

3.5 Alcohols

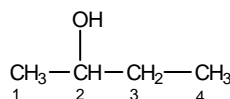
General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

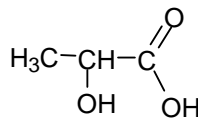
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

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-**:

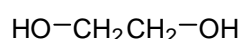
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



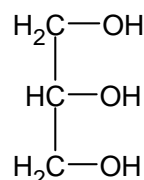
butan-2-ol



2-hydroxypropanoic acid



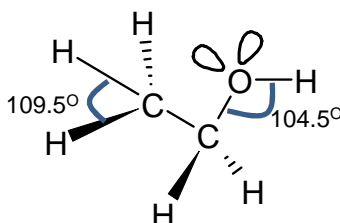
ethane-1,2-diol



propane-1,2,3-triol

Bond angles in Alcohols

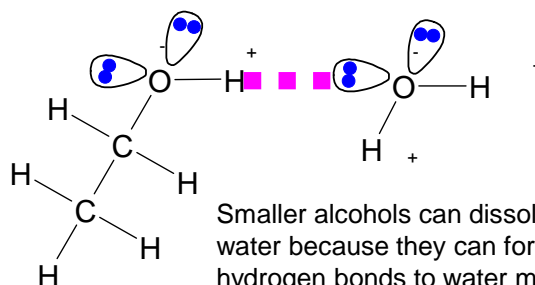
All the H-C-H bonds and C-C-O are 109.5° (tetrahedral shape), because there are 4 bonding pairs of electrons repelling to a position of minimum repulsion.



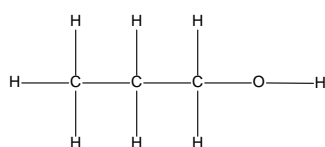
The H-O-C bond is 104.5° (bent line shape), because there are 2 bonding pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bonding pairs so the bond angle is reduced.

Boiling points

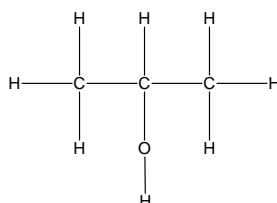
The alcohols have relatively low volatility and high boiling points due to their ability to form hydrogen bond between alcohol molecules.



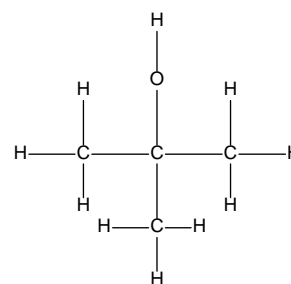
Different types of alcohols



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.

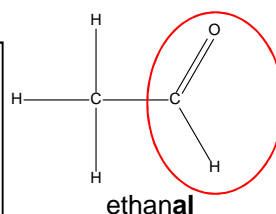
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

Reaction: primary alcohol \rightarrow aldehyde

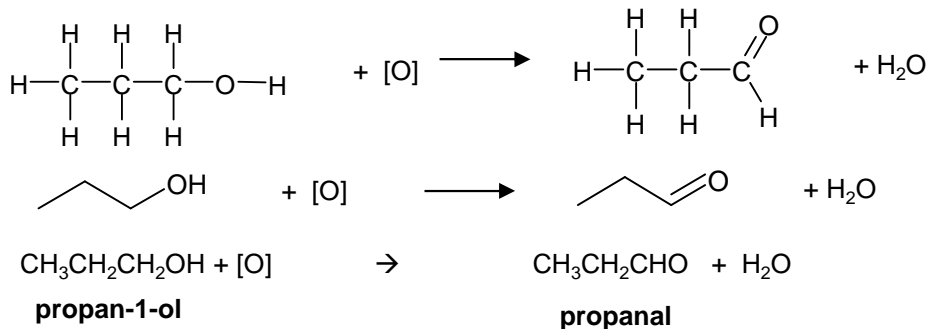
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.

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

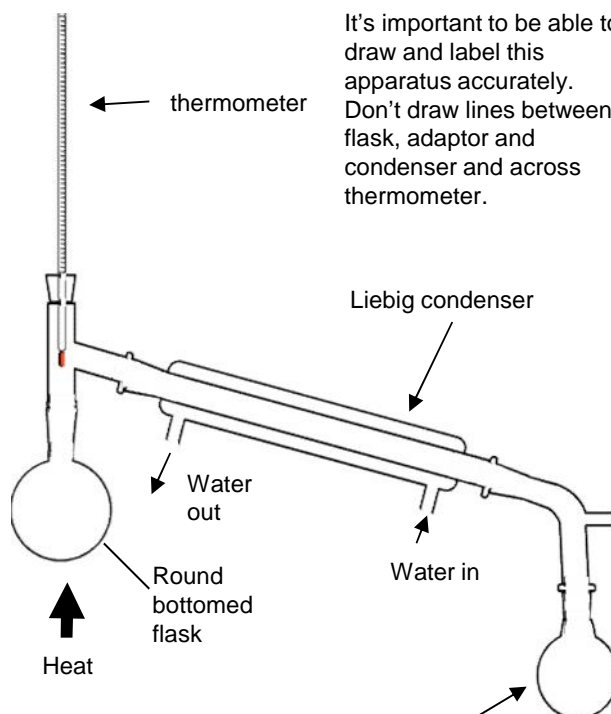
Distillation

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.

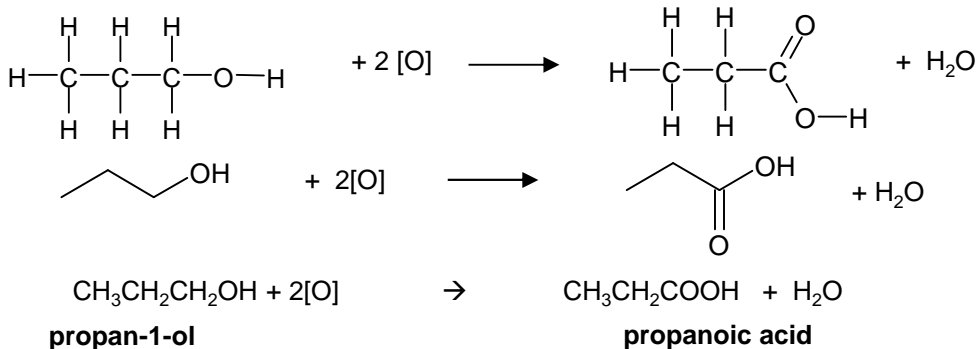
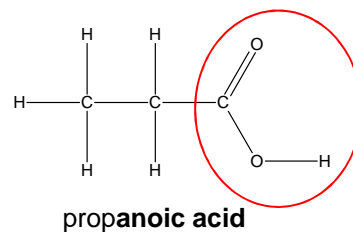
The collection flask can be cooled in ice to help improve the yield of distillate

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)



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

Reflux

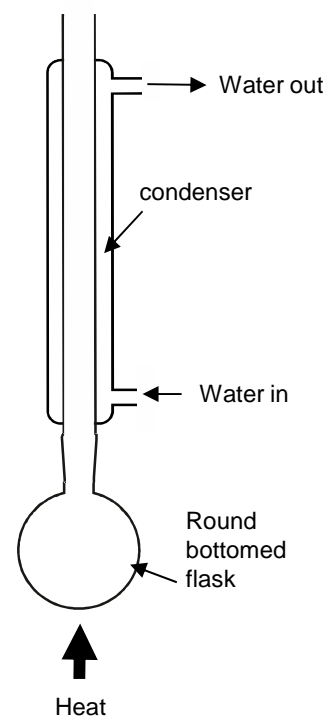
Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

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.

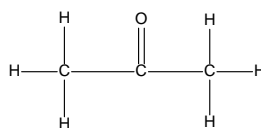
It's important to be able to draw and label this apparatus accurately.

- 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

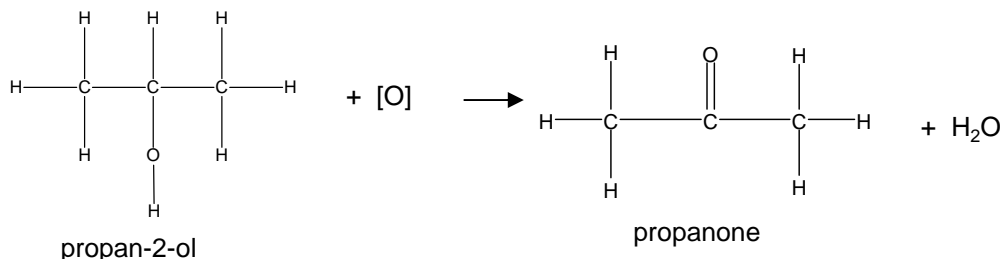
Reaction: secondary alcohol → ketone
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid.
Conditions: heat under reflux



propanone

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 (Cr₂O₇²⁻) reduces to the green Cr³⁺ 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.

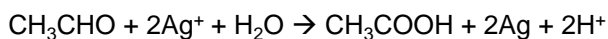
Tollens' Reagent

Reagent: Tollens' reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)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



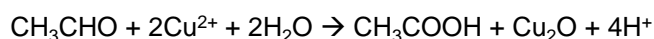
Fehling's solution

Reagent: Fehling's solution containing blue Cu²⁺ 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 Cu²⁺ ions in solution change to a red precipitate of Cu₂O. **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

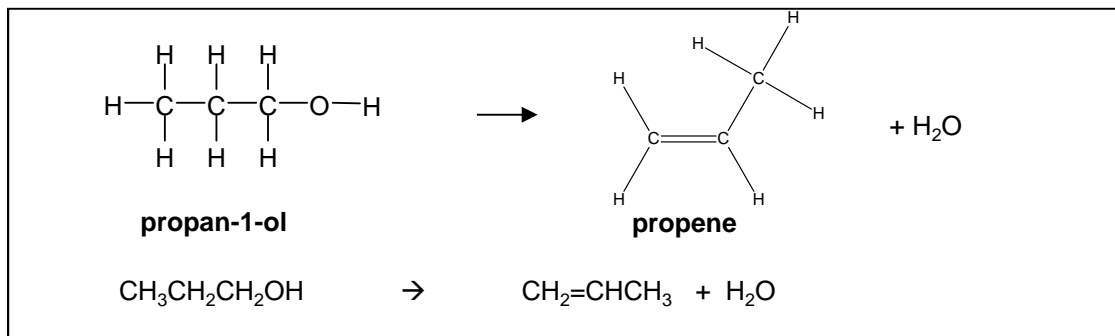
Reagents: Concentrated sulfuric or phosphoric acids

Conditions: warm (under reflux)

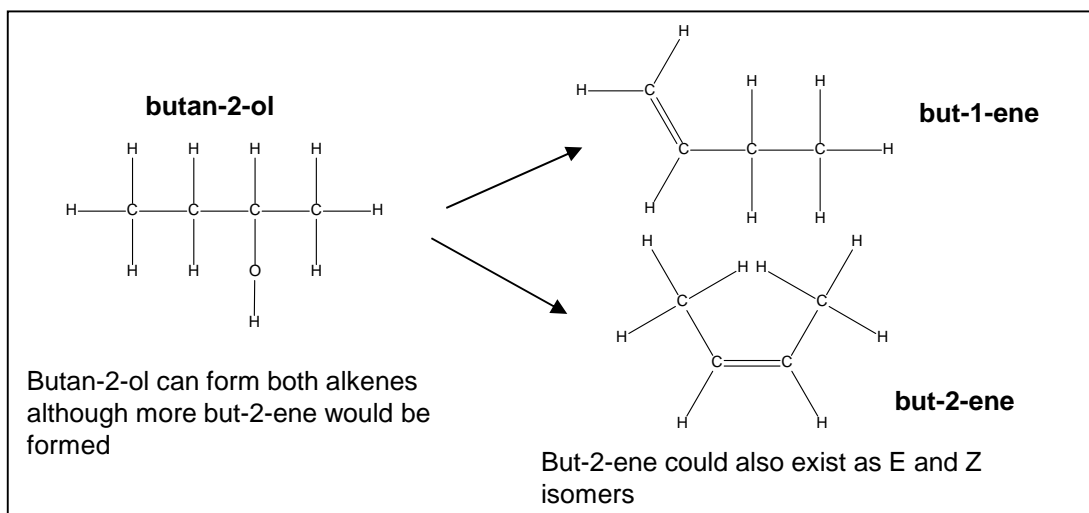
Role of reagent: dehydrating agent/catalyst

Type of reaction: acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule

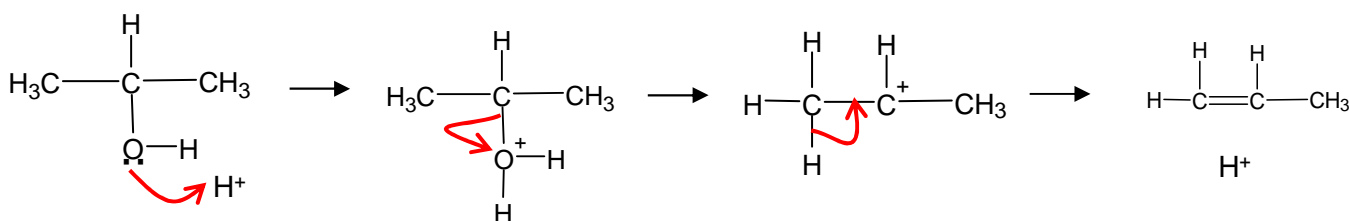


Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms



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

Acid catalysed elimination mechanism

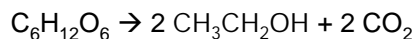


The H^+ comes from the conc H_2SO_4 or conc H_3PO_4

Forming ethanol Comparing two methods for producing ethanol: Fermentation or industrial formation from ethene

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

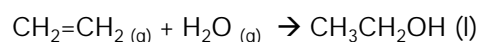
- sugar is a renewable resource
- production uses low level technology / cheap equipment

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 H₃PO₄**

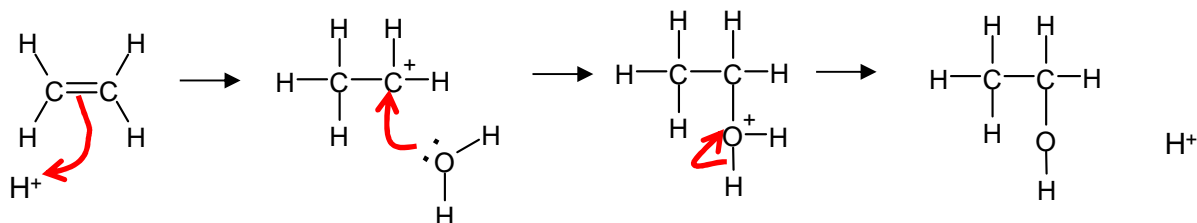
Advantages:

- 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^+ comes from the conc H_3PO_4

Ethanol as biofuel

A biofuel is a fuel produced from plants

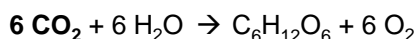
The term carbon neutral refers to “an activity that has **no net annual carbon** (greenhouse gas) emissions **to the atmosphere**”

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 CO₂ emission into the atmosphere.

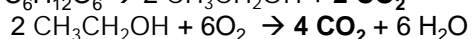
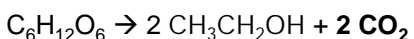
Equations to show no net contribution to CO₂

Removal of CO₂ by photosynthesis



6 CO₂ molecules are removed from the atmosphere when the plants grow by photosynthesis to produce one molecule of glucose.

Production of CO₂ by fermentation and combustion



When 1 molecule of glucose is fermented 2 molecules of CO₂ is emitted. The two ethanol molecules produced will then produce 4 molecules of CO₂ when they are combusted.

Overall for every 6 molecules of CO₂ absorbed, 6 molecules of CO₂ are emitted. There is no net contribution of CO₂ 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.