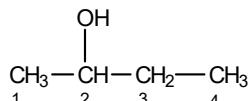


## 3.5 Alcohols

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

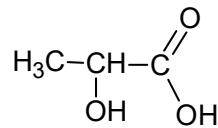
### Naming Alcohols

These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

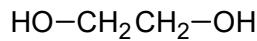


butan-2-ol

If the compound has an **-OH** group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix **hydroxy**):



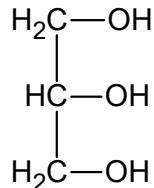
2-hydroxypropanoic acid



ethane-1,2-diol

If there are two or more **-OH** groups then **di**, **tri** are used.

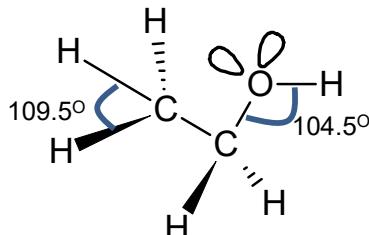
Add the **'e'** on to the stem name though



propane-1,2,3-triol

### Bond angles in Alcohols

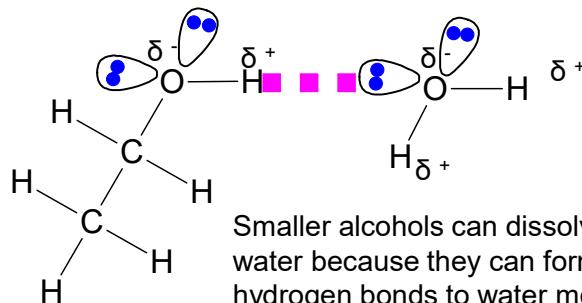
All the H-C-H bonds and C-O are  $109.5^\circ$  (tetrahedral shape), because there are 4 bonding pairs of electrons repelling to a position of minimum repulsion.



The H-O-C bond is  $104.5^\circ$  (bent line shape), because there are 2 bonding pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bonding pairs so the bond angle is reduced.

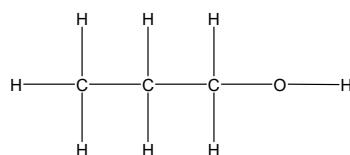
### Boiling points

The alcohols have relatively low volatility and high boiling points due to their ability to form hydrogen bond between alcohol molecules.

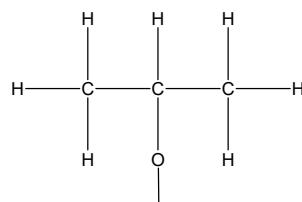


Smaller alcohols can dissolve in water because they can form hydrogen bonds to water molecules.

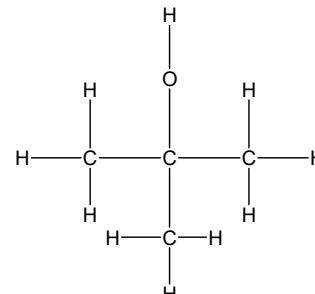
### Different types of alcohols



propan-1-ol  
Primary



propan-2-ol  
Secondary



methylpropan-2-ol  
Tertiary

Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen.

Secondary alcohols are alcohols where 2 carbon are attached to the carbon adjoining the oxygen.

Tertiary alcohols are alcohols where 3 carbon are attached to the carbon adjoining the oxygen.

# Oxidation Reactions of the Alcohols

Potassium dichromate  $K_2Cr_2O_7$  is an oxidising agent that causes alcohols to oxidise.

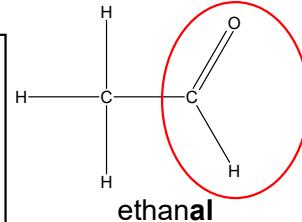
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

## Partial Oxidation of Primary Alcohols

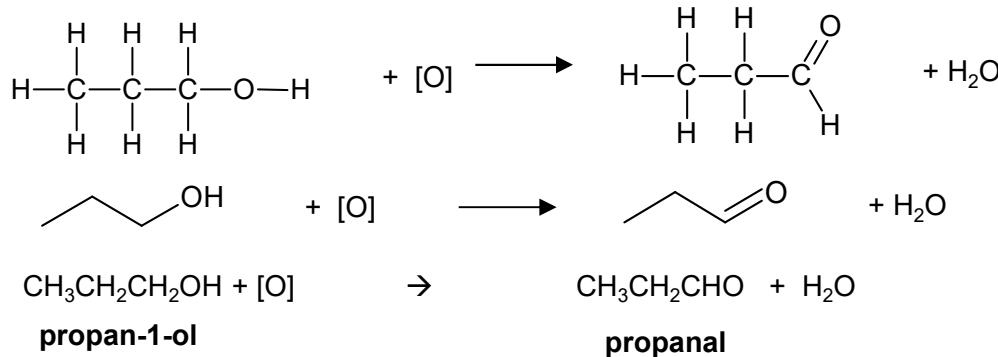
**Reaction:** primary alcohol  $\rightarrow$  aldehyde

**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.

**Conditions:** (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



An aldehyde's name ends in **-al**  
It always has the C=O bond on the first carbon of the chain so it does not need a number in its name.



Observation: the orange dichromate ion ( $Cr_2O_7^{2-}$ ) reduces to the green  $Cr^{3+}$  ion

Write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent

When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g.  $CH_3CH_2CHO$

## Distillation

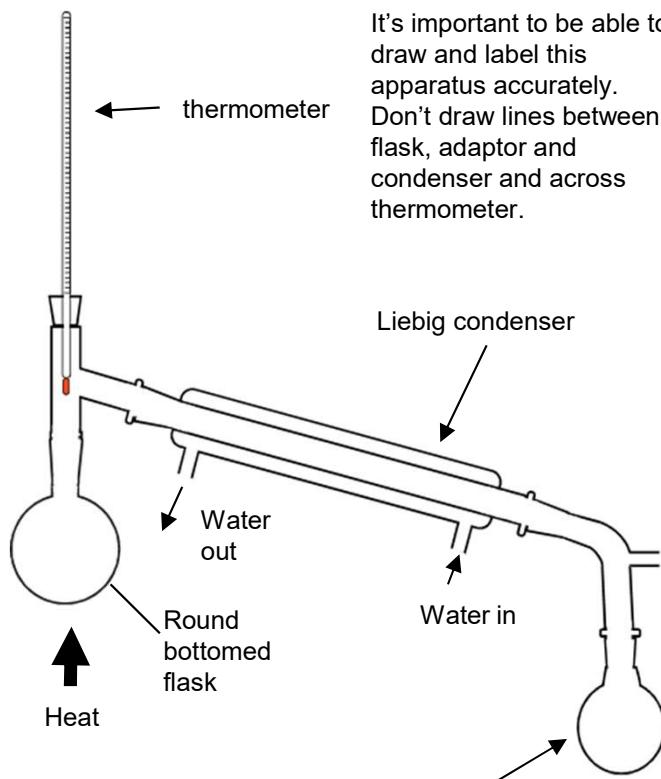
In general used as separation technique to separate an organic product from its reacting mixture. In order to maximise yield collected, only collect the distillate at the approximate boiling point of the desired aldehyde and not higher.

The bulb of the thermometer should be at the T junction connecting to the condenser to measure the correct boiling point.

Note the water goes in to the bottom of the condenser to go against gravity. This allows more efficient cooling and prevents back flow of water.

Electric heaters are often used to heat organic chemicals. This is because organic chemicals are normally highly flammable and could set on fire with a naked flame.

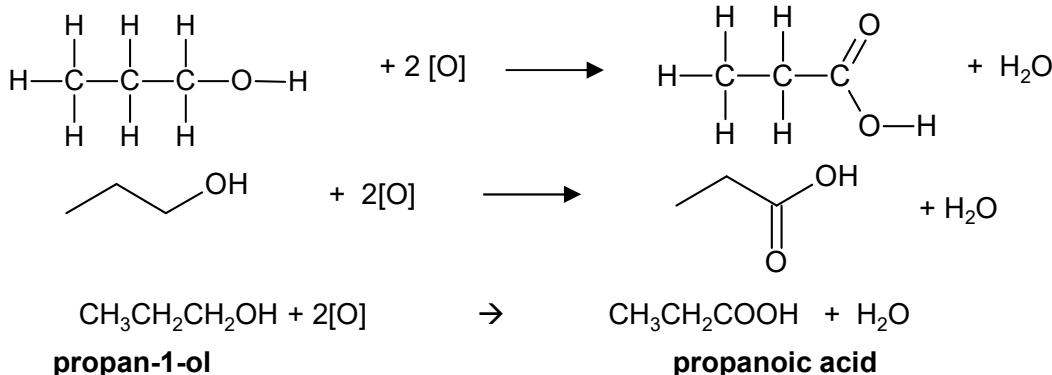
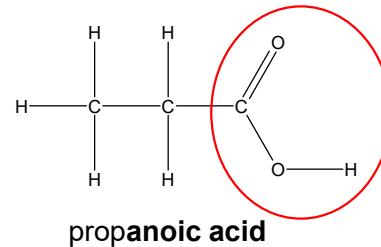
It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser and across thermometer.



The collection flask can be cooled in ice to help improve the yield of distillate

## Full Oxidation of Primary Alcohols

**Reaction:** primary alcohol  $\rightarrow$  carboxylic acid  
**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid  
**Conditions:** use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)



## Reflux

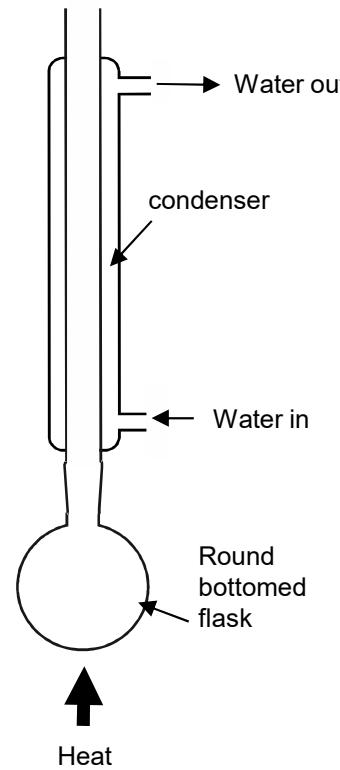
Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

**Never seal the end of the condenser** as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated including the distillation set up.

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles.

It's important to be able to draw and label this apparatus accurately.

- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

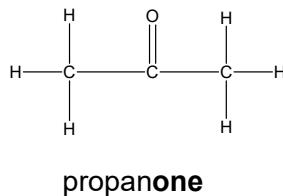


## Oxidation of Secondary Alcohols

**Reaction:** secondary alcohol  $\rightarrow$  ketone

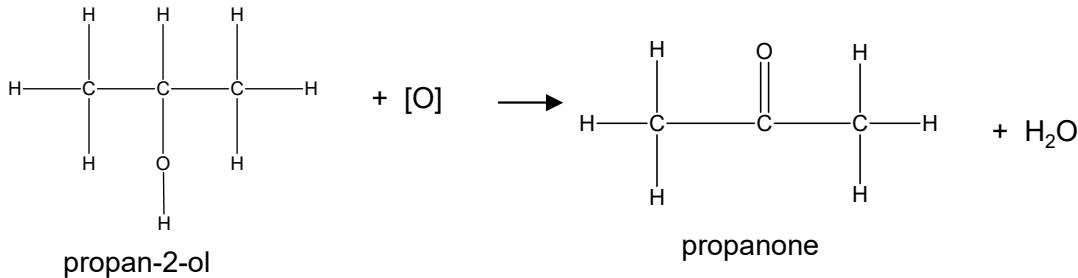
**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid.

**Conditions:** heat under reflux



Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



**Observation:** the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion

There is no further oxidation of the ketone under these conditions.

**Tertiary alcohols** cannot be oxidised at all by potassium dichromate: This is because there is no hydrogen atom bonded to the carbon with the -OH group

## Distinguishing between Aldehydes and Ketones

Aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised. This is the chemical basis for two tests that are commonly used to distinguish between aldehydes and ketones.

### Tollens' Reagent

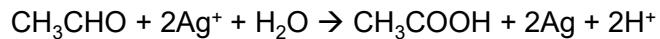
**Reagent:** Tollens' reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of  $[\text{Ag}(\text{NH}_3)_2]^+$ .

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Tollens' reagent into a carboxylic acid. The silver(I) ions are reduced to silver atoms

**Observation:** with aldehydes, a silver mirror forms coating the inside of the test tube.

Ketones result in no visible change



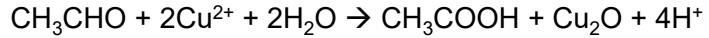
### Fehling's solution

**Reagent:** Fehling's solution containing blue  $\text{Cu}^{2+}$  ions.

**Conditions:** heat gently

**Reaction:** **aldehydes only** are oxidised by Fehling's solution into a carboxylic acid. The copper (II) ions are reduced to copper(I) oxide.

**Observation:** **Aldehydes** :Blue  $\text{Cu}^{2+}$  ions in solution change to a red precipitate of  $\text{Cu}_2\text{O}$ . **Ketones do not react**



The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide.

## Reaction of Alcohols with Dehydrating Agents

**Reaction:** Alcohol  $\rightarrow$  Alkene

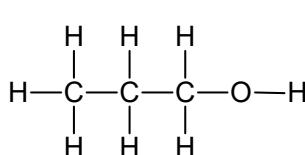
**Reagents:** Concentrated sulfuric or phosphoric acids

**Conditions:** warm (under reflux)

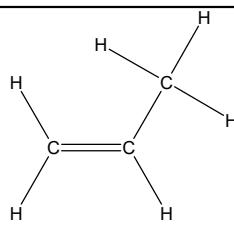
**Role of reagent:** dehydrating agent/catalyst

**Type of reaction:** acid catalysed elimination

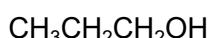
**Dehydration Reaction:** removal of a water molecule from a molecule



propan-1-ol

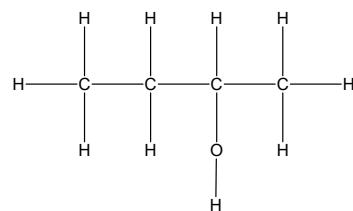


propene

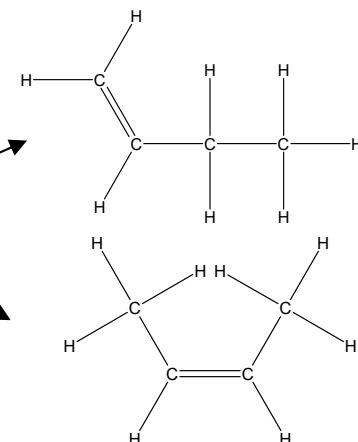


Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms

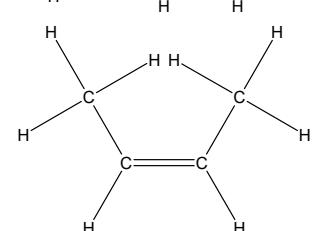
butan-2-ol



Butan-2-ol can form both alkenes although more but-2-ene would be formed



but-1-ene

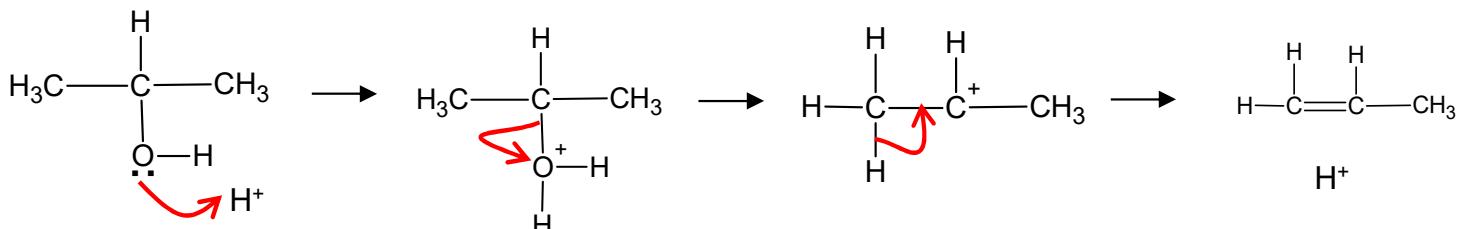


but-2-ene

But-2-ene could also exist as E and Z isomers

Producing alkenes from alcohols provides a possible route to polymers without using monomers derived from oil.

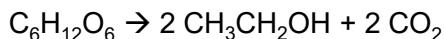
### Acid catalysed elimination mechanism



The  $\text{H}^+$  comes from the conc  $\text{H}_2\text{SO}_4$  or conc  $\text{H}_3\text{PO}_4$

### Fermentation

glucose  $\rightarrow$  ethanol + carbon dioxide



The conditions needed are:

- Yeast
- No air
- temperatures 30 –40°C

Type of reaction: **Fermentation**

The **optimum temperature** for fermentation is around 38°C

At lower temperatures the reaction is too slow.

At higher temperatures the yeast dies and the enzymes denature.

Fermentation is done in an **absence of air** because the presence of air can cause extra reactions to occur.

It oxidises the ethanol produced to ethanoic acid (vinegar).

### Advantages

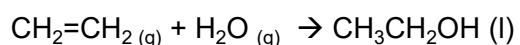
- sugar is a renewable resource
- production uses low level technology / cheap equipment

### Disadvantages

- batch process which is slow and gives high production costs
- ethanol made is not pure and needs **purifying by fractional distillation**
- depletes land used for growing food crops

### From ethene

Reagent: **ETHENE** - from cracking of fractions from distilled crude oil



Type of reaction: **Hydration/addition**

**Definition:** **Hydration** is the addition of water to a molecule

#### Essential Conditions

high temperature 300 °C

high pressure 70 atm

strong acidic catalyst of **conc H<sub>3</sub>PO<sub>4</sub>**

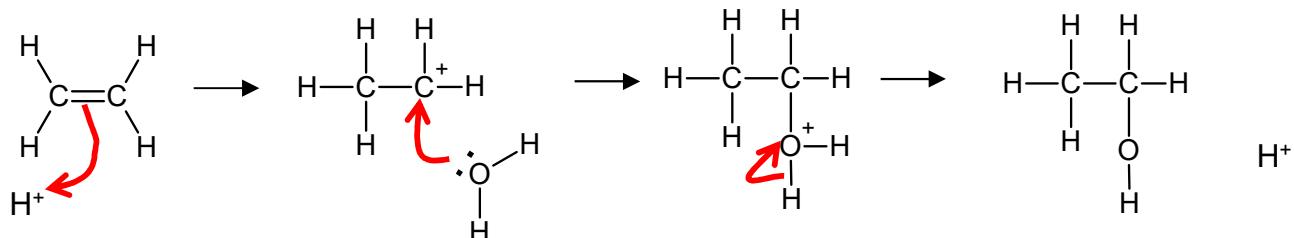
#### Advantages:

- faster reaction
- purer product
- continuous process (which means cheaper manpower)

#### Disadvantages:

- high technology equipment needed (expensive initial costs)
- ethene is non-renewable resource (will become more expensive when raw materials run out)
- high energy costs for pumping to produce high pressures

### Acid catalysed addition mechanism for hydration of ethene



The H<sup>+</sup> comes from the conc H<sub>3</sub>PO<sub>4</sub>

## Ethanol as biofuel

A biofuel is a fuel produced from plants

The term carbon neutral refers to “an activity that has **no net annual carbon** (greenhouse gas) emissions **to the atmosphere**”

Ethanol produced from fermentation is a biofuel.

It can be argued that ethanol produced from this method is classed as carbon–neutral because any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew. There would be no net CO<sub>2</sub> emission into the atmosphere.

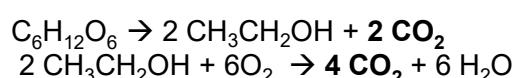
### Equations to show no net contribution to CO<sub>2</sub>

Removal of CO<sub>2</sub> by photosynthesis



6 CO<sub>2</sub> molecules are removed from the atmosphere when the plants grow by photosynthesis to produce one molecule of glucose.

Production of CO<sub>2</sub> by fermentation and combustion



When 1 molecule of glucose is fermented 2 molecules of CO<sub>2</sub> is emitted. The two ethanol molecules produced will then produce 4 molecules of CO<sub>2</sub> when they are combusted.

Overall for every 6 molecules of CO<sub>2</sub> absorbed, 6 molecules of CO<sub>2</sub> are emitted. There is no net contribution of CO<sub>2</sub> to the atmosphere.

This does not take into account any energy needed to irrigate plants, fractionally distil the ethanol from the reaction mixture or process the fuel. If the energy for these processes comes from fossil fuels then the ethanol produced is not carbon neutral.