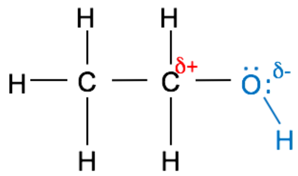
3.5 The Alcohols

Introduction:

General formula $C_nH_{2n+1}OH$

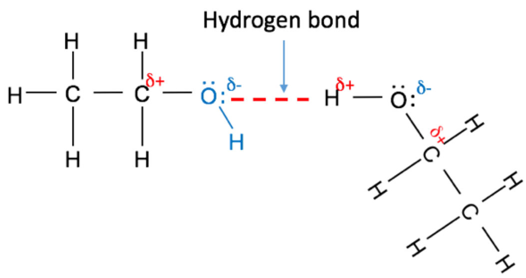
Reactivity



The more electronegative oxygen produces a polar bond

This makes the alcohols more reactive

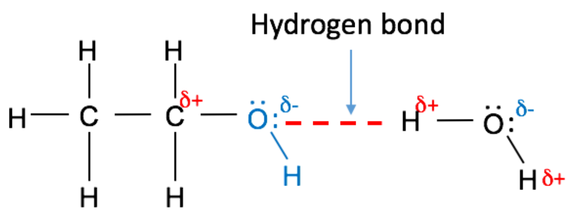
Boiling points



They can form hydrogen bonds with each other

This gives the alcohols a higher boiling point than their corresponding alkanes

Solubility



They can form hydrogen bonds with water

This makes the first 3 alcohols soluble in water. After that, the long alkyl chain interferes with the H bonds

Naming the alcohols

- The suffix '**ol'** is used used, as it starts with a vowel, we insert '**an**' between the stem and the suffix:-

$CH_3 – OH$ Meth**anol**

$CH_3 – CH_2 – OH$ Eth**anol**

- For the above examples numbers are not required. However, after these the OH can be in different positions, **position isomers**:

$CH_3 – CH_2 – CH_2 – OH$ Prop**an – 1 – ol**

$CH_3 – CH(OH) – CH_3$ Prop**an – 2 – ol**

Naming alcohols

Give the IUPAC name of the following alcohols:

Alcohol	IUPAC name
$CH_3CH_2CH_2CH_2CH_2OH$	
$CH_3CH(OH)CH_2CH_3$	
$CH_3CH_2CH(OH)CH_2CH(OH)CH_3$	

Draw the structure of the following alcohols:

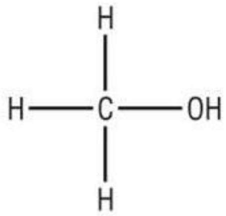
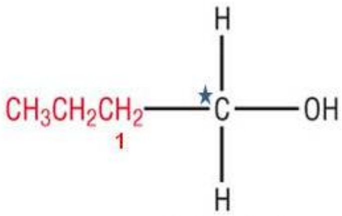
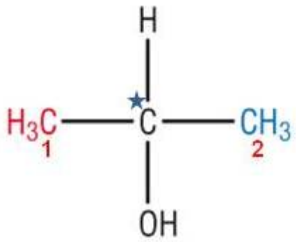
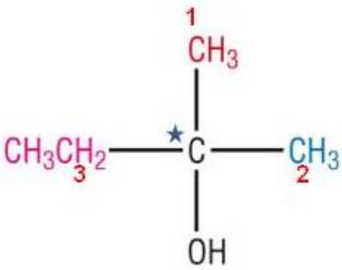
Alcohol	Structural formula	Skeletal formula
Propan – 2 – ol		
Pentan – 2 – ol		
Hexan – 1,3 – diol		

Complete the table below for pentan – 1 – ol

Structural formula	Position Isomer	Chain Isomer

Classification of alcohols:

- Alcohols can be classified as primary, secondary or tertiary based upon their structures.
- The reactions of the alcohols can depend upon its structure and therefore classification so it is important you can classify them

Primary (1°)	 Methanol  Butan-1-ol	**Primary (1°)** alcohol. The OH carbon (*) is attached to **1 other carbon atom**.
Secondary (2°)		**Secondary (2°)** alcohol. The OH carbon (*) is attached to **2 other carbon atoms**.
Tertiary (3°)		**Tertiary (3°)** alcohol. When the OH carbon (*) is attached to **3 other carbon atoms**.

Draw the following molecules as structural formula and classify them as 1°,2° or 3°

a. Propan-2-ol

b. 2-methylpropan-2-ol

c. Propan-1-ol

d. 3-methyl hexan-3-ol

Making ethanol

- Ethanol is made in 1 of 2 ways:

1) Fermentation:

$C_6H_{12}O_{6(aq)}$ → $2CH_3CH_2OH_{(g)}$ + $2CO_{2(g)}$

Conditions: Yeast / anaerobic conditions (without oxygen) / 30 – 40°C

- Fermentation is exothermic.
- At low temperatures the reaction is slow.
- At high temperatures the enzymes in yeast are denatured.
- When the ethanol concentration reaches 15%, the alcohol kills the yeast.
- Fractional distillation is required to purify ethanol.

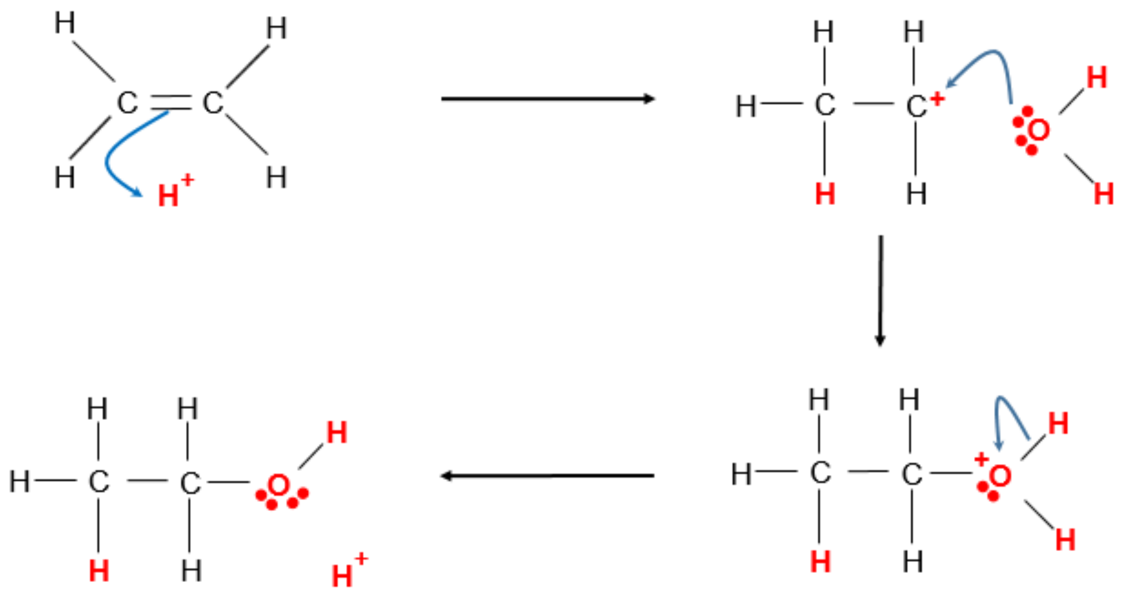
2) Hydration of ethene:

$H_2C{=}CH_{2(g)}$ + $H_2O_{(g)}$ ⇌ $CH_3CH_2OH_{(g)}$

Conditions: Steam / 300°C / 60 atm / solid H_3PO_4 catalyst

- This is a reversible reaction and only about 5% of ethene is converted to ethanol.
- Unreacted gases are recycled - this gives a 95% conversion.

The mechanism:



- This mechanism was covered in the alkenes.

Comparing the processes:

Process	Hydration of Ethene	Fermentation
Raw material	Ethene from crude oil – finite – non renewable	Sugar – renewable resource
Quality of product	Pure	Impure – requires fractional distillation
Rate of reaction	Fast	Slow
Type of process	Continuous	Batch
Costs	High set up cost / low labour costs – Low cost	Low set up costs / high labour costs – High cost

Use of alcohols:

Ethanol as a fuel:

- Ethanol can make up 10% of petrol, it gives it a higher octane rating so burns more efficiently.
- As the ethanol is made from a biological material, it can be described as a **biofuel** or **bioethanol** and can be added to petrol

Advantages	Disadvantages
Sugar – renewable resource, not finite like oil	Food vs Fuel
Carbon neutral – only release the same amount of CO_2 that was absorbed in photosynthesis	Deforestation to grow crop – removes trees that absorb CO_2
	Trees from deforestation are often burnt – CO_2 released
	Loss of habitats
	Fertilisers used – can pollute water systems / produce NO (greenhouse gas)
	Modern car engines need to be modified

Carbon neutral

1. Photosynthesis

$6CO_2$	+	$6H_2O$	→	$C_6H_{12}O_6$	+	$6O_2$

2. Fermentation

$C_6H_{12}O_6$			→	$2C_2H_5OH$	+	**$2CO_2$**

3. Combustion

$2C_2H_5OH$	+	$6O_2$	→	$6H_2O$	+	**$4CO_2$**

Overall: The amount of CO_2 taken in through photosynthesis is equal to the amount of CO_2 released through fermentation and combustion

However: This process will require machinery which will inevitably be run from the use of fossil fuels which will produce CO_2

Questions:

1) Write balanced chemical reactions for the hydration of:

   a. $CH_2{=}CH_2$

   b. $CH_3CH{=}CHCH_3$

   c. Explain why you would get 2 possible alcohols when $CH_3CH{=}CH_2$ undergoes hydration. Use balanced chemical reactions in your answer.

   d. Outline the mechanism for the hydration of $CH_3CH{=}CH_2$

2) State and explain the trend in solubilities of the alcohols. Draw a labelled diagram to illustrate your answer.

3) For each of the 2 processes, give one advantage and one disadvantage for the production of alcohols.

Process	Advantage	Disadvantage
Fermentation		
Hydration		

Reactions of the alcohols

There are 3 types of reactions of the alcohols:

1) Combustion
2) Dehydration (elimination)
3) Oxidation

1. Combustion

- In a plentiful supply of oxygen, alcohols will burn to form carbon dioxide and water.
- Balancing is more tricky due to the oxygen in the alcohol.

	$C_2H_5OH_{(l)}$	+	$3O_{2(g)}$	→	$2CO_{2(g)}$	+	$3H_2O_{(g)}$
C	**2**				**1 x2 = 2**		
H	**6**						**2 x3 =6**
O	**(7-1 = 6)**		**2 x3 = 6**		**=**	**7**	

- You have to **take one oxygen away** before you multiply the $\mathbf{O_2}$'s up

Have a go at the following:

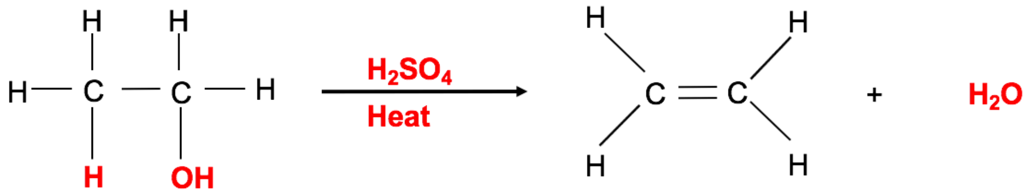
- Complete combustion of methanol

- Complete combustion of pentan – 1 – ol

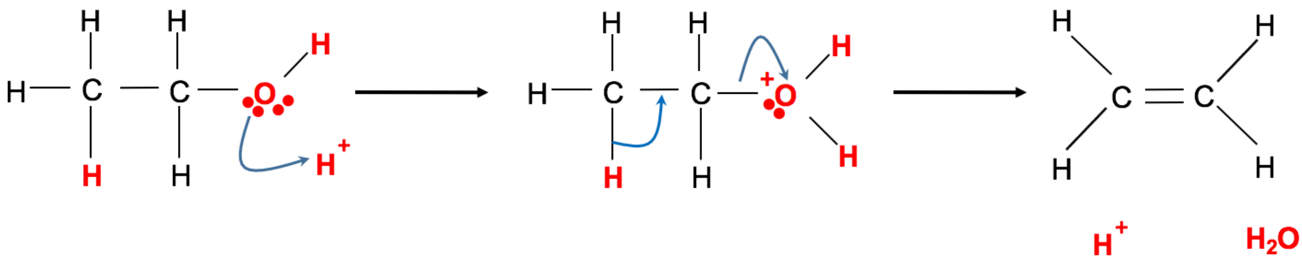
- Incomplete combustion of ethanol

- Incomplete combustion of propan – 2 – ol

2. Dehydration of an alcohol – Elimination reaction



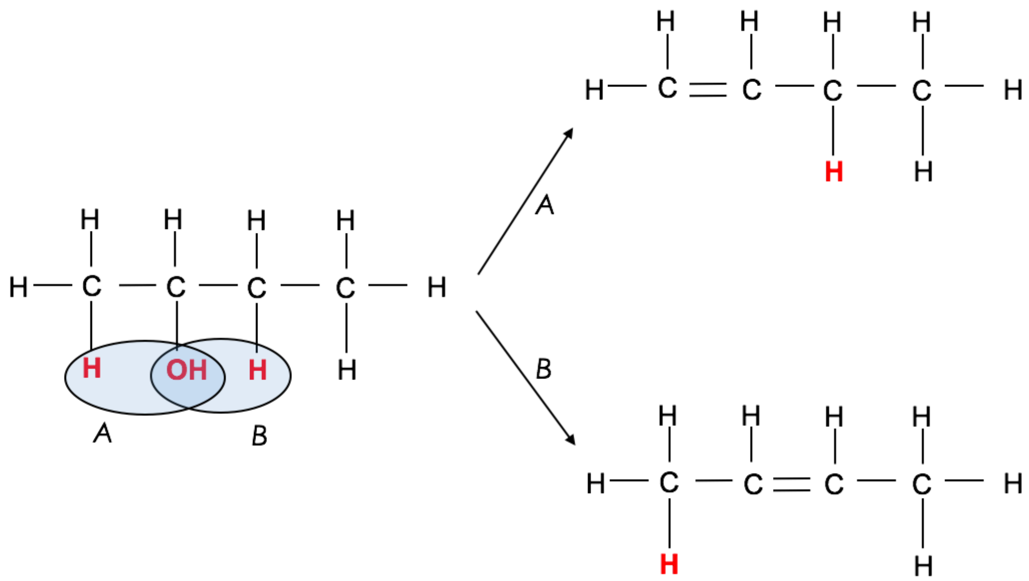
The mechanism:



- The catalyst is concentrated sulphuric acid, H_2SO_4
- The reaction requires heat

Unsymmetrical alcohols

- Dehydration of unsymmetrical alcohols gives rise to 2 alkenes, **position isomers**

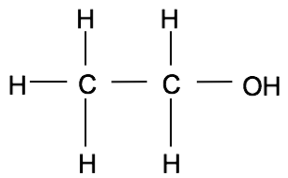


- The dehydration using 'B' would also give **E/Z isomerism**

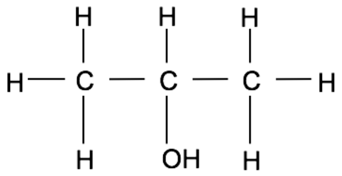
Questions:

1) Draw and name the organic products formed from the dehydration of the following alcohols

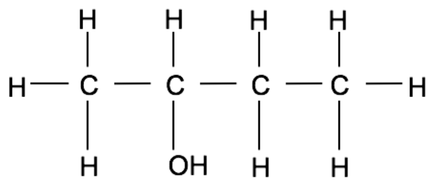
a.



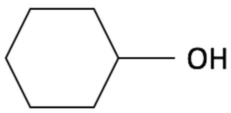
b.



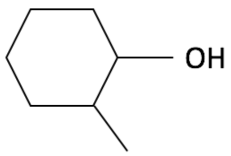
c.



d.



e.

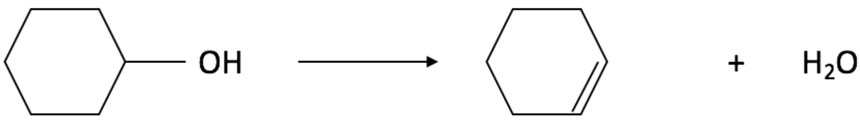


2) Draw the mechanism for the reaction in 1b

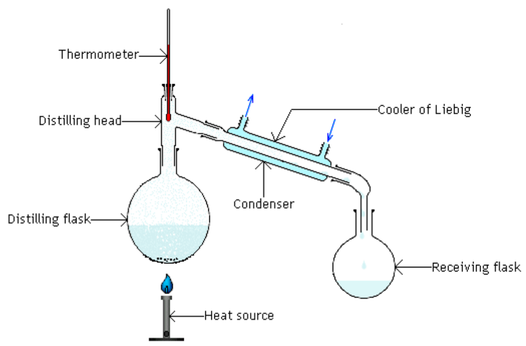
Required Practical 5 – Purification of a product

Dehydration of an alcohol

$C_6H_{11}OH \rightarrow C_6H_{10} + H_2O$



1) Heat and 1st distillation



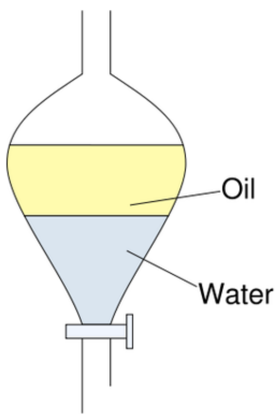
- The heat for the reaction is provided from a distillation process.
- The reason that distillation is used as the source of heat is that the product can be distilled off as it forms.
- The product is usually in a water / acid / reactant mixture.

Intermolecular forces of the reaction mixture

Cyclohexanol	Water	Sulphuric acid	Cyclohexene
H - Bonding	H - Bonding	H - Bonding	Van Der Waals
Strong – High boiling point	Strong – High boiling point	Strong – High boiling point	Weak – Low boiling point

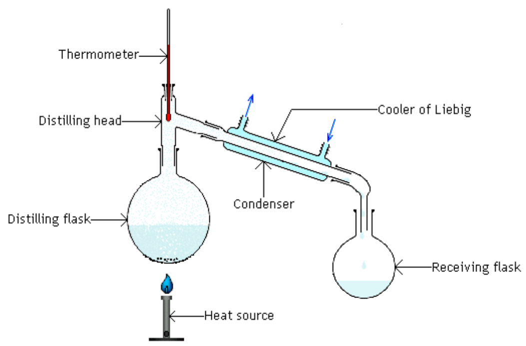
- The alkene only has the weakest VDW forces of attraction it will evaporate 1st
- This allows the crude alkene to be collected as it is formed at its boiling point – 83°C

2) Separation



- The crude cyclohexene will contain water soluble impurities that need separating from the alkene.
- The cyclohexene is transferred to a separating funnel.
- Water is added to the separating funnel and shaken to remove water soluble impurities from the cyclohexene and transfer them to the water.
- Allow to settle. The cyclohexene (hydrocarbon) is less dense than water and does not mix due to their different intermolecular forces.
- Run off the aqueous layer (waste)

3) Purification – 2nd distillation



- Pour the cyclohexene into a round bottom flask.
- Add $CaCl_2$ – a drying agent. This removes any droplets of water trapped in the cyclohexene, allow 20 minutes for this.
- Any other (hydrocarbon based) impurities are removed from a 2nd distillation.
- Only the liquid around cyclohexene's boiling point is collected.
- This is the pure cyclohexene.

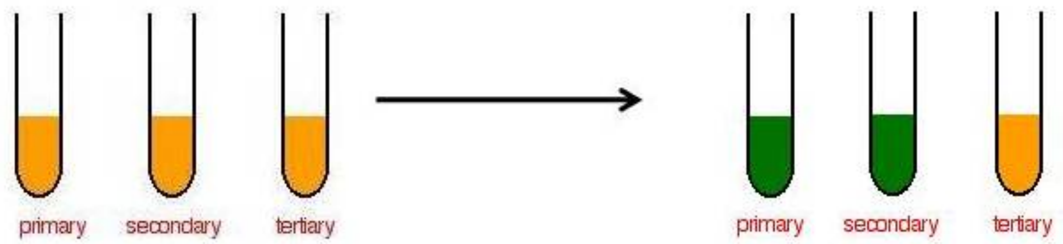
3. Oxidation of alcohols:

The oxidising agent – Potassium dichromate (VI) / sulphuric acid

$$Cr_2O_7^{2-}{}_{(aq)} \quad + \quad 14H^+{}_{(aq)} \quad + \quad 6e^- \quad \rightarrow \quad 2Cr^{3+}{}_{(aq)} \quad + \quad 7H_2O$$

Orange ($Cr_2O_7^{2-}$) → **Green** (Cr^{3+})

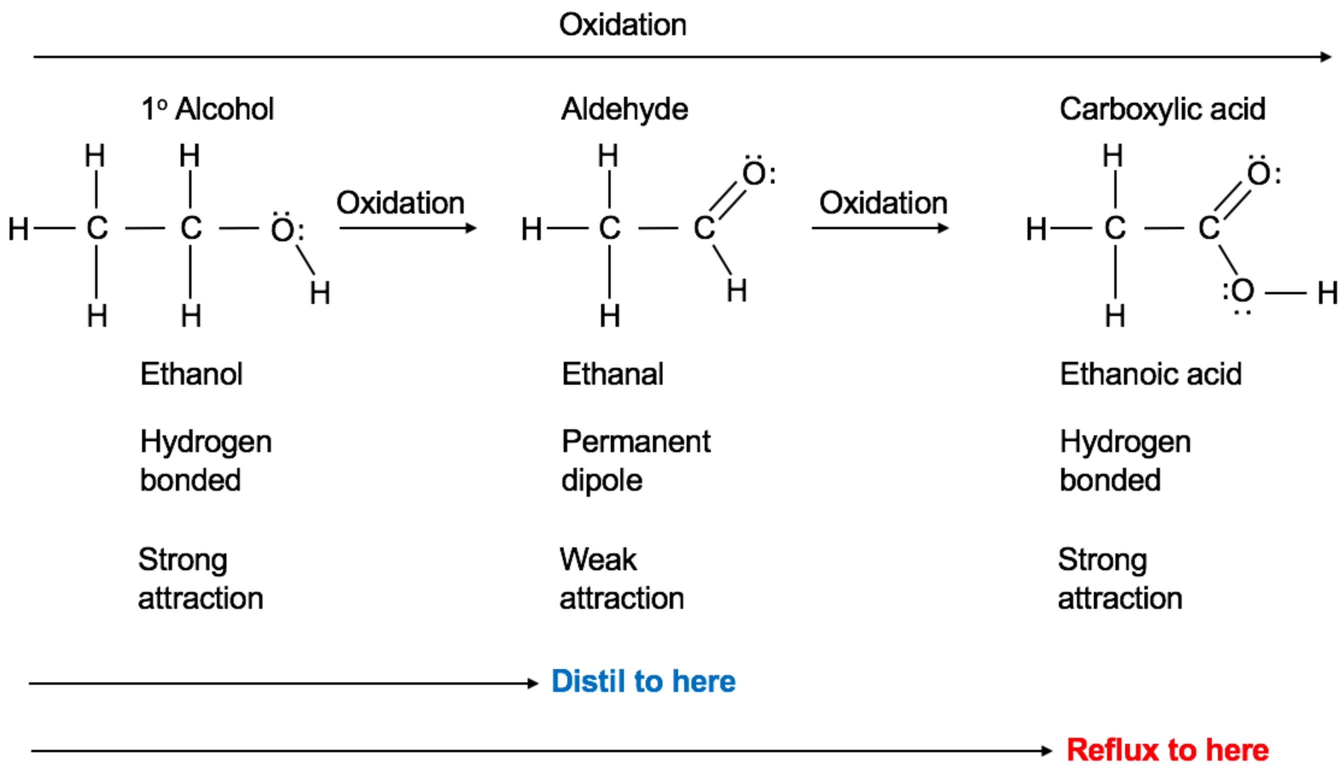
- This is orange in colour and is a mixture of Sulphuric acid, H_2SO_4 (H^+) and $K_2Cr_2O_7$.
- When added to primary, secondary and tertiary alcohols we get different results:



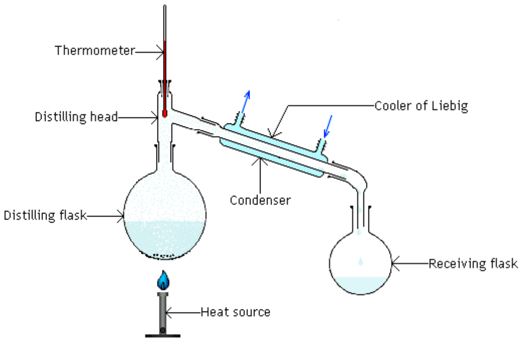
- The results show that only **primary** and **secondary alcohols** can be **oxidised** / tertiary alcohols cannot be oxidised.

a) Primary alcohols

- Primary alcohols when oxidised form an **Aldehyde** first
- Then oxidise further to a **Carboxylic acid**:



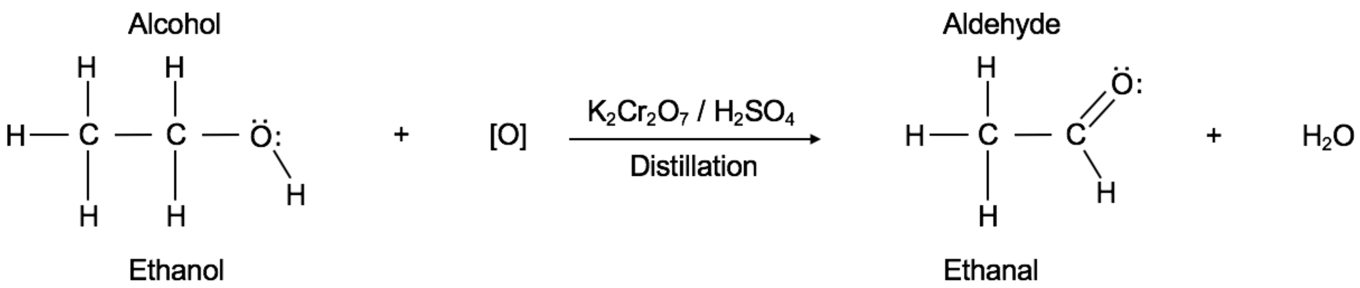
i) Primary alcohol → Aldehyde:



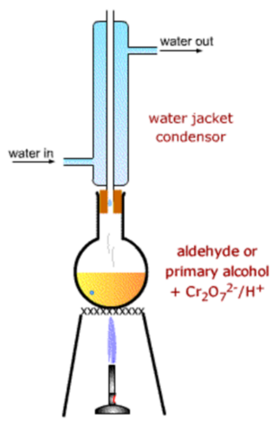
- The aldehyde has to be distilled off as it forms to prevent further oxidation.
- As it has the weakest intermolecular force it evaporates first.

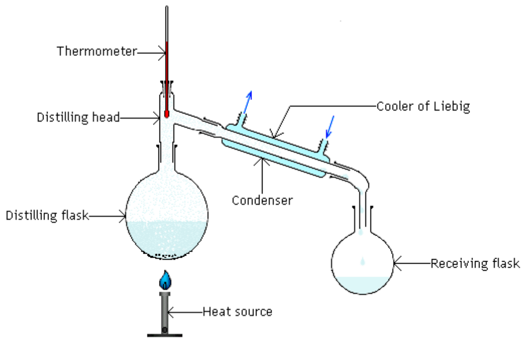
Balanced chemical reaction:

- [O] is used as the oxidising agent and used to balance the chemical equation
- Balance H first with H_2O
- Then O with [O]



ii) Primary alcohol → Carboxylic acid:



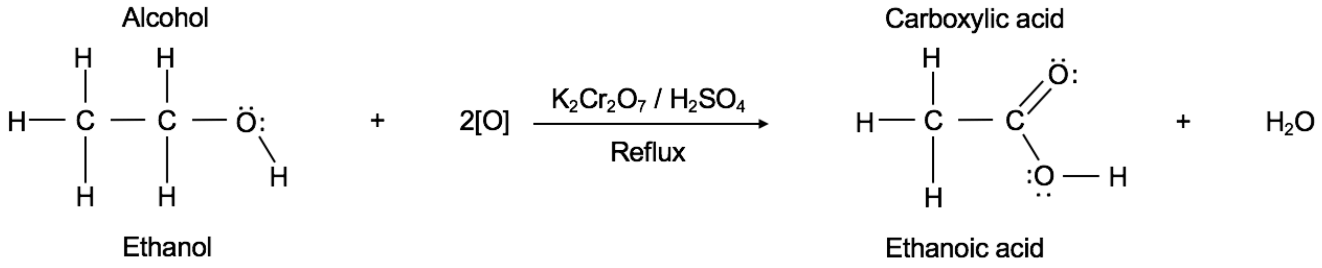


- The mixture is refluxed. Anything that evaporates is condensed back into the reaction mixture.
- We don't worry about further oxidation of the aldehyde as we want this to oxidise further to form the carboxylic acid.

- The carboxylic acid is then distilled off from the mixture

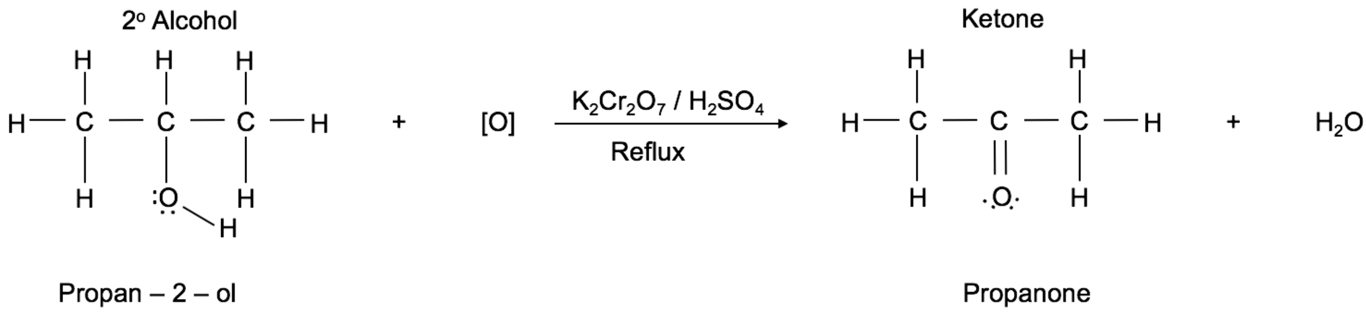
Balanced chemical reaction:

- Balance H first with H_2O
- Then O with [O]



b) Secondary alcohols:

- secondary alcohols only oxidised to form a **Ketone**
- Balance H first with H_2O
- Then O with [O]



c) Tertiary alcohols:

- These cannot be oxidised with sodium dichromate (VI) / sulphuric acid.
- They are only oxidised by combustion.

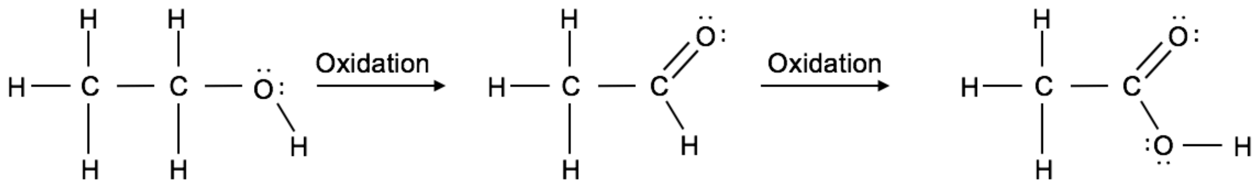
Summary of alcohol oxidation

1° alcohol → Aldehyde → Carboxylic acid

2° alcohol → Ketone

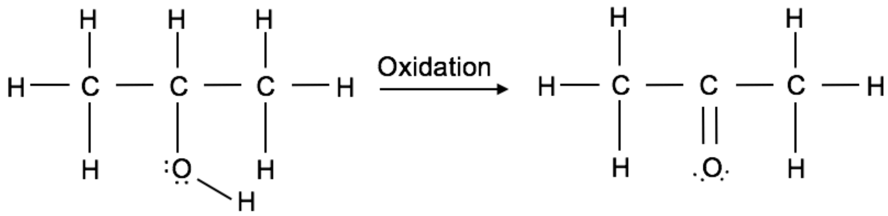
3° alcohol

1° Alcohol Aldehyde Carboxylic acid



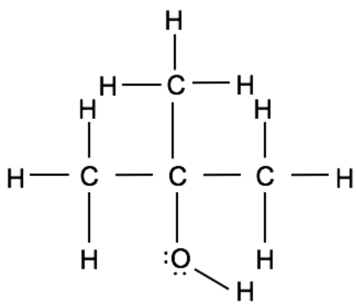
Ethanol Ethanal Ethanoic acid

2° Alcohol Ketone



Propan – 2 – ol Propanone

3° Alcohol



2 – methyl Propan – 2 – ol

Test for aldehydes and ketones

- The key difference between aldehydes and ketones is:
- Aldehyde can be oxidised further
- Ketones cannot be oxidised further
- This allows us to identify the aldehyde using an oxidising agent as the ketone will not react

1) Tollens' reagent – Silver mirror test

Reagents	**Silver nitrate dissolved in ammonia**	
Observations	**Aldehyde**	**Silver precipitate / mirror formed**
	Ketone	**No reaction**

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

Reagent: Silver ions are reduced to silver

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$

Colourless → Silver ppt

2) Fehling's solution –

Reagents	**$CuSO_4$ / NaOH / Warm**	
Observations	**Aldehyde**	**Red precipitate**
	Ketone	**No reaction**

Chemical reactions

Organic: Aldehyde is oxidised to a carboxylic acid

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

Reagent: Cu^{2+} ions are reduced to Cu^+

$$CuSO_{4(aq)} \rightarrow Cu_2O_{(s)}$$

Blue → Red

$$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(s)}$$

Questions:

1) Classify the following alcohols as primary, secondary or tertiary:

   a. $CH_3CH_2CH_2OH$

   b. $CH_3CH(OH)CH_2CH_3$

   c. $CH_3CH(OH)CH(CH_3)_2$

   d. Pentan – 2 – ol

   e. Butan – 1 – ol

   f. 2 – Methyl propan – 2 – ol

2) Draw the oxidation products of the alcohols in question 1:

   a.

   b.

   c.

   d.

   e.

   f.

3) Write balanced chemical reactions for:

   a. Oxidation of $CH_3CH_2CH_2OH$

   b. Oxidation of $CH_3CH(OH)CH_2CH_3$

   c. Oxidation of $CH_3CH(OH)CH(CH_3)_2$

   d. Oxidation of Pentan – 2 – ol

   e. Partial oxidation of Butan – 1 – ol

4) State and explain the process to oxidise the alcohol in question 3e

5) An unknown alcohol with molecular formula C_3H_8O was oxidised using $K_2Cr_2O_7$ / H_2SO
The oxidation product collected and tested:

The oxidation product was added to $AgNO_3$ dissolved in ammonia and heated. The inside of the tube gave a silver precipitate.

a. What functional group must the oxidation product have?

b. Suggest a structure and name the oxidation product.

c. Suggest a structure and name the unknown alcohol.

d. Write a balanced chemical equation for the oxidation of the unknown alcohol. Use [O] as the oxidising agent to balance the reaction.

e. What colour change would be observed during the oxidation reaction, explain your answer.

f. Write an ionic equation to show what happened to the silver ions in the test

g. Draw the organic product formed after the reaction with $AgNO_3$