Organic chemistry – crib notes

Alcohols

General

Alcohols are a group of compounds containing one or more -OH group on the chain. They occur naturally by the fermentation of yeast mould and sugars (e.g. cider is made by fermenting apple or pear sugars with yeast and leaving to mature) and can be oxidised to produce a number of other useful compounds (such as carboxylic acids and aldehydes)

Structure and bonding

The alcohol group has an overall negative charge on the oxygen due to the lone pair of electrons on the oxygen. This gives a slight dipole on the carbon-oxygen bond which makes the cationic carbon more prone to attack from more nucleophilic groups.

The negative charge on the alcohol also enables hydrogen bonding to occur. This is where the slightly positive H forms an electrostatic bond with the negative charge on the oxygen. This is not a real bond, more an attraction bond.

Alcohols can hydrogen bond with themselves (forming "dimers") or with water to some extent.

Short carbon chain alcohols are soluble in water (up to 5 carbons can go into solution). After that, the solubility of the OH group is not enough to drag the carbonyl chain into the solution

The ability to hydrogen bond increases the boiling point of alcohols. At room temperature and 1 atmosphere pressure, all alcohols are liquid.

Importance of alcohol

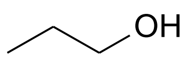
Alcohols are a very important group of compounds as virtually all other types of organic compounds can be formed from them (such as esters and aldehydes, both of which are essential as food flavourings).

Naming alcohols

Naming an alcohol is simple.

1. Find the longest carbon chain
2. Find the position of any multiple bonds
3. Find the position of any alcohols
4. Find the position of any groups.

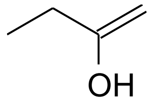
The naming goes from the highest priority (the multiple bond) being on the lowest carbon. To change the carbonyl to an alcohol, add -ol to the end



Longest chain = 3 = propan

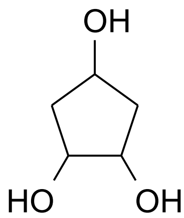
Any multiple bonds : no
Alcohol on carbon : 1
Any other groups : no

Full name : propan-1-ol



Longest chain = 4 = butan
Any multiple bonds : yes, C1
Alcohol on carbon : 2
Any other groups : no

Full name : but-1-ene-2-ol

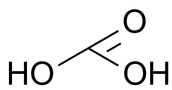


Longest chain = 5 = pentan
Any multiple bonds : no, but it's cyclic, name is now cyclopentan
Alcohol on carbon : 1, 3 and 5
Any other groups : no

Full name : cyclopentan-1,3,5-ol

<u>Special rule for naming.</u>

If there is a terminal group (can only ever be on the end of the carbonyl chain) on the carbonyl chain (such as a carboxylic acid or aldehyde), the alcohol becomes “hydroxy” and is placed before the start of the main chain



Longest chain = 2 – ethan
Any multiple bonds : no
Any other groups : carboxylic acid (terminal group)
Alcohol on carbon : 2

Full name : 2-hydroxy-ethanoic acid (**not** ethanoic acid-2-ol)

Types of alcohol

Alcohols can be primary (1º), secondary (2º) or tertiary (3º). These have already been covered in the alkene chemistry handouts. In terms of stability, 3º > 2º > 1º.

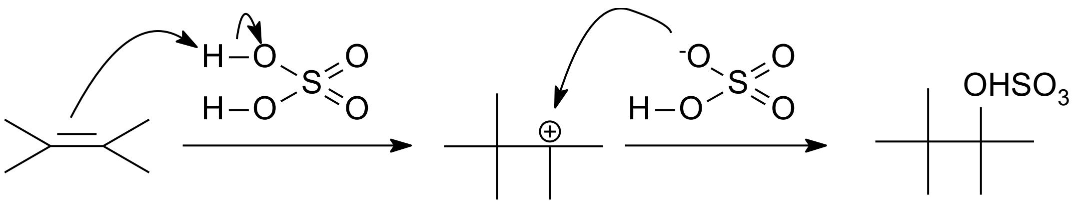
Preparation of alcohols

Alcohols can be produced in a number of ways : the oxidation of an alkene or the reduction of an aldehyde

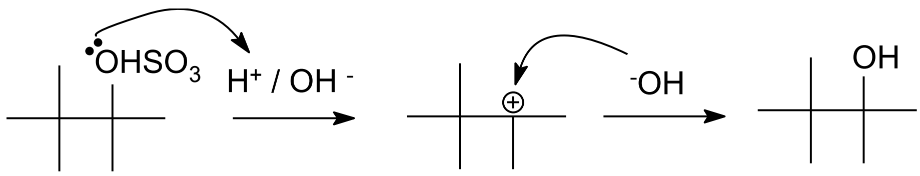
Oxidation of an alkene with sulfuric acid

This is a two stage process. The first step is the opening of the double bond using concentrated sulfuric acid to form the hydrogen sulfonate alkane. This can then be reacted with OH^- to produce the alcohol. OH^- can be obtained from water. Note : adding water to an alkene will **NOT** produce an alcohol!

Stage 1 – opening the alkene to form the hydrogen sulfonate

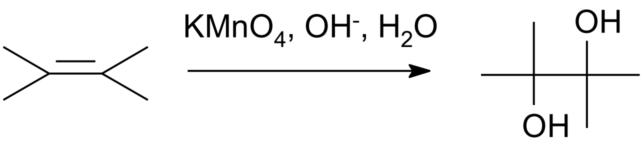


Stage 2 – removal of hydrogen sulfonate and hydration



Partial oxidation of an alkene with $KMnO_4$

Potassium manganate (VII) (also known as potassium permanganate) is a relatively mild oxidising agent. In this case, when the alkene is reacted with KMnO4, the double alcohol is formed along with solid MnO_2 (a brown solid which sinks to the bottom of the flask). The vibrant purple colour vanishes during this reaction.



The only exception to this is the preparation of methanol.

Methanol is prepared by reacting CO with H_2. CO can be prepared by the incomplete combustion of methane.

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2H_2O$$

$$CO + 2H_2 \rightarrow CH_3OH$$

Reactions of alcohols

Reaction with alkali metals (Grp I metals)

The group I elements are highly reactive. When they react with an alcohol, H_2 gas is evolved and a metal alkoxide formed. Metal alkoxide are very strong nucleophiles and useful in organic chemistry for the production of other compounds.

Oxidation with Copper (II) Oxide

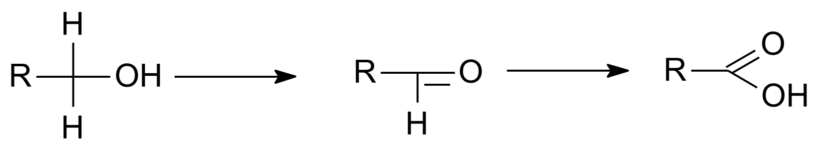
The alcohol is passed over heated copper(II) oxide. When the alcohol is oxidised, the brown solid turns pinkish-brown (it has been reduced to copper(I) oxide).

Oxidation with hot potassium dichromate.

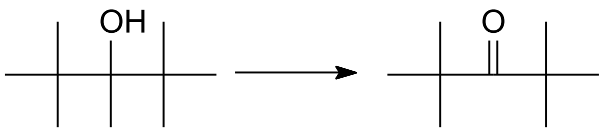
K_2CrO_7 is an orange liquid. When heated gently with an alcohol, the alcohol reduces the Cr^{6+} to Cr^{3+} and the solution goes a deep green.

Reactions of alcohols

When a primary alcohol is oxidised, it first forms the aldehyde. If it is further oxidised, the carboxylic acid forms.



When a secondary alcohol is oxidised, it forms the ketone

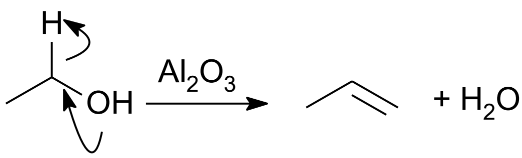


Further oxidation of a ketone is possible, but very difficult and usually breaks the carbon skeleton.

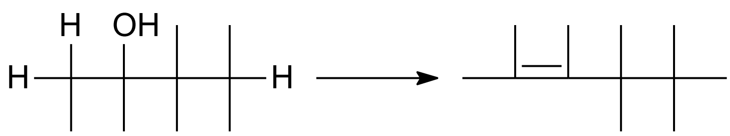
Tertiary alcohols are unreactive (*no hydrogen to replace*).

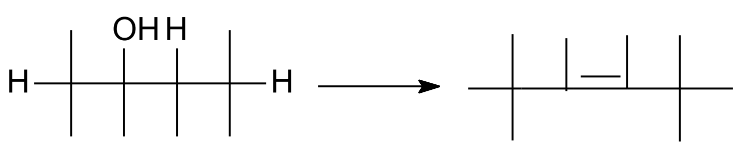
Dehydration reactions

When an alcohol is dehydrated, the alkene is reformed. For example, passing propan-1-ol over Al_2O_3 will result in propene and water being formed. The OH group is removed as well as a hydrogen from the next carbon to give the alkene



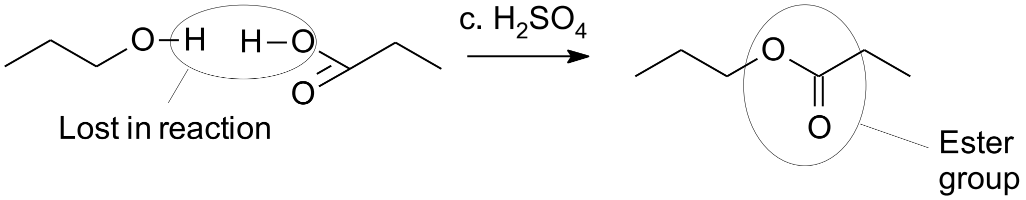
When propan-1-ol or propan-2-ol are dehydrated, only prop-1-ene is formed. When butan-1-ol is dehydrated, only but-1-ene is formed. However, when butan-2-ol is dehydrated both but-1-ene and but-2-ene can be formed





Forming esters

The formation of an ester requires an alcohol and carboxylic acid in the presence of sulfuric acid. This is known as a condensation reaction as it gives out H_2O.

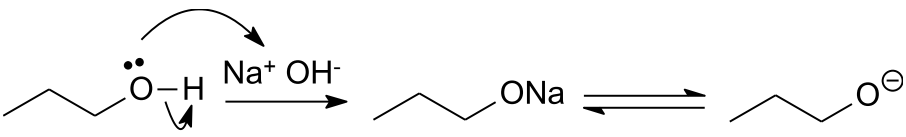


Ester chemistry is continued in another crib sheet.

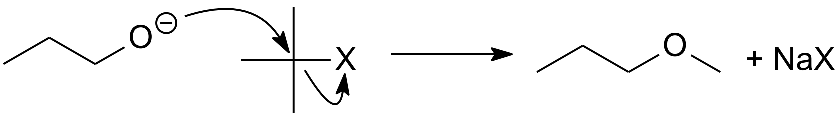
Forming ethers

Ethers are formed by the nucleophilic reaction of a metal alkoxide with a monohalogenated hydrocarbon.

Stage 1 : alcohol reacts with Na^+. Na^+ has a stronger charge than H^+, so replaces it to give the alkoxide



Stage 2 : alkoxide reacts with the haloalkane to give the ether



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