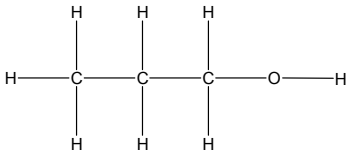
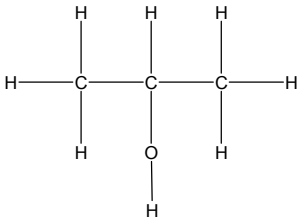
10. Alcohols

Different types of alcohols



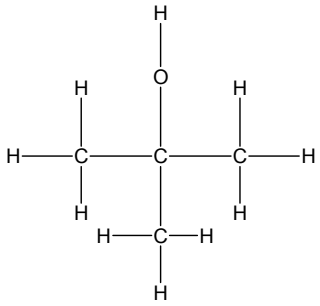
Propan-1-ol
Primary

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



Propan-2-ol
Secondary

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



2 methyl propan-2-ol
Tertiary

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

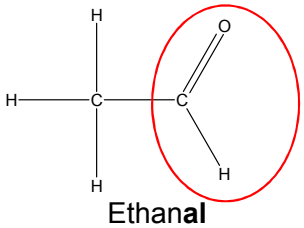
Oxidation reactions of the alcohols

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.

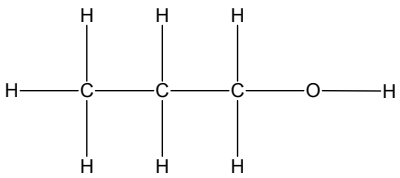
Partial Oxidation of Primary Alcohols

Reaction: primary alcohol → aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.
Conditions: (use a limited amount of dichromate) warm gently and **distil** out the aldehyde as it forms:



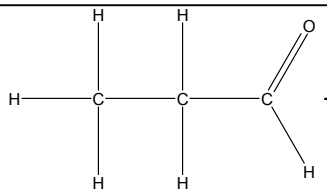
Ethan**al**

An aldehyde's name ends in **–al**
It always has the C=O bond on the last carbon of the chain so it does not need an extra number



propan-1-ol

+ [O] →



+ H_2O

propanal

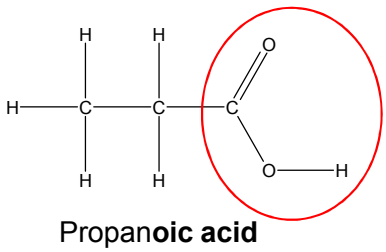
Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

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

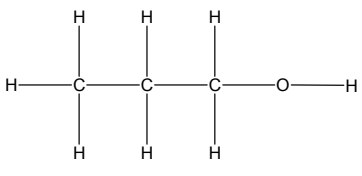
When writing the formulae of aldehydes in a condensed way wire **CHO** and not COH e.g.CH_3CH_2**CHO**

Full Oxidation of Primary Alcohols

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

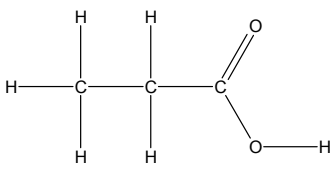


Propan**oic acid**



propan-1-ol

+ 2 [O] →



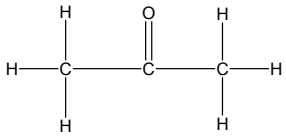
+ H_2O

Propanoic acid

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

Oxidation of Secondary Alcohols

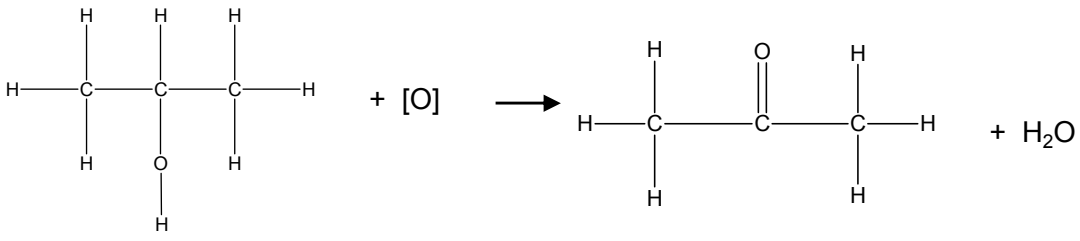
Reaction: secondary alcohol → ketone
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid.
Conditions: heat under reflux



Propan**one**

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



propan-2-ol + [O] → Propanone + H_2O

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

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

Tertiary alcohols cannot be oxidised at all by potassium dichromate

Distinguishing between Aldehydes and Ketones

The fact that aldehydes can be further oxidised to carboxylic acids whereas ketones cannot be further oxidised is the chemical basis for two tests that are commoly used to distinguish between aldehydes and ketones

Tollen's Reagent

Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[Ag(NH_3)_2]^+$.
Conditions: heat gently
Reaction: aldehydes only are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to a silver atoms
Observation: with aldehydes, a silver mirror forms coating the inside of the test tube Ketones result in no change

$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$

Fehling's solution

Reagent: Fehling's Solution containing blue Cu^{2+} ions.
Conditions: heat gently
Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide . .
Observation: Aldehydes : Blue Cu^{2+} ions in solution change to to red precipitate of Cu_2O. **Ketones do not react**

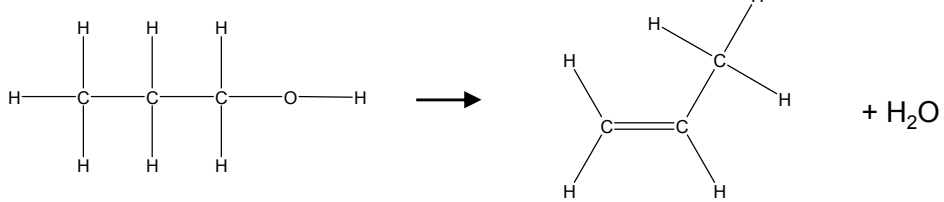
$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$

Reaction of alcohols with Dehydrating agents

Reaction : Alcohol → Alkene

Reagents : Concentrated Sulphuric or Phosphoric acids
Conditions: warm (under reflux)
Role of reagent: dehydrating agent/catalyst
Type of reaction: **acid catalysed** elimination

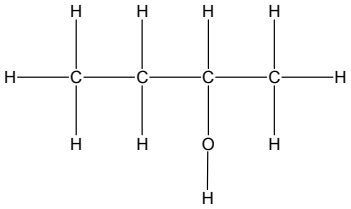
Dehydration Reaction: removal of a water molecule from a molecule

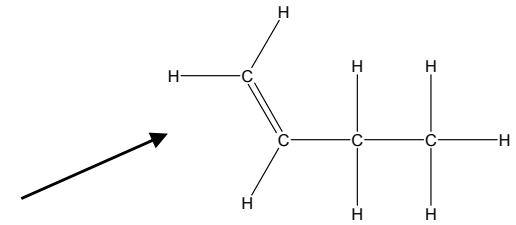


propan-1-ol → **Propene** + H_2O

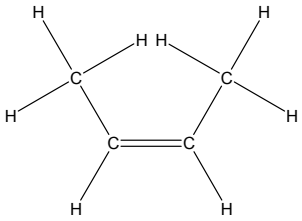
Some 2º and 3º alcohols can give more than one product, when the double bond forms between different carbon atoms

Butan-2-ol





But-1-ene



But-2-ene

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

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

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

Fermentation

glucose → ethanol + carbon dioxide

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$

The conditions needed are:
- Yeast
- No air
- temperatures 25 –55ºC

The **optimum temperature** for fermentation is around 38ºC

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

From ethene

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

$CH_2{=}CH_{2\ (g)} + H_2O_{\ (g)} \rightarrow CH_3CH_2OH\ (l)$

Essential Conditions

high temperature 300 °C

high pressure 70 atm

strong acidic catalyst of H_3PO_4

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

Disadvantage:
- High technology equipment needed (expensive initial costs)
- ethene is non-renewable resource (will become more expensive when raw materials run out)
- High energy costs

Ethanol as biofuel

A biofuel is a fuel produced from plants

Ethanol produced from fermentation is a biofuel.

It can be argued that ethanol produced from this method is classed as carbon–neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

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 this process comes from fossil fuels then the ethanol produced is not carbon neutral