

6.5 Alcohols

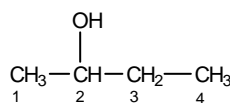
General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

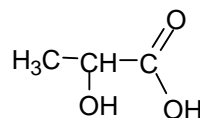
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

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-**:

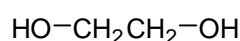
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



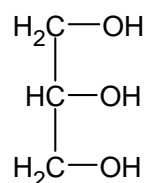
Butan-2-ol



2-hydroxypropanoic acid



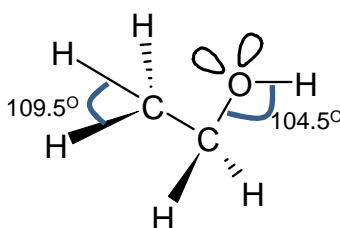
Ethane-1,2-diol



propane-1,2,3-triol

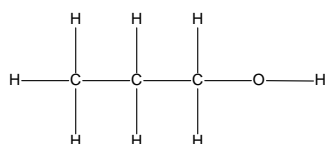
Bond angles in Alcohols

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



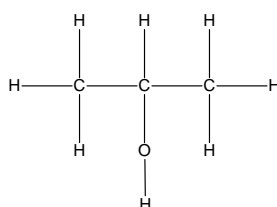
The H-O-C bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

Different types of alcohols



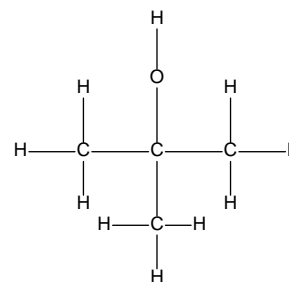
Propan-1-ol
Primary

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

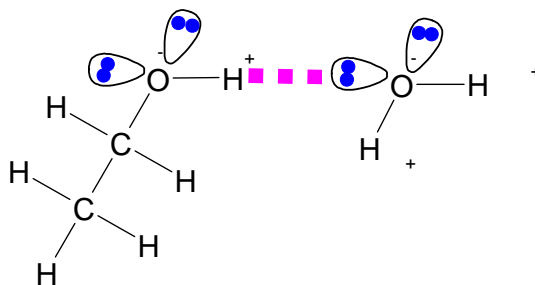


methylpropan-2-ol
Tertiary

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

Solubility of simple alcohols

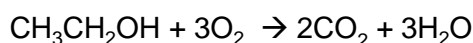
The smaller alcohols are soluble in water because they can form hydrogen bonds with water. The longer the hydrocarbon chain the less soluble the alcohol.



Reactions of Alcohols

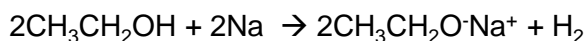
Combustion of Alcohols

Alcohols combust with a clean flame



Reaction of Alcohols with Sodium

Sodium reacts with alcohols



This reaction can be used as a test for alcohols

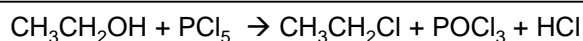
Observations:

- effervescence,
- the mixture gets hot,
- sodium dissolves,
- a white solid is produced.

Substitution reactions of Alcohols to form Halogenoalkanes

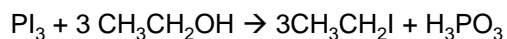
Various halogenating compounds can be used to substitute the $-\text{OH}$ group for a halogen

Reaction with phosphorous (V) halide



This reaction with PCl_5 (phosphorous(V)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.

Reaction with phosphorous (III) halide



The **phosphorous (III) halide** can also be produced in situ by reacting red phosphorus and the halogen.

$\text{PCl}_5 / \text{PCl}_3 / \text{conc HCl} / \text{SOCl}_2 /$
mixture of $\text{NaCl} + \text{H}_2\text{SO}_4$ can all be
uses for substituting a Cl

For Br and I it is best to use PI_5, PI_3
and Br equivalents. It is not suitable
to use NaBr , or $\text{NaI} + \text{H}_2\text{SO}_4$ to
produce HBr or HI because the
sulphuric acid will oxidise the
hydrogen halides to other products

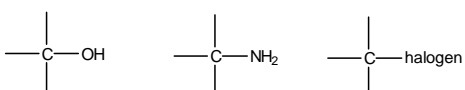
Oxidation and Reduction in organic chemistry

Oxidation and reduction reactions are common in organic chemistry. Whilst it is possible to assign individual atoms in an organic molecule an oxidation state/number, it can be quite complicated to work them out. Instead some chemists use the concept of functional group level to scaffold their ideas about oxidation and reduction.

The functional group level of a carbon atom can be worked out by counting the number of bonds to electronegative atoms on the carbon.

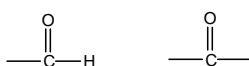
- No such bonds is called the Hydrocarbon level
- one bond is called the Alcohol level
- two bonds is the Carbonyl level
- three bonds the Carboxylic Acid level
- four bonds the Carbon Dioxide level

Alcohol level



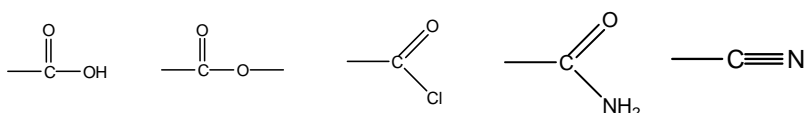
common examples within the Alcohol level include alcohols, amines, halogenoalkanes

Carbonyl level



examples in the Carbonyl level: aldehydes, ketones

Carboxylic Acid level



Examples in the Carboxylic Acid level: carboxylic acids, esters, acyl chlorides, amides, nitriles;

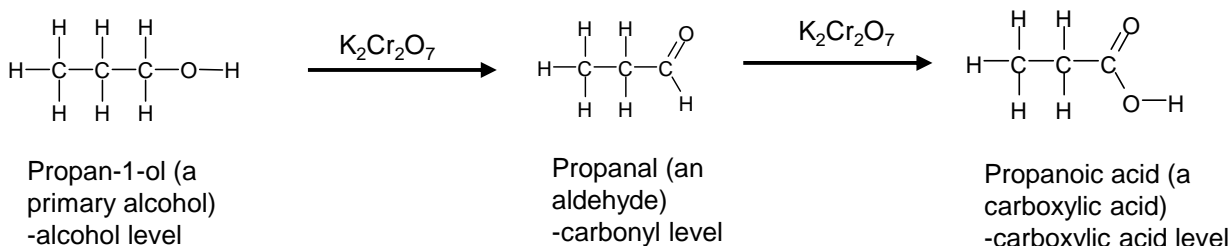
Moving a carbon atom up a level is oxidation and requires an oxidizing agent. Moving a carbon atom down a level is reduction and requires a reducing agent

Oxidation reactions of the alcohols

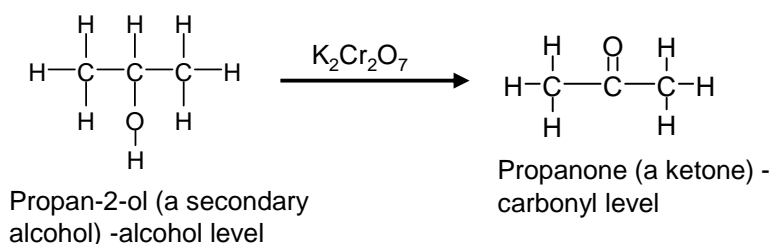
Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols to oxidise.

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

Primary alcohols can be oxidised up one level to an aldehyde, or two levels to a carboxylic acid



Secondary alcohols can only be oxidised up one level to a ketone

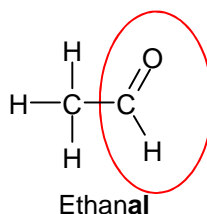


Partial Oxidation of Primary Alcohols

Reaction: primary alcohol \rightarrow aldehyde

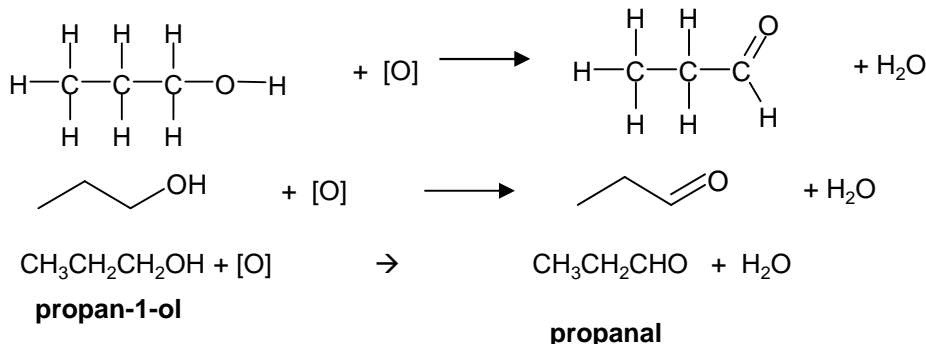
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.

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 an extra number

Primary alcohols can be oxidised to aldehydes or up an extra level to carboxylic acids. If we just want to oxidise the alcohol up to an aldehyde and no further then we need to choose the conditions carefully. The main condition is to conduct the reaction in a distillation set up, as shown below, and by application of gentle heat distil off the aldehyde as it forms, which will prevent it from reacting with more dichromate to produce a carboxylic acid. Using a limited amount of the oxidising agent will also help prevent further oxidation



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

Generally we write the oxidation equations in a simplified form using [O] which represents O from the oxidising agent rather than a full balanced equation with the dichromate ion as shown below.



When writing the formulae of aldehydes in a condensed way write **CHO** and not COH e.g. $\text{CH}_3\text{CH}_2\text{CHO}$

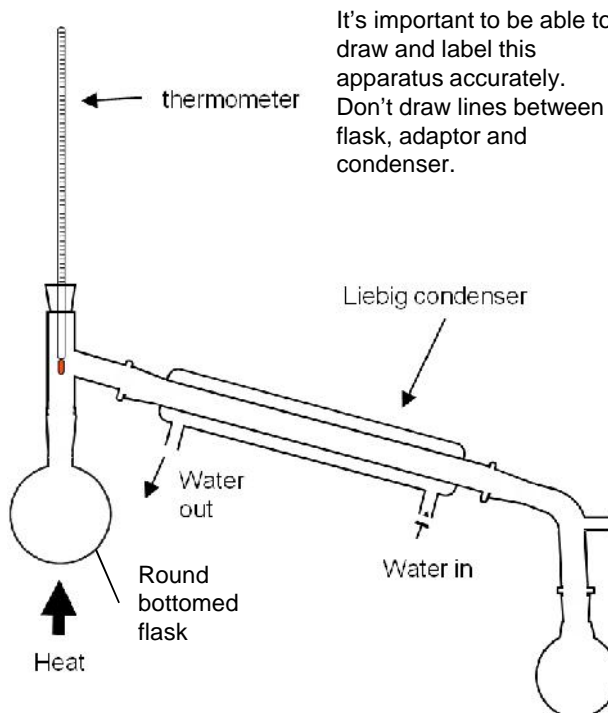
Distillation

In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Note 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 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.



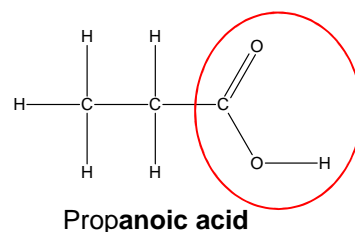
It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

Full Oxidation of Primary Alcohols

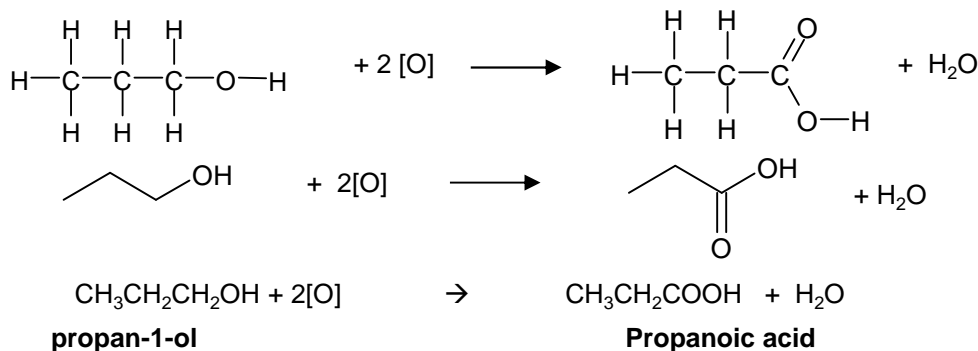
Reaction: primary alcohol \rightarrow carboxylic acid

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)



If we want to oxidise the primary alcohol up two levels to a carboxylic acid then we need to use more vigorous conditions. Heating under reflux allows the reaction to happen quicker.



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

Reflux

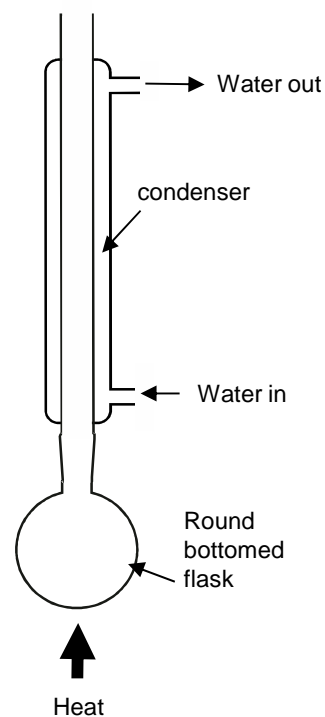
Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

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

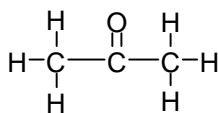


Oxidation of Secondary Alcohols

Reaction: secondary alcohol \rightarrow ketone

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

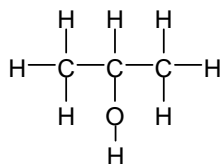
Conditions: heat under reflux



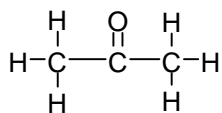
Propanone

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



propan-2-ol



Propanone



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

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 commonly used to distinguish between aldehydes and ketones

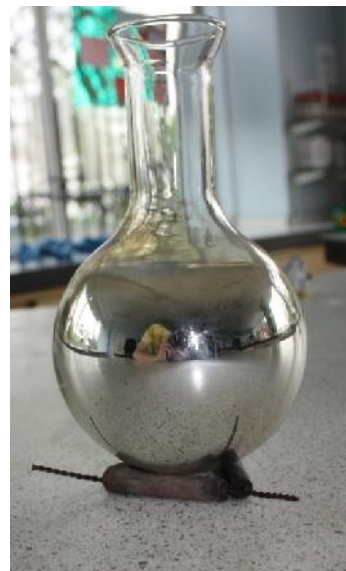
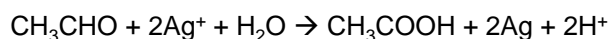
Tollen's Reagent

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

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's 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



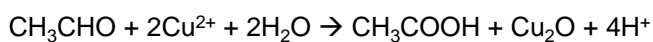
Fehling's solution

Reagent: Fehling's Solution containing blue Cu^{2+} ions.

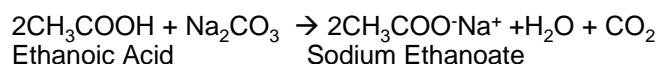
Conditions: heat gently

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 Cu^{2+} ions in solution change to a red precipitate of Cu_2O .
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



Elimination Reaction of Alcohols with Dehydrating Agents

Reaction: Alcohol \rightarrow Alkene

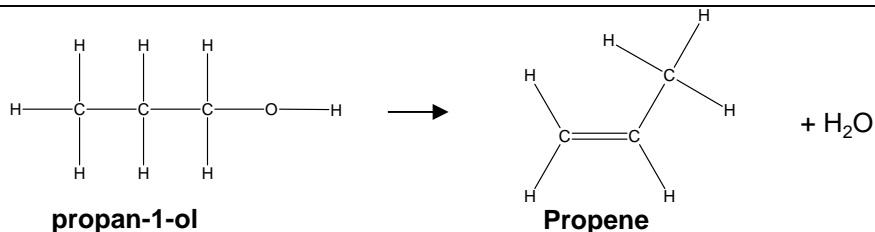
Reagents: Concentrated Sulfuric or Phosphoric acids

Conditions: warm (under reflux)

Role of reagent: dehydrating agent/catalyst

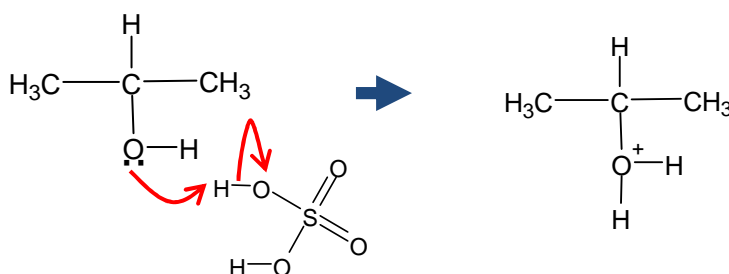
Type of reaction: acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule



E1 Elimination Reaction

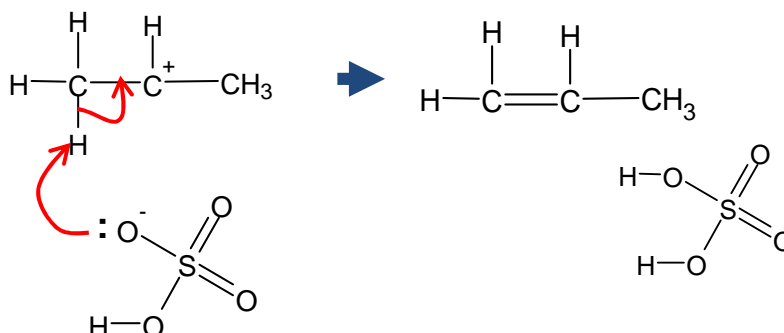
Step 1: The oxygen on the alcohol with its lone pair accepts a proton from the sulphuric acid



Step 2: The protonated alcohol loses water forming a carbocation

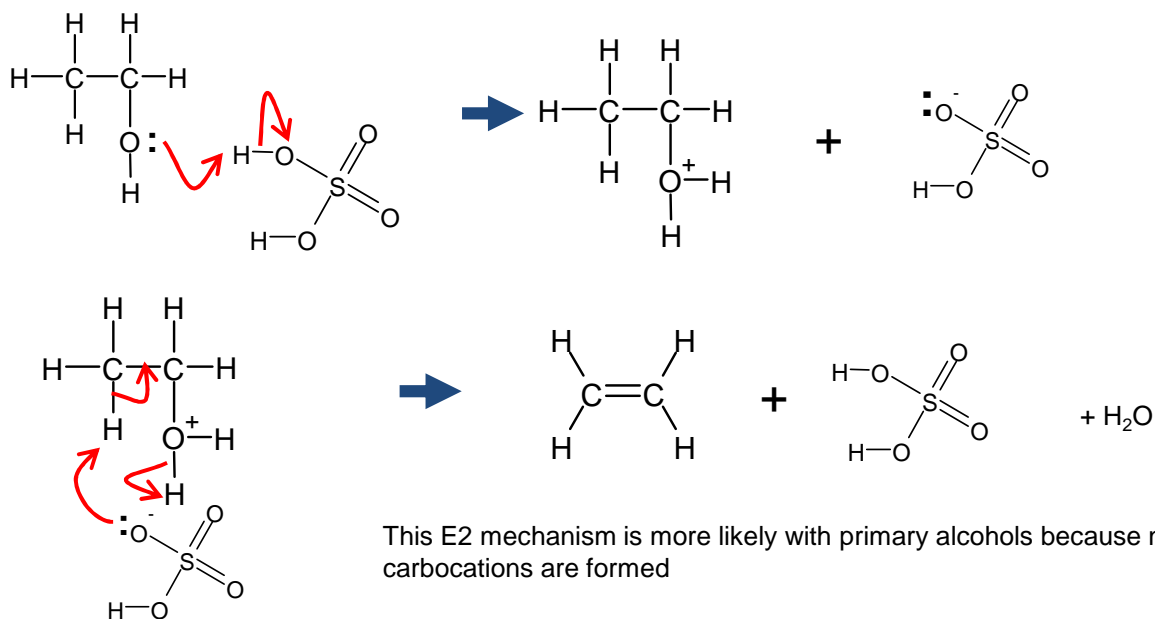


Step 3: The carbocation loses a proton and forms a double bond, regenerating the sulphuric acid catalyst in the process



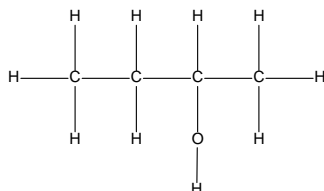
The Elimination reaction is called an E1 reaction. It is most likely to occur with tertiary alcohols because the carbocation formed in step 2 is stabilised by the electron releasing alkyl groups around it. Secondary alcohols will react by this reaction less readily. This mechanism is unlikely for primary alcohols because it would result in the formation of an unstable primary carbocation

E2 Elimination Reaction – primary alcohols

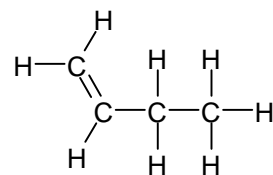


Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms

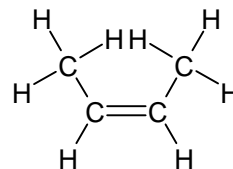
Butan-2-ol



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

Questions on Alcohols

1. Draw skeletal formula of the four structurally isomeric alcohols of molecular formula $C_4H_{10}O$.

Name each isomer and identify whether they are primary, secondary or tertiary alcohols

2) Draw displayed formulae of compound formed by the following oxidations

a) propan-1-ol + acidified $K_2Cr_2O_7$ (heated under reflux with excess oxidising agent)

b) propan-1-ol + acidified $K_2Cr_2O_7$ (gently heated and product distilled off with limited oxidising agent)

c) propan-2-ol + acidified $K_2Cr_2O_7$ (heated under reflux with excess oxidising agent)

d) cyclohexanol + acidified $K_2Cr_2O_7$ (heated under reflux with excess oxidising agent)

e) 2-methylpropan-1-ol + acidified $K_2Cr_2O_7$ (gently heated and product distilled off with limited oxidising agent)

3 a) Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, was oxidised by adding it dropwise to acidified potassium dichromate(VI) and distilling off the organic product immediately. Write an equation for this reaction showing the skeletal formula of the organic substances. You may use [O] to represent the oxidising agent.

b) Butan-2-ol, $CH_3CH_2CH(OH)CH_3$, was oxidised by heating it under reflux with acidified potassium dichromate(VI). Write an equation for this reaction the skeletal formula of the organic substances. You may use [O] to represent the oxidising agent.

c) Fehling's solution could be used to distinguish between the products formed in 3a and 3b. Describe the observations that would be made with both products. The product that reacts with Fehling's solution turns into another organic substance. Draw the displayed formula of the organic product that is formed from the reaction of Fehling's solution with the substance that reacts. What type of reaction is this?

4 Ethanol can be oxidised to an aldehyde and to a carboxylic acid.

a) Draw the structure of this aldehyde and of this carboxylic acid.

b) Give a suitable reagent and reaction conditions for the oxidation of ethanol to form the carboxylic acid as the major product. Explain what colour change would be observed in this reaction and identify which species is responsible for each colour.

c) Draw the structure of an alcohol containing four carbon atoms which is resistant to oxidation. Explain why this compound cannot be oxidised.

d) Draw the structure of an alcohol containing four carbon atoms which can be oxidised to a ketone.

5 a) Describe two chemical tests that could be done to distinguish between a sample of propanal and a sample of propanone. Describe the relevant colour changes for each test

b) Describe a chemical test that could be done to distinguish between a sample of propanone and a sample of propanoic acid. Describe the relevant observations.

c) Describe a chemical test that could be done to distinguish between a sample of propan-1-ol and a sample of 2-methylpropan-2-ol acid. Describe the relevant observations.

6. Methanol is the first member of the homologous series of alcohols
- (a) Write the general formula for this homologous series.
- (b) Methanol can be oxidised to methanoic acid. State the reagent(s) which you would use to perform this oxidation and give any colour change which might be seen during the reaction.
- (c) Write an equation for the oxidation of methanol to methanoic acid, using displayed formulae to show the structures of the organic substances. You may use the symbol [O] for the oxidising agent.
- (d) By considering the structure of methanoic acid, explain why it can easily be oxidised further and suggest the product(s) formed by further oxidation.

7. Most alcohols can be readily dehydrated.

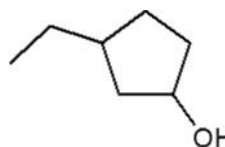
- (a) Explain what is meant by the term *dehydration*.
- (b) State the type of compound formed by dehydration of alcohols.
- (c) What are the reagent(s) and condition(s) necessary for the dehydration of alcohols.
- (d) Draw the displayed formula of the product that would be formed if propan-2-ol was dehydrated.
- (e) Choose an alcohol with the formula C_4H_9OH which, on dehydration, would give a single product. Draw the displayed formula of the alcohol and the displayed formula of the product.
- (f) Choose an alcohol with the formula C_4H_9OH which, on dehydration, would give three products, A, B and C which are isomeric. A and B are E-Z stereoisomers of each other and C is a structural isomer of A and B. Draw skeletal formulae for the alcohol and for these three isomers and explain why the formation of these isomers is possible in this case.

8. Outline the mechanism for the reaction for the reaction where water is eliminated from a molecule of propan-1-ol

9. Outline the mechanism for the reaction for the reaction where water is eliminated from a molecule of butan-2-ol to form but-2-ene

10. Draw the products that would be formed by reacting the cyclic alcohol shown on the right with:

- a) Acidified potassium dichromate (heat under reflux)
b) concentrated sulphuric acid



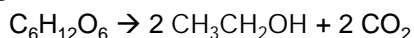
- 11a) Draw the skeletal formula of an alcohol with 7 carbon atoms that could be dehydrated to form 3 different structurally isomeric organic products
- b) Draw the skeletal formula of an alcohol with 7 carbon atoms that could be dehydrated to form 2 different structurally isomeric organic products
- c) Draw the skeletal formula of an alcohol with 7 carbon atoms that could be dehydrated to form 1 organic products
- d) Draw the skeletal formula of an alcohol with 7 carbon atoms that could **not** be dehydrated

Formation of Ethanol

Ethanol can be produced in two main ways. One way is from the fermentation of sugars. The other way is by reacting ethene with Steam

Fermentation

glucose \rightarrow ethanol + carbon dioxide



Type of reaction: **Fermentation**

The conditions needed are:

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

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

At lower temperatures the rate of 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.

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

The solution produced by fermentation will only contain around 15% ethanol. Above this concentration of ethanol the yeast will not survive. Therefore to get pure ethanol it is necessary to fractionally distil the solution made by fermentation

Advantages of producing ethanol from fermentation

- Sugar is a renewable resource so producing ethanol by this method would not use up non-renewable crude oil
- Production by this method uses low level technology and cheap equipment and will have low energy costs.

Disadvantages of producing ethanol from fermentation

- This is a batch process which has a slow rate of reaction. The need to be refilling and emptying batch containers will require labour and this will lead to higher production costs.
- The ethanol made by this process is not pure and will need purifying by fractional distillation which is an extra stage in the process with extra costs.
- Using land to produce sugar for fermentation will potentially deplete the land bank used for growing food crops which could have a knock on effect on food prices. If the land came from destruction of rain forests this would obviously be a disadvantage too

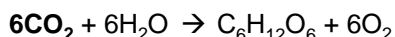
Ethanol as a carbon neutral biofuel

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 so there is not net annual addition to carbon dioxide levels in the atmosphere

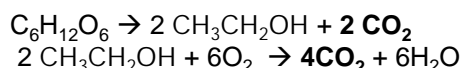
Equations to show no net contribution to CO₂

Removal of CO₂ by photosynthesis



6CO₂ 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



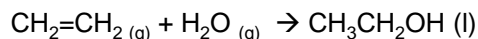
When 1 molecule of glucose is fermented 2 molecules of CO₂ is emitted. The two ethanol molecules produced will then produce 4 molecules of CO₂ when they are combusted

Overall for every 6 molecules of CO₂ absorbed , 6 molecules of CO₂ are emitted

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

Forming ethanol industrial formation from ethene

Ethene - from cracking of fractions from distilled crude oil is reacted with steam at high temperatures in the presence of an acid catalyst



Type of reaction: **Hydration/addition**

Essential Conditions

high temperature 300 °C
high pressure 70 atm
strong acidic catalyst of **conc H₃PO₄**

Definition: Hydration is the addition of water to a molecule

Advantages of producing ethanol from ethene

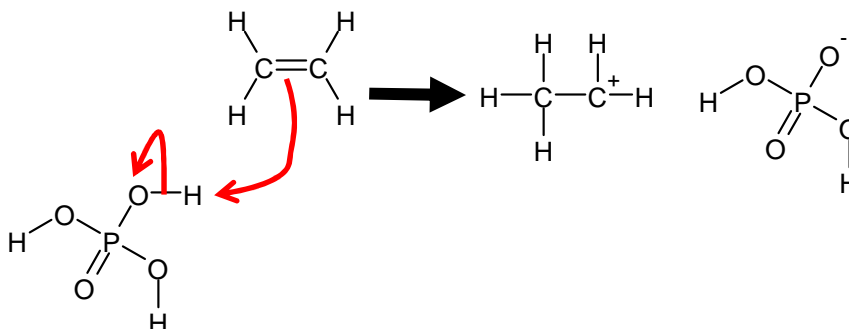
This is a large scale industrial process that will have a faster rate of reaction and will produce a purer product. It is suitable for making large amounts of pure ethanol quickly. It is a continuous process which means cheaper manpower costs.

Disadvantages of producing ethanol from ethene

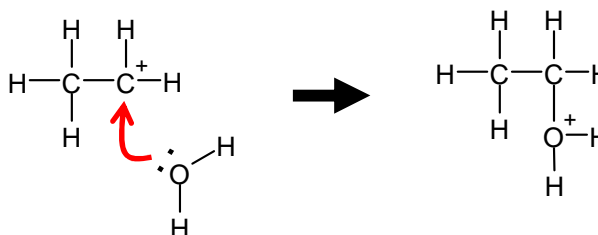
High technology equipment is needed so there are expensive initial capital costs. Ethene is non-renewable resource and will become more expensive when the raw material crude oil run out. The process will also have high energy costs for pumping to produce the high pressures needed.

Mechanism for acid catalysed addition of steam to ethene

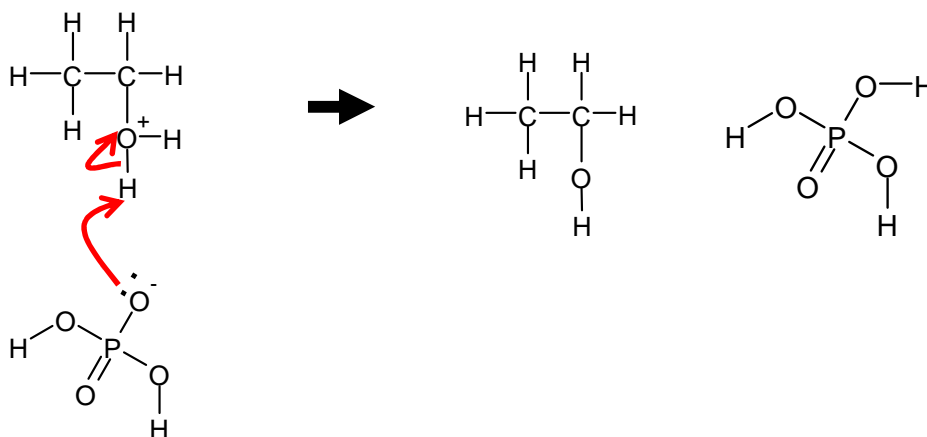
Step 1: A pair of electrons from the double bond in the alkene forms a bond with a proton from the phosphoric acid forming a carbocation intermediate



Step 2: The lone pair of electrons on the water form a bond to the carbocation forming a protonated alcohol



Step 3: The protonated alcohol loses a proton to the phosphate ion regenerating the phosphoric acid catalyst in the process



Questions Making Ethanol: Fermentation or Hydration?

- Ethanol can be manufactured by the direct hydration of ethene
 - 1.1) State what is meant by the term **hydration**.
 - 1.2) What are the reactants and essential conditions necessary for the hydration of ethene?
 - 1.3) Write an equation using skeletal formulae for this reaction
 - 1.4) Outline the mechanism for this reaction using curly arrows for this reaction
 - 1.5) By referring to the mechanism explain why it is classed as '**acid -catalysed addition**'
 - 1.6) What are the advantages and disadvantages of making ethene by this method?

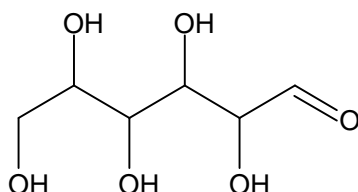
- Ethanol can also be produced commercially by fermentation of aqueous glucose, $C_6H_{12}O_6$
 - 2.1) Write an equation for the production of ethanol by fermentation

 - 2.2) State all the conditions which are necessary for fermentation.
 - 2.3) Explain why neither a low temperature nor a high temperature is suitable for this reaction.

 - 2.4) Describe the process used to separate ethanol from the dilute aqueous solution made by the fermentation process.
 - 2.5) Give advantages of this method of production over that by the direct hydration of ethene.

 - 2.6) Give disadvantages of this process when it is used to make ethanol on a large scale

3. In aqueous solution, some glucose molecules have the structure shown below.



- 3.1) Give the empirical formula of glucose and name the two different types of functional group in this form of glucose.

Scientists have used bacteria to ferment glucose and produce the biofuel butan-1-ol
- 3.2) Write an equation for the fermentation of glucose $C_6H_{12}O_6$ to form butan-1-ol, carbon dioxide and water only.
- 3.3) State one condition necessary to ensure complete combustion of a fuel in air.
- 3.4) Write an equation for the complete combustion of butan-1-ol.
- 3.5) Explain why butan-1-ol made in this way can be classed as a biofuel. Discuss some of the advantages and disadvantages of using biofuels.

4 Ethanol produced by fermentation can be classed as a carbon neutral biofuel

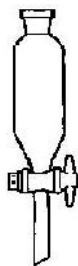
- 4.1) Define the term carbon neutral.
- 4.2) Write an equation for the complete combustion of ethanol.
- 4.3) Write an equation for the formation of ethanol from glucose by fermentation
- 4.4) Write an equation for the formation of glucose from CO_2 by photosynthesis
- 4.5) By considering the 3 equations written in 4.2, 4.3, 4.4, show how this process could be classed as carbon neutral
- 4.6) In reality it is not valid to say producing ethanol from fermentation is carbon neutral. Give reasons why this is the case.

Purifying an organic liquid

General method

- Put the distillate of impure product into a separating funnel
- wash product by adding either
 - sodium hydrogencarbonate solution, shaking and releasing the pressure from CO_2 produced.
 - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (e.g. anhydrous sodium sulfate, calcium chloride) to dry the organic liquid. When dry the organic liquid should appear clear.
- Carefully decant the liquid into the distillation flask
- Distil to collect pure product

Separating funnel



Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

The layer with lower density will be the upper layer. This is usually the organic layer

The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid

Decant means carefully pour off organic liquid leaving the drying agent in the conical flask