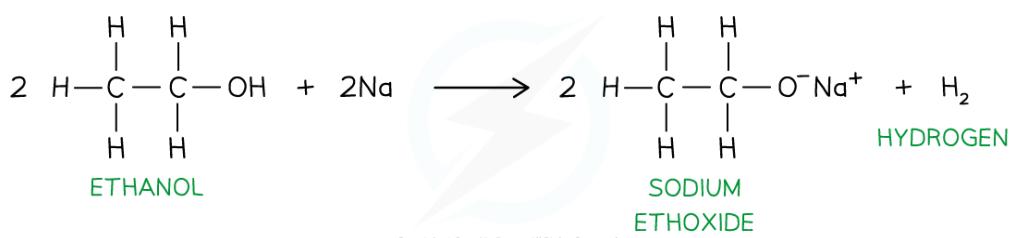
## Reaction with Na

- When an alcohol reacts with a **reactive metal** such as sodium (Na), the oxygen-hydrogen bond in the hydroxy group **breaks**
- Though the reaction is less vigorous than sodium reacting with water, **hydrogen gas** is given off and a **basic** compound (**alkoxide**) is formed
  - If the excess ethanol is evaporated off after the reaction a white crystalline solid of **sodium alkoxide** is left



- The longer the hydrocarbon chain in the alcohol, the less **vigorous** the reaction becomes
- 

## The reaction of ethanol with sodium metal



**Alcohols react with Na to form a basic sodium alkoxide salt and hydrogen gas**

## Oxidation of alcohols

- Primary alcohols can be oxidised:
  - They form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- Secondary alcohols can be oxidised
  - They form **ketones** only
- Tertiary alcohols do not undergo oxidation

## Oxidising agents

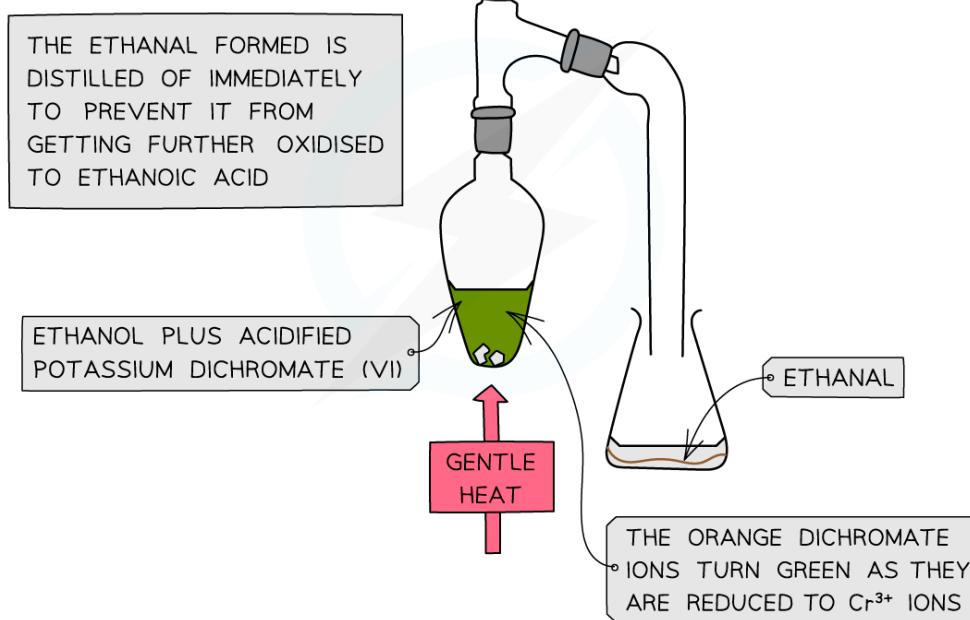
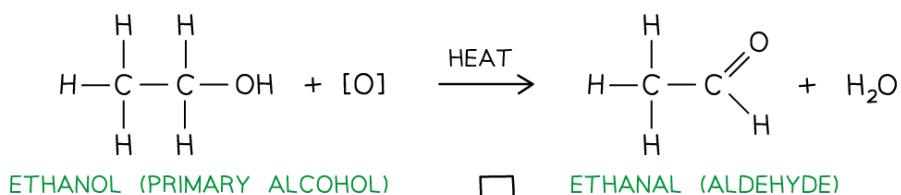
- The oxidising agents of alcohols include **acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>** or **acidified KMnO<sub>4</sub>**
- **Acidified potassium dichromate(VI)**, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, is an orange oxidising agent
  - Acidified means that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
  - For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
  - This reduction requires hydrogen (H<sup>+</sup>) ions which are provided by the acidic medium
    - When alcohols are **oxidised** the orange dichromate ions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) are reduced to green Cr<sup>3+</sup> ions
- **Acidified potassium manganate(VII)**, KMnO<sub>4</sub>, is a purple oxidising agent
  - As with acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> the potassium manganate(VII) is in an acidic medium to allow reduction of potassium manganate(VII) to take place
    - When alcohols are **oxidised**, the purple manganate ions (MnO<sub>4</sub><sup>-</sup>) are reduced to colourless Mn<sup>2+</sup> ions
- When a **warm primary alcohol** is treated with an oxidising agent, it is initially oxidised to an **aldehyde**
  - The aldehyde has a **lower boiling point** than the alcohol, so it can be **distilled off as it forms** to prevent further oxidation
  - If it is **not distilled**, continued heating under **reflux with excess oxidising agent** will convert the aldehyde into a **carboxylic acid**

- In contrast, **secondary alcohols** are oxidised to **ketones**, which **cannot be further oxidised**, so there is **no need to distil them off immediately**



Your notes

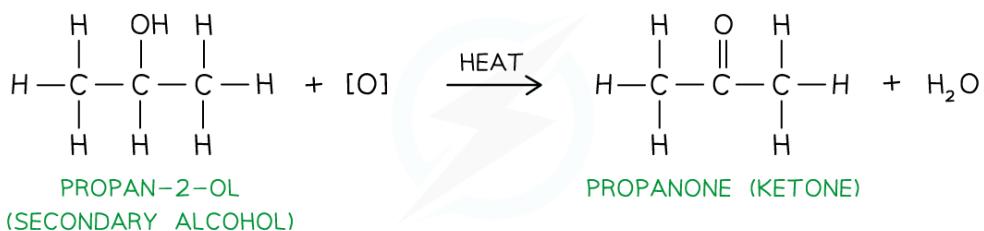
## The reflux setup to convert an alcohol to an aldehyde



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**The oxidation of ethanol by acidified potassium dichromate forms ethanal by distillation and ethanoic acid by refluxing**

## Oxidation of propan-2-ol by acidified $\text{K}_2\text{Cr}_2\text{O}_7$



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**The oxidation of secondary alcohols by acidified potassium dichromate forms a ketone, under distillation**

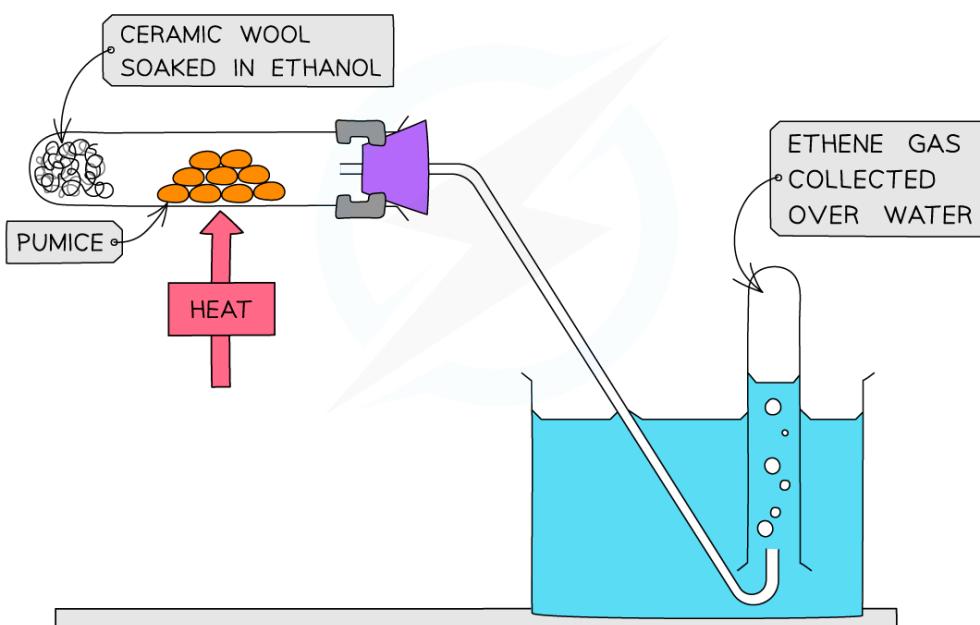
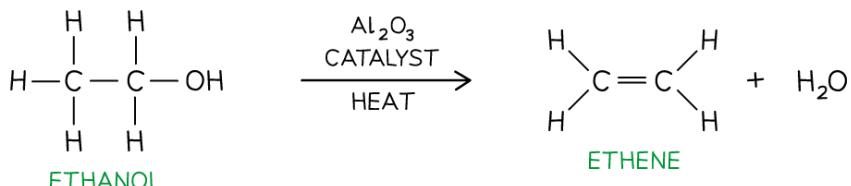
## Dehydration of alcohols

- Alcohols can also undergo **dehydration** to form alkenes

- Dehydration is a reaction in which a water molecule is removed from a larger molecule
    - A dehydration reaction is a type of **elimination** reaction
  - Alcohol vapour is passed over a **hot catalyst** of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) powder OR pieces of porous pot or pumice as well as concentrated acid can be used as catalysts



# Dehydration of ethanol



**Dehydration of ethanol using aluminium oxide as a catalyst forms ethene gas, which can be collected over water.**

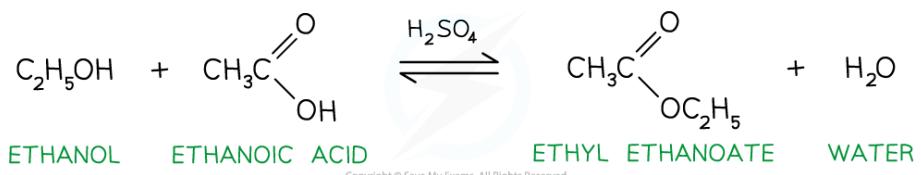
## Esterification of Alcohols

- Esterification is a **condensation** reaction between a carboxylic acid and an alcohol to form an **ester** and a water molecule
  - For esterification to take place, the carboxylic acid and alcohol are **heated under reflux** with a **strong acid catalyst** (such as  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ )



- The reaction is reversible so an equilibrium mixture can be established with all the reactants and products
  - Esters have **sweet, fruity smells**

## Example esterification reaction



Your notes

**Esterification of ethanol and ethanoic acid using a strong acid catalyst to form ethyl ethanoate and water**



### Examiner Tips and Tricks

The first part of an ester's name comes from the alcohol, whereas the second part comes from the carboxylic acid

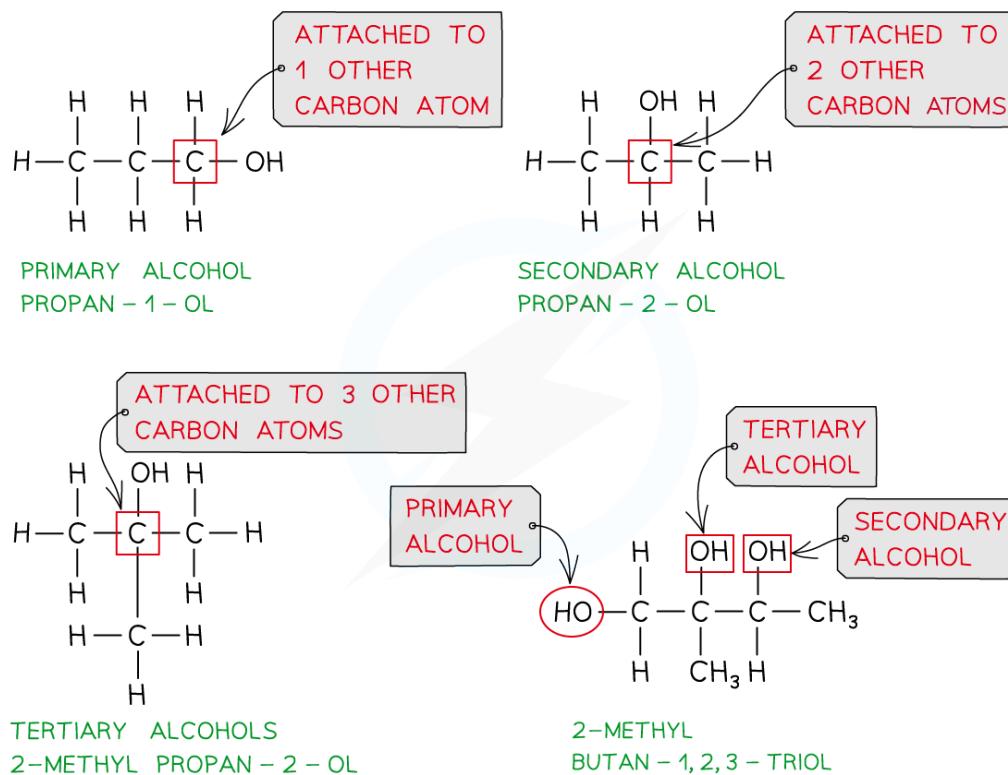
So, if ethanol and propanoic acid react together, this will make the ester **ethyl propanoate**



# Classifying Alcohols

- **Primary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **one** other carbon atom (or alkyl group)
- **Secondary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **two** other carbon atoms (or alkyl groups)
- **Tertiary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **three** other carbon atoms (or alkyl groups)

## Primary, secondary and tertiary alcohols



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## Classifying primary, secondary and tertiary alcohols and alcohols with more than one alcohol group

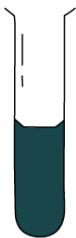
- Only **primary** and **secondary alcohols** can get oxidised when **mildly oxidised** with acidified  $K_2Cr_2O_7$ 
  - Primary alcohols get mildly oxidised to aldehydes
  - Secondary alcohols get mildly oxidized to ketones
- **Tertiary alcohols** do **not** undergo oxidation with acidified  $K_2Cr_2O_7$

- Therefore, only the oxidation of primary and secondary alcohols will change the colour of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution as the **orange**  $\text{Cr}_2\text{O}_7^{2-}$  ions are reduced to **green**  $\text{Cr}^{3+}$  ions

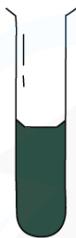
## Testing for alcohols



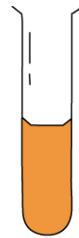
Your notes



PROPAN-1-OL  
(PRIMARY ALCOHOL)



PROPAN-2-OL  
(SECONDARY ALCOHOL)



2-METHYL-PROPAN-2-OL  
(TERTIARY ALCOHOL)

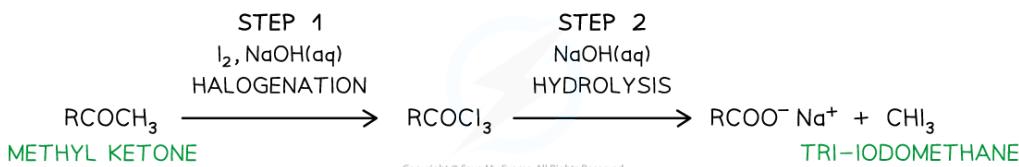
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Only propan-1-ol and propan-2-ol, which are **primary and secondary alcohols** respectively, can get oxidised, turning the orange solution green; no colour change is observed with 2-methyl-propan-2-ol, which is a **tertiary alcohol**

## Test for Alcohols

- Tri-iodomethane (also called **iodoform**) is a **yellow precipitate**
- It is formed from the reaction of **iodine** in an **alkaline solution** with **methyl ketones**
  - Methyl ketones are compounds that have a  $\text{CH}_3\text{CO}-$  group
  - Ethanal** also contains a  $\text{CH}_3\text{CO}-$  group and therefore also forms a yellow precipitate with iodoform
- The reagent is **heated** with an **alkaline** solution of **iodine**
- This reaction involves a **halogenation** and **hydrolysis** step
  - In the **halogenation** step, all three H-atoms in the  $-\text{CH}_3$  (methyl) group are replaced with iodine atoms, forming a  $-\text{Cl}_3$  group
  - The intermediate compound is hydrolysed by an **alkaline** solution to form a sodium salt ( $\text{RCO}_2^- \text{Na}^+$ ) and a yellow precipitate of  $\text{CHI}_3$

## The iodoform reaction



The reaction of methyl ketones with iodoform results in the formation of a yellow  $\text{CHI}_3$  precipitate

## Iodoform & alcohols

- The position of a **secondary alcohol group** in a molecule can be identified using the iodoform test with iodine in alkaline solution



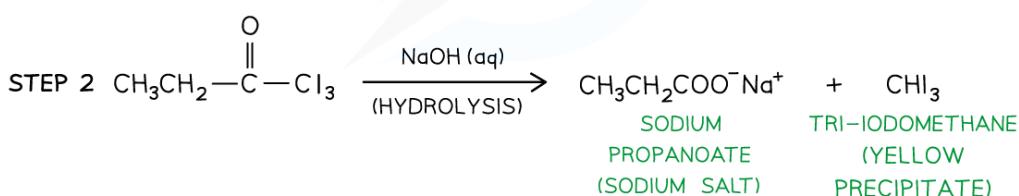
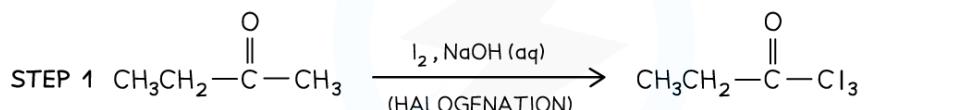
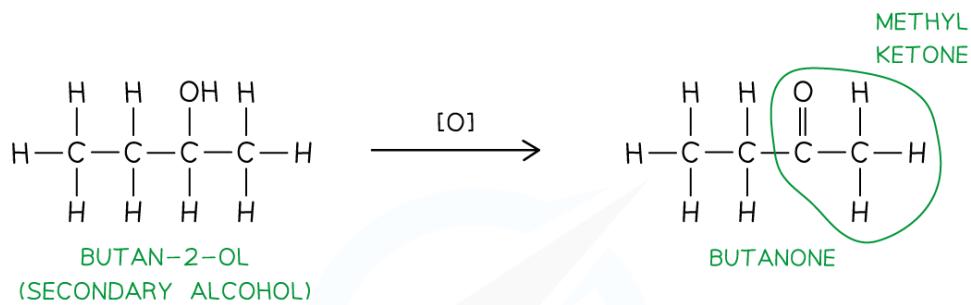
Your notes

- If the **-OH group** is attached to a carbon atom that is **next to a methyl group**, the alcohol can be **oxidised** by the alkaline iodine to form a **methyl ketone** ( $\text{RCOCH}_3$ )
- The methyl ketone then undergoes:

- Halogenation**, where the three hydrogen atoms of the methyl group are replaced by iodine atoms ( $-\text{Cl}_3$ ), followed by
- Hydrolysis**, forming a **sodium carboxylate salt** and a **yellow precipitate of iodoform** ( $\text{CHI}_3$ )

- A positive result (yellow precipitate) indicates that the alcohol has the structure  $\text{CH}_3\text{CH}(\text{OH})\text{R}$
- No precipitate means the secondary alcohol is not adjacent to a methyl group and therefore cannot form a methyl ketone intermediate

## Using the iodoform test



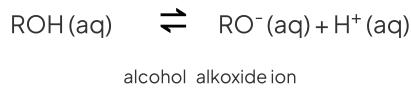
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The secondary alcohol butan-2-ol will firstly get oxidised to the methyl ketone butanone which will form a yellow precipitate when reacted with alkaline iodine

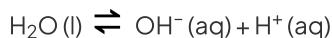


# Acidity of Alcohols

- Alcohols have a **low degree of dissociation**
    - This means, that when dissolved in water, alcohol molecules do not **dissociate** (split up) to a great extent



- The **position** of the equilibrium lies to the left, meaning that there are far more alcohol molecules than  $\text{RO}^-$  and  $\text{H}^+$  ions
  - When water dissociates, the position of the equilibrium still lies to the **left**, but there are more  $\text{H}^+$  ions compared to the dissociation of alcohols

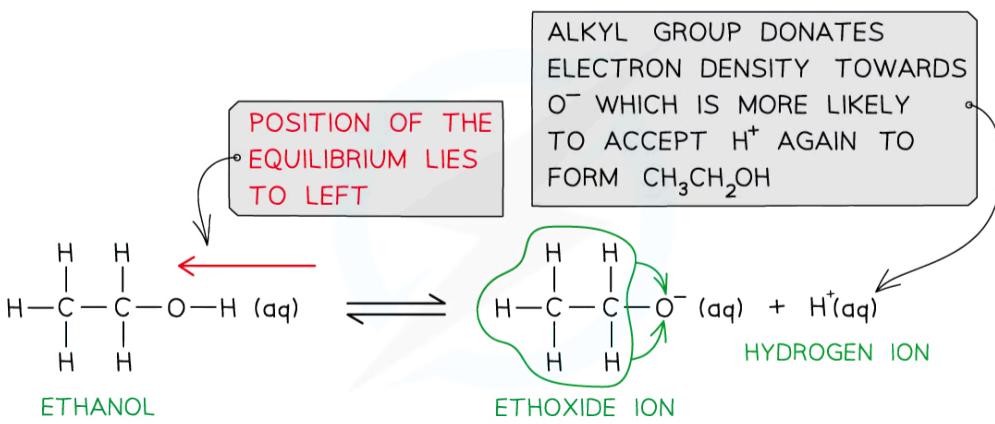


- As alcohols have a lower  $[H^+(aq)]$  in solution compared to water, **alcohols are weaker acids than water**

# The inductive effect in alcohols

- Electron-donating species such as alkyl groups push electrons into a covalent bond and are said to have a positive inductive effect
  - In alcohols, the **oxygen** atom in the **alkoxide ion** is bonded to an **electron-donating** alkyl group
  - This means that there is more electron density on the  $\text{O}^-$  atom
  - The alkoxide ion is, therefore, more likely to **accept** an  $\text{H}^+$  ion and form the alcohol again

## The inductive effect in alcohols

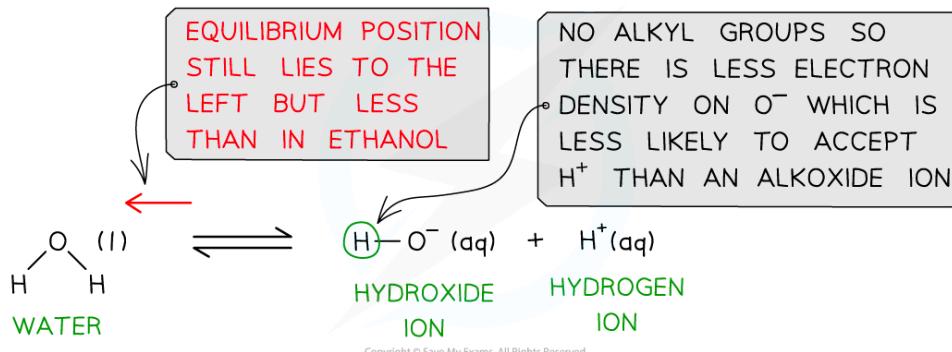


**Alkyl groups in the alkoxide ion donate electron density to the negatively charged oxygen, causing it to more readily accept a proton and form the alcohol again.**

- When water dissociates, the **hydroxide ion** only has one other **hydrogen atom**
- There is no extra **electron density** on the oxygen which is less likely to **accept** an  $\text{H}^+$  ion
- Water is therefore a **stronger** acid than alcohols



## The equilibrium of water and hydroxide ions



Water is a stronger acid than alcohols as there are no electron-donating groups in the hydroxide ion, causing the  $\text{O}^-$  to be less likely to accept a proton and reform water