

Alcohols

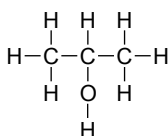
General

The functional group is -OH

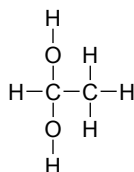
The homologous series has general formula $C_nH_{2n+1}OH$

The names end in -ol, with a number if needed to indicate where on the carbon skeleton the -OH group is located. When more than one -OH group is present the name ends in -diol or -triol etc. as shown below. Note that when there is more than one -OH group the 'e' is not dropped from the name just before the numbers, whereas the 'e' is dropped when there is only one -OH group.

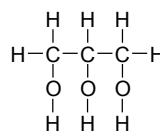
e.g. propan-2-ol



ethane-1,1-diol

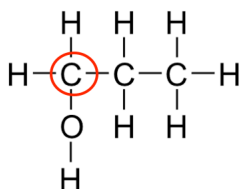


propane-1,2,3-triol

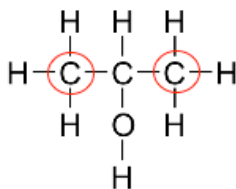


Classifying alcohols

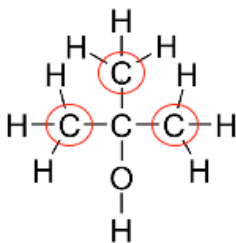
We describe alcohols as PRIMARY, SECONDARY or TERTIARY depending on the number of carbon atoms attached to the carbon with the -OH group.



A primary alcohol has only one other carbon attached to the carbon with the -OH group.



A secondary alcohol has two carbons attached to the carbon with the -OH group



A tertiary alcohol has three carbons attached to the carbon with the -OH group.

Check your understanding:

Draw displayed formulae, then classify the following alcohols as primary, secondary or tertiary

- | | |
|------------------------|-------------------------|
| i) 3-methylpentan-1-ol | ii) hexan-3-ol |
| iii) cyclobutanol | iv) 3-methylpentan-2-ol |
| v) 3-methylpentan-3-ol | |

Physical Properties

Solubility trend

Alcohols are miscible (solids which dissolve are soluble, liquids which dissolve are miscible) with water but as the hydrocarbon chain gets longer their solubility gets less.

Explanation: When methanol or ethanol mix with water, the hydrogen bonds between water molecules are disrupted but just as many new hydrogen bonds to C_2H_5OH or CH_3OH are formed. With longer chain alcohols, although the $-OH$ group can still form hydrogen bonds to water, the longer alkyl chain disrupts the hydrogen bonding between other water molecules. There are not strong intermolecular forces between the alkyl chains and the water molecules because the alkyl chains are essentially non-polar.

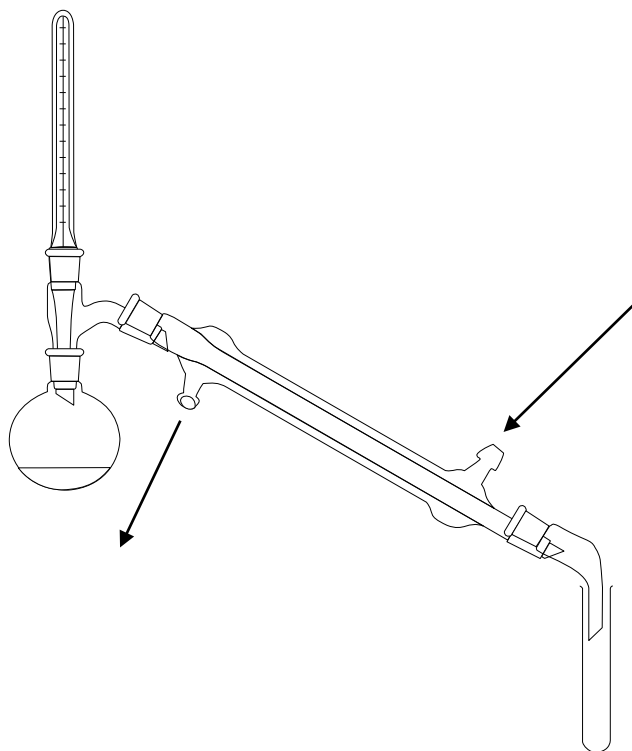
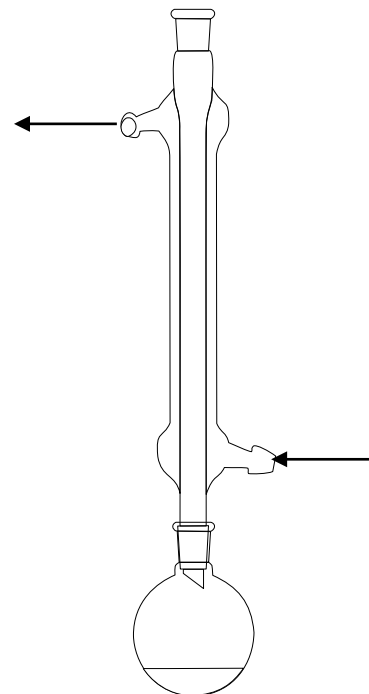
Volatility trend	(boiling points $^{\circ}C$)		
ethanol	325	compared to propane	231 (similar length)
propan-1-ol	371	butane	271
butan-1-ol	390	pentane	309

Explanation: Hydrogen bonding between alcohols reduces their volatility (ease of separating molecules into gas phase), compared to similar sized alkanes which have only London forces. The intermolecular forces between alcohol molecules are therefore much stronger, and much more energy is required to overcome these forces to vapourise alcohols.

Diols and triols can form more hydrogen bonds (because they have more $-OH$ groups) leading to even greater intermolecular forces and increased viscosity, density and boiling points compared to corresponding sized alcohols.

Practical techniques

Refluxing – heating a reaction mixture to continually vaporize and recondense it, preventing volatile components from escaping while keeping the temperature high to increase reaction rate.



Distillation – separating a component from a reaction mixture because it has a lower boiling point than the rest of the mixture.

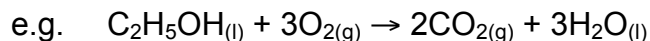
Involves evaporating the component then condensing it and collecting it separately.

Water must flow into the bottom of the condenser and out of the top to ensure efficient cooling, by keeping the water jacket full of water.

Reactions of alcohols

i) Combustion

Alcohols are fully oxidised to H_2O and CO_2 on combustion with excess oxygen. The reactions are exothermic: alcohols are useful fuels. Ethanol burns with a pale blue flame - hard to see in sunlight making ethanol a dangerous fuel since it is also volatile and ignites easily.



Check your understanding:

vi) Write a balanced symbol equation, including state symbols, to show the complete combustion of propan-2-ol.

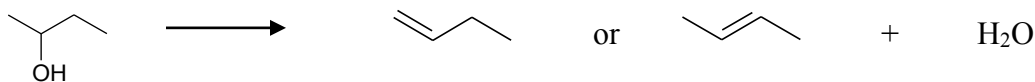
ii) Dehydration to form alkenes

Alcohols can be dehydrated, eliminating water, when refluxed in the presence of an acid catalyst. Hot (170°C) concentrated sulphuric or phosphoric acid can be used:



How it works: The OH group is removed from one C atom, and an H group is removed from an adjacent carbon – these form water. A double bond forms between the two carbons. Note that it doesn't work if there isn't a hydrogen on the carbon adjacent to the one with the –OH group.

Note that if the alcohol is asymmetrical then there are two possible products, depending on which –H is removed along with the –OH group



Check your understanding:

vii) Write equations to show the three isomeric products that could be produced when butan-2-ol vapour is treated in this way, and name the products.

viii) Write a balanced equation to show how buta-1,3-diene could be produced from a suitable starting material using this reaction.

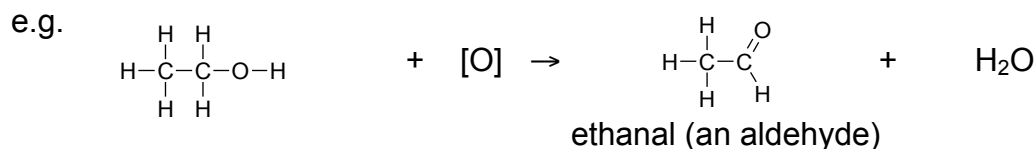
iii) Oxidation of alcohols

When heated with acidified aqueous potassium dichromate(VI), alcohols can be oxidised (dichromate ions are powerful oxidising agents) to form a compound with a **carbonyl group**. The orange dichromate ions are reduced to green chromium(III) ions in this reaction.

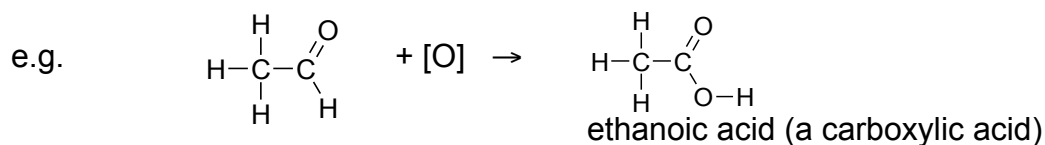
The oxidising agent can be shown in the reaction as [O], simplifying the equations.

Primary alcohols are **partially oxidized** to form **aldehydes**

Conditions: warm with acidified sodium/potassium dichromate(VI), and collect the product by distillation as it forms



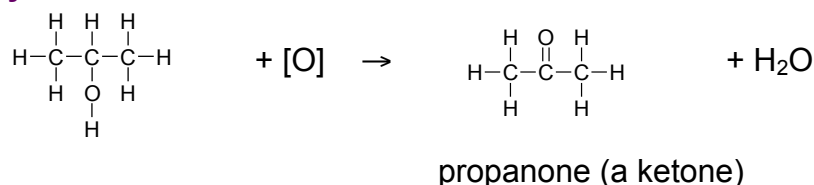
Primary alcohols can be **completely oxidized** (or aldehydes can be further oxidized) to form **carboxylic acids** on stronger heating and refluxing with excess acidified dichromate(VI).



Conditions: heat and reflux with excess acidified sodium/potassium dichromate(VI)

Note that the first oxidation to form an aldehyde makes water as an additional product, while the second oxidation forms no additional products.

Secondary alcohols are oxidized to form **ketones**



Conditions: heat and reflux with acidified sodium/potassium dichromate(VI)

Note that ketones do not react further even with prolonged refluxing with an excess of the reactants.

Tertiary alcohols are **not oxidized** by acidified dichromate(VI) ions. The dichromate(VI) ions remain orange.

Check your understanding:

ix) Complete the table showing oxidation reactions of different alcohols:

Name:	Type:	Conditions:	Product:	Functional group:
Pentan-1-ol				Aldehyde
	Primary	Heat with excess acidified sodium dichromate	Hexanoic acid	
Pentan-2-ol		Heat with acidified sodium dichromate		
2-methylbutan-2-ol		Heat with acidified sodium dichromate		Alcohol

Write balanced equations for the following oxidations:

- x) ethane-1,2-diol refluxed with excess acidified sodium dichromate
- xi) propane-1,2-diol refluxed with excess acidified sodium dichromate
- xii) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{OH}$ warmed with acidified sodium dichromate and the product collected by distillation as it forms

iv) substitution to form haloalkanes

Alcohols undergo substitution reactions with hydrogen halides where the –OH group can be replaced by a halogen group, e.g. –Cl or –Br. The reaction mixture is heated under reflux.

The hydrogen halide is formed in-situ by reacting a sodium halide with sulphuric acid.

e.g. 2-bromopropane can be formed from propan-2-ol by heating and refluxing with sulphuric acid and sodium bromide.

Hydrogen bromide is formed: $\text{H}_2\text{SO}_{4(\text{aq})} + \text{NaBr}_{(\text{s})} \rightarrow \text{HBr}_{(\text{aq})} + \text{NaHSO}_{4(\text{aq})}$

The HBr then reacts with the alcohol: $\text{HBr} + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{CHBrCH}_3 + \text{H}_2\text{O}$

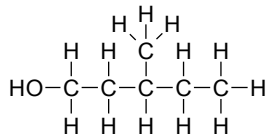
Overall equation: $\text{H}_2\text{SO}_4 + \text{NaBr} + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{CHBrCH}_3 + \text{NaHSO}_4 + \text{H}_2\text{O}$

Check your Understanding:

- xiii) Write the overall equation for the substitution reaction that takes place when cyclohexanol is refluxed with sulphuric acid and sodium iodide.

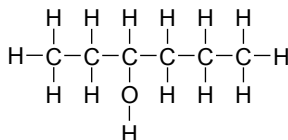
Answers to "Check your understanding" questions:

i) *3-methylpentan-1-ol*



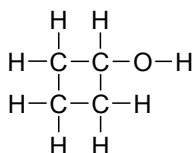
Primary

ii) *hexan-3-ol*



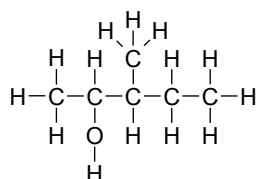
Secondary

iii) *cyclobutanol*



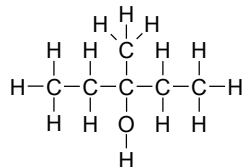
Secondary

iv) *3-methylpentan-2-ol*



Secondary

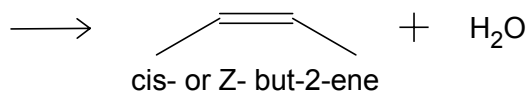
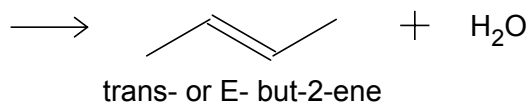
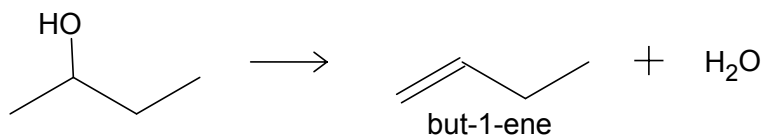
v) *3-methylpentan-3-ol*



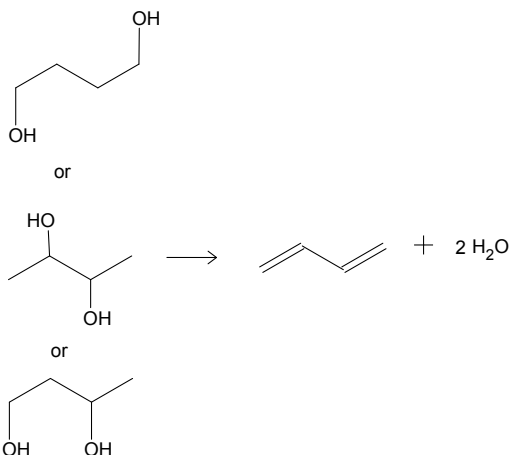
Tertiary



vii)



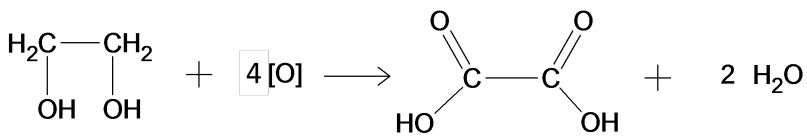
viii)



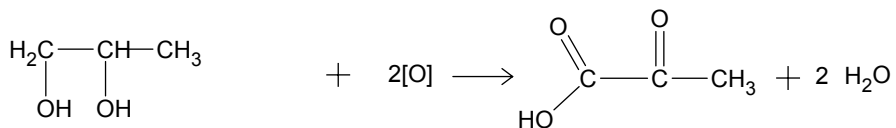
ix)

<i>Name:</i>	<i>Type:</i>	<i>Conditions:</i>	<i>Product:</i>	<i>Functional group:</i>
<i>Pentan-1-ol</i>	<i>Primary</i>	<i>Warm with acidified sodium dichromate</i>	<i>Pentanal</i>	<i>Aldehyde</i>
<i>Hexan-1-ol</i>	<i>Primary</i>	<i>Heat with excess acidified sodium dichromate</i>	<i>Hexanoic acid</i>	<i>Carboxylic acid</i>
<i>Pentan-2-ol</i>	<i>Secondary</i>	<i>Heat with acidified sodium dichromate</i>	<i>Pentan-2-one</i>	<i>Ketone</i>
<i>2-methylbutan-2-ol</i>	<i>Tertiary</i>	<i>Heat with acidified sodium dichromate</i>	<i>No reaction</i>	<i>Alcohol</i>

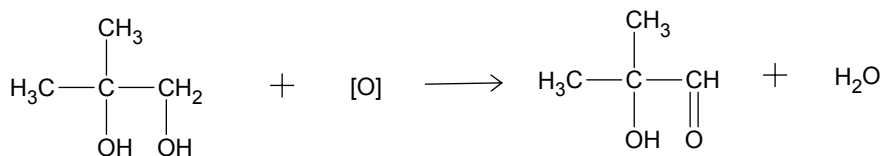
x)



xi)



xii)



xiii)

