

17 Alcohols

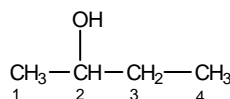
General formula alcohols $C_nH_{2n+1}OH$

Naming Alcohols

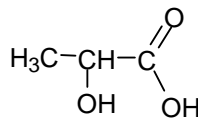
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the **-ol**

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-**:

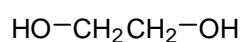
If there are two or more **-OH** groups then di, tri are used. Add the 'e' on to the stem name though



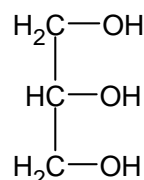
Butan-2-ol



2-hydroxypropanoic acid



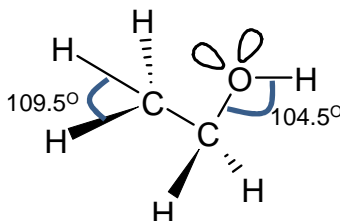
Ethane-1,2-diol



propane-1,2,3-triol

Bond angles in Alcohols

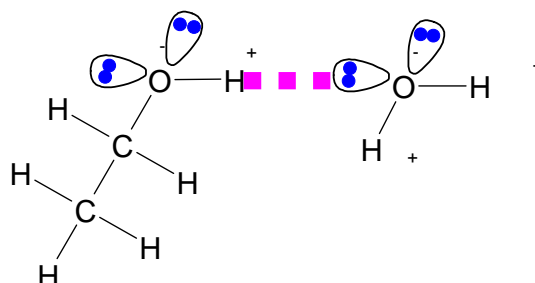
All the **H-C-H** bonds and **C-C-O** are 109.5° (tetrahedral shape), because there are 4 bond pairs of electrons repelling to a position of minimum repulsion.



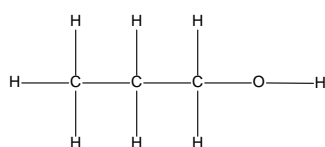
The **H-O-C** bond is 104.5° (bent line shape), because there are 2 bond pairs of electrons and 2 lone pairs repelling to a position of minimum repulsion. Lone pairs repel more than bond pairs so the bond angle is reduced.

Boiling points

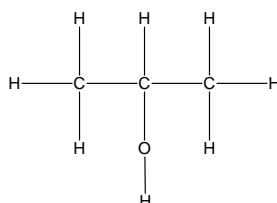
The alcohols have relatively low volatility and high boiling points due to their ability to form hydrogen bond between alcohol molecules.



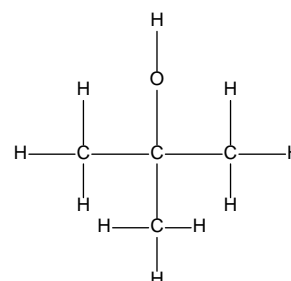
Different types of alcohols



Propan-1-ol
Primary



Propan-2-ol
Secondary



methylpropan-2-ol
Tertiary

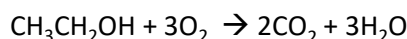
Primary alcohols are alcohols where 1 carbon is attached to the carbon adjoining the oxygen

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

1. Combustion of Alcohols

Alcohols combust with a clean flame

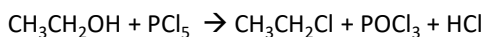


2. Substitution reactions of Alcohols to form Halogenoalkanes

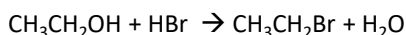
Various halogenating compounds can be used to substitute the -OH group for a halogen

PCl_5 / PCl_3 / conc HCl / SOCl_2 / mixture of NaCl + H_2SO_4 can all be used for substituting a Cl

Reaction with phosphorous (V) halide

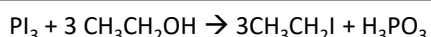


This reaction with PCl_5 (phosphorous(v)chloride) can be used as a test for alcohols. You would observe misty fumes of HCl produced.



For Br use KBr, 50% concentrated H_2SO_4 to produce HBr

Reaction with phosphorous (III) iodide

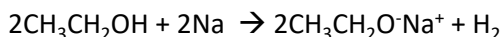


The **phosphorous (III) iodide** is produced in situ by reacting red phosphorus and iodine.

The reaction of KI and conc H_2SO_4 can't be used to produce HI because the sulphuric acid will oxidise the hydrogen halides to other products

3. Reaction of Alcohols with Sodium

Sodium reacts with alcohols



Observations:

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

This reaction can be used as a test for alcohols

Oxidation reactions of the alcohols

Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ is an oxidising agent that causes alcohols to oxidise.

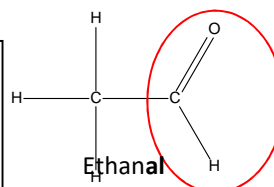
The exact reaction, however, depends on the type of alcohol, i.e. whether it is primary, secondary, or tertiary, and on the conditions.

Partial Oxidation of Primary Alcohols

Reaction: primary alcohol \rightarrow aldehyde

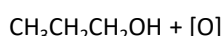
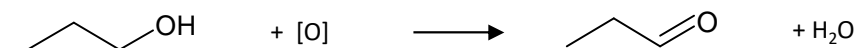
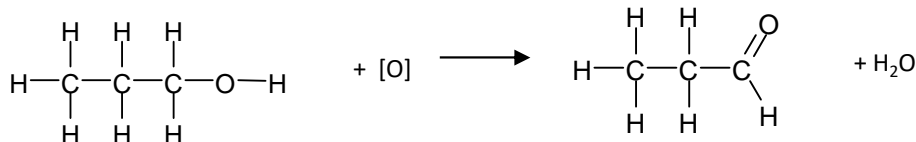
Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

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



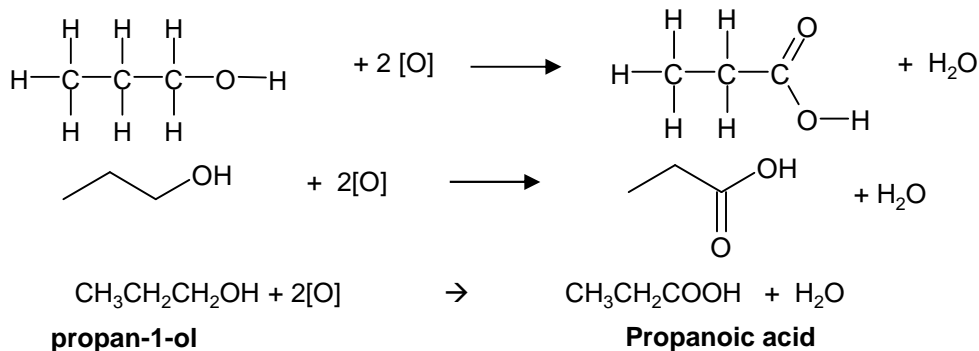
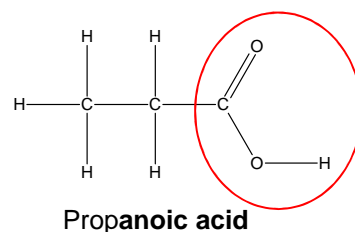
Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

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. $\text{CH}_3\text{CH}_2\text{CHO}$

Full Oxidation of Primary Alcohols

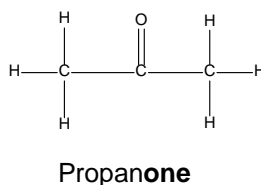
Reaction: primary alcohol \rightarrow carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulphuric acid
Conditions: use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished)



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

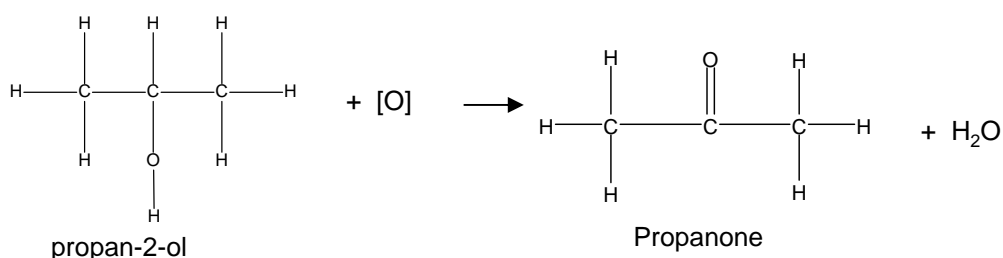
Oxidation of Secondary Alcohols

Reaction: secondary alcohol \rightarrow ketone
Reagent: potassium dichromate(VI) solution and dilute sulphuric 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 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

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

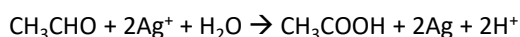
Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[\text{Ag}(\text{NH}_3)_2]^+$.

Conditions: heat gently

Reaction: **aldehydes only** are oxidised by Tollen's reagent into a carboxylic acid and 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



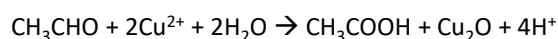
Fehling's solution

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 and the copper 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

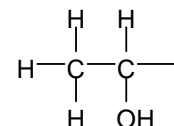
Reaction of ethanol with iodine in presence of alkali

Reagents: Iodine and sodium hydroxide

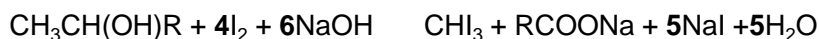
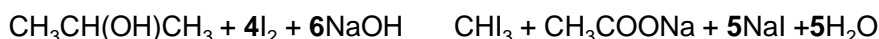
Conditions: warm very gently

The product tri-iodomethane CHI_3 is a yellow crystalline precipitate with an antiseptic smell

Only alcohols with a methyl group next to the C-O-H bond will do this reaction.



This reaction is called the Iodoform test



Reaction of Alcohols with Dehydrating Agents

Reaction: Alcohol \rightarrow Alkene

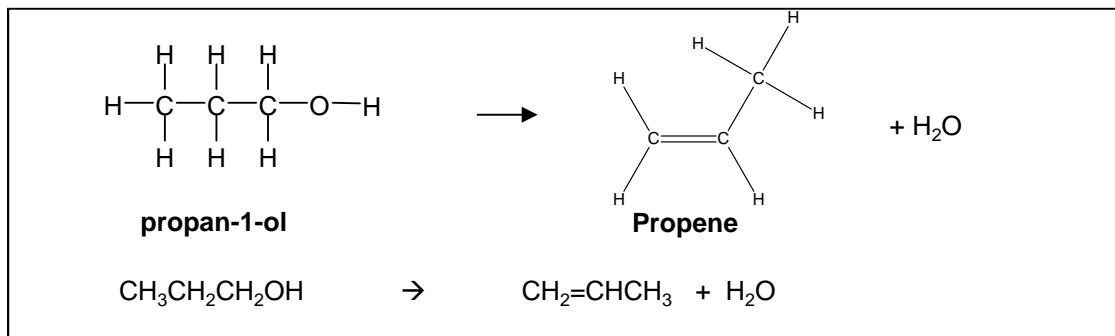
Reagents: Concentrated Sulphuric or Phosphoric acids

Conditions: warm (under reflux)

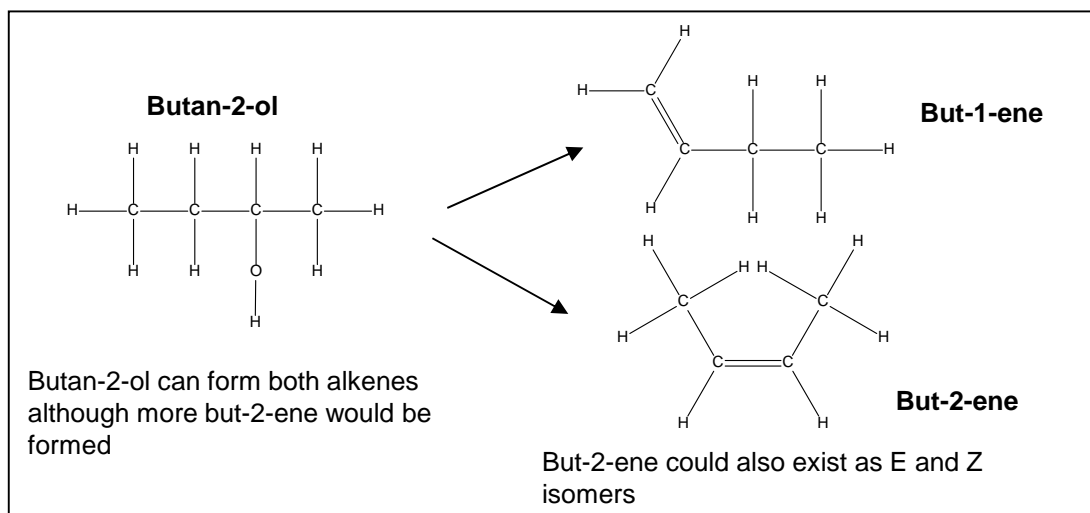
Role of reagent: dehydrating agent/catalyst

Type of reaction: acid catalysed elimination

Dehydration Reaction: removal of a water molecule from a molecule

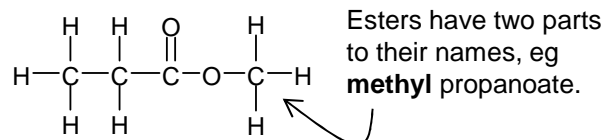


Some 2° and 3° alcohols can give more than one product, when the double bond forms between different carbon atoms



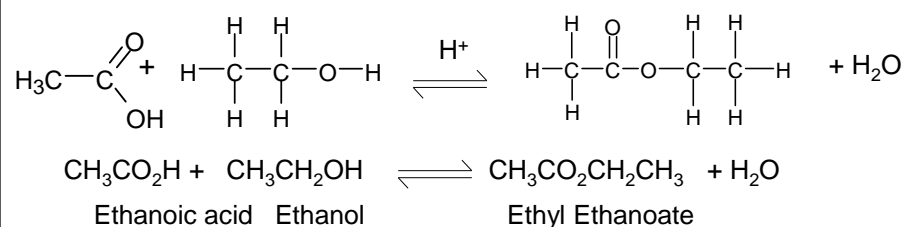
Esterification

Carboxylic acids react with alcohols, in the presence of a strong sulfuric acid catalyst, to form esters and water.



The bit ending in **-anoate** comes from the carboxylic acid and includes the C in the C=O bond.

The bit ending in **-yl** comes from the alcohol that has formed it and is next to the single bonded oxygen.



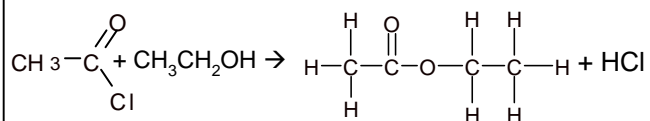
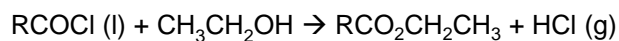
The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst (H_2SO_4) is needed.

Esterification with acyl chlorides

Change in functional group: **alcohol** → **ester**

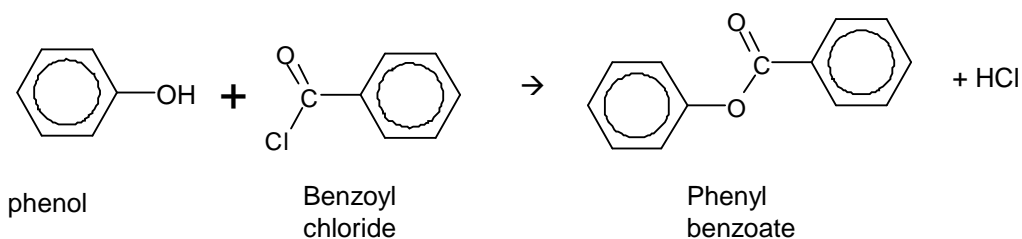
Reagent: **alcohol**

Conditions: **room temp.**

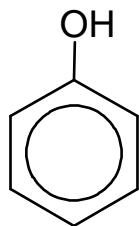


Observation: Steamy white fumes of HCl are given off

This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction

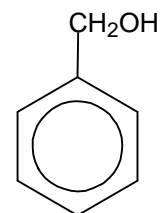


Phenols



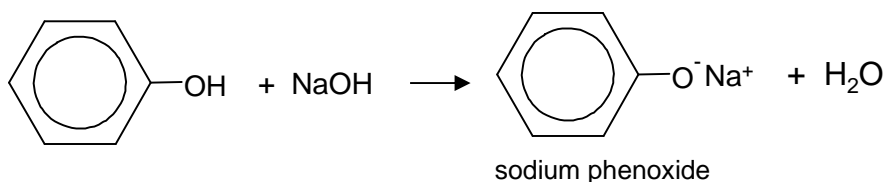
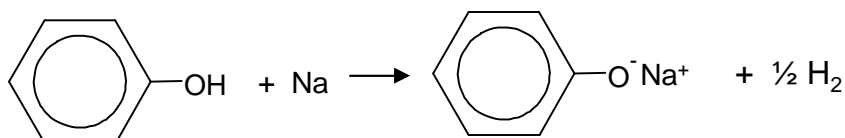
In a phenol the OH group is directly attached to the benzene ring.

In a phenol the lone pair of electrons on the oxygen is delocalised with the electron charge cloud of the arene ring. The delocalised bonding changes the reactivity of the OH group and the arene ring.



This is not a phenol, but is an alcohol because the OH group is attached to an alkyl group rather than the benzene ring.

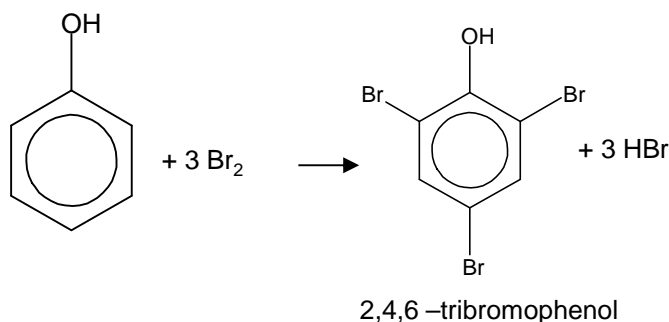
Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Both phenols and carboxylic acids will react with sodium metal and sodium hydroxide. Only carboxylic acids will react with sodium carbonate as a phenol is not strong enough an acid to react.



The sodium phenoxide compound is more soluble than the original phenol. So the solid phenol dissolves on addition of NaOH

Reaction with Bromine

Reagents: Br₂
Conditions: room temp



Phenol does not need a FeBr₃ catalyst like benzene and undergoes multiple substitution whereas benzene will only add one Br.

The product in this reaction is a white solid

In phenol the lone pair of electrons on the oxygen (p-orbital) is partially **delocalised** into the ring. The electron density increases and the Br₂ is more polarised

Phenols are used in the production of plastics, antiseptics, disinfectants and resins for paints.

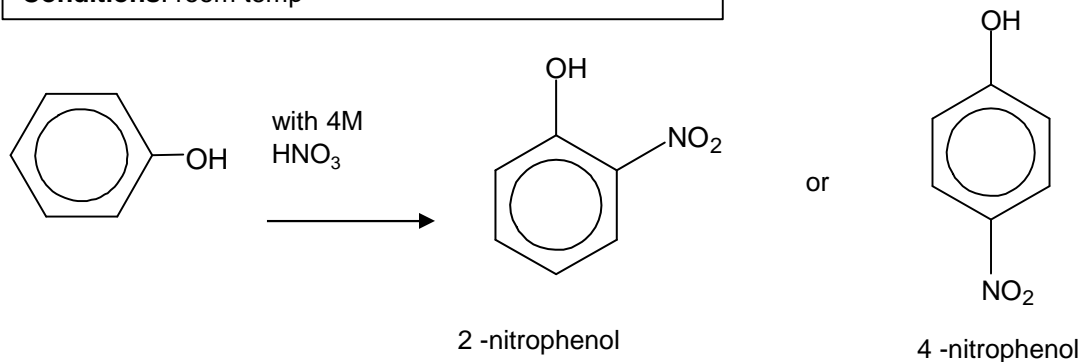
Reaction of Phenol with Nitric acid

In comparison with benzene, phenol does not need the concentrated sulphuric acid catalyst

With 4M HNO_3 single substitution occurs (in comparison to the conc HNO_3 needed for benzene)

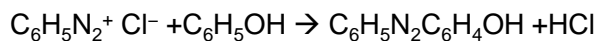
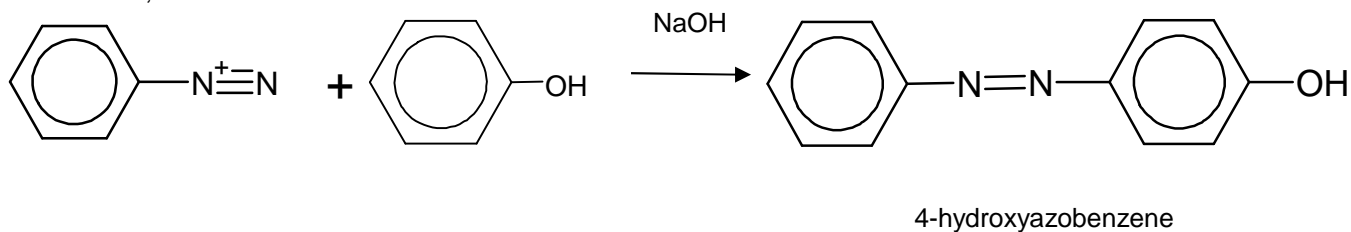
Reagent 4M HNO_3

Conditions: room temp



Reaction with diazonium ion

coupling of diazonium ion with a phenol under alkaline conditions;



Azo dyes are used for dyes, pigments and colourings