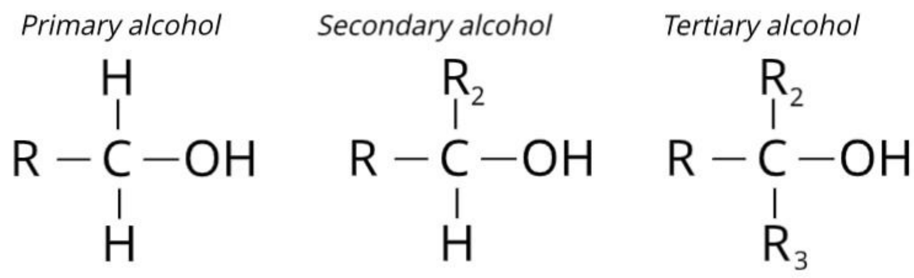
CAIE Chemistry A-level

16: Hydroxy Compounds

Notes

Alcohols

Alcohols are organic compounds which contain a **hydroxyl group**, -OH. Alcohols can be separated into three different classifications:



Formation of Alcohols

<u>Electrophilic Addition with Steam:</u>

Alkenes are hydrated when they react with steam to form alcohols. This requires an **acid catalyst** such as phosphorus acid or sulfuric acid.

$$CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$$

When steam reacts with propene, according to **Markovnikov's rule of addition**, the OH group joins to the carbon atom in the double bond which is directly bonded to the most carbons atoms. This can be seen in the equation below:

$$CH_3CHCH_2 + H_2O \rightarrow CH_3C(OH)CH_3$$

Using Markovnikov's rule, propan-2-ol is the major product and propan-1-ol is the minor product. The reaction will mostly produce propan-2-ol.

<u>Cold, Dilute Acidified Manganate(VII) Ions</u>

Potassium manganate(VII) contains manganate(VII) ions meaning it is a **strong oxidising agent.** Manganate(VII) ions can oxidise alkenes to form diols (alkane with two alcohol groups). For this reaction to take place, the manganate ions must be cold, dilute and acidified.
In the reaction below, [O] denotes the oxidising agent:

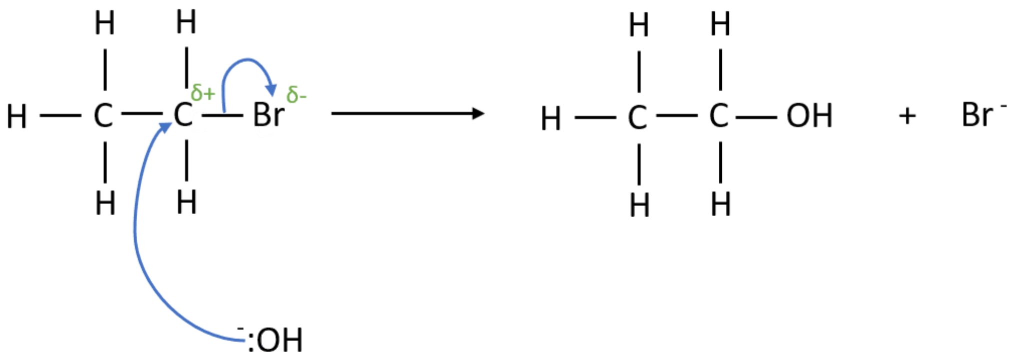
$$CH_2CH_2 + H_2O + [O] \rightarrow CH_2(OH)CH_2(OH)$$

During this reaction, the purple solution will decolourise.

<u>Nucleophilic Substitution</u>

An alcohol is produced when a halogenoalkane undergoes nucleophilic substitution with a **hydroxide ion**.

For example bromoethane reacts to form ethanol. **Warm aqueous sodium hydroxide** is required:

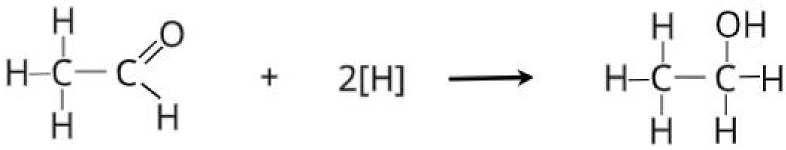


Reduction of Aldehydes

The symbol [H] is used in equations to represent the reducing agent- **$LiAlH_4$**.

$$RCHO + 2[H] \rightarrow RCH_2OH$$

For example, the reduction of **ethanal to ethanol**:

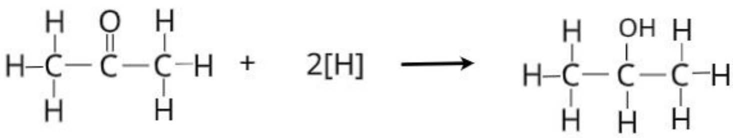


Reduction of Ketones

The reducing agent is **$LiAlH_4$:**

$$R_1COR_2 + 2[H] \rightarrow RC(OH)HR_2$$

For example, the reduction of **propanone to propanal**:



Reduction of Carboxylic Acids

Carboxylic acids can be **reduced** to primary alcohols using **$LiAlH_4$**. The reduction process occurs in **two stages** because the carboxylic acid is converted into an **aldehyde** before becoming a **primary alcohol**. The overall equation for this reaction is:

$$RCOOH + 4[H] \rightarrow RCH_2OH + H_2O$$

Acid Hydrolysis of Ester

When esters react with water an **acid catalyst** is required. This reaction is **reversible** so **excess water** must be used to ensure the position of equilibrium is shifted as far towards the products as possible. This reaction can occur when the ester is mixed with dilute acid.

$$CH_3CH_2COOCH_3 + H_2O \rightleftharpoons CH_3CH_2COOH + CH_3OH$$

Combustion of Alcohol

Water and carbon dioxide are produced when alcohols undergo **complete combustion**. A relatively large amount of **energy** is produced meaning they can be used as **fuels**.

$$CH_3OH + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Incomplete combustion of alcohols occurs when there is a **limited supply of oxygen**. This produces water as well as carbon monoxide, carbon and/or carbon dioxide:

$$2CH_3CH_2OH + 3O_2 \rightarrow 2CO + 2C + 6H_2O$$

Substitution to form Halogenoalkanes

Alcohols can react with **halides** to form halogenoalkanes. During this substitution reaction, the hydroxyl group is replaced by a halogen atom.

Reactions with Hydrogen Halides

- **Primary** and **secondary** alcohols react **very, very slowly** with **hydrogen chloride**, HCl. **Tertiary** alcohols react rapidly with concentrated hydrochloric acid at room temperature:
$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

- **Hydrogen bromide** reacts with alcohols. Typically the alcohol is treated with **potassium bromide** and **concentrated sulfuric acid** as these two reactants will produce hydrogen bromide:
$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$

- **Hydrogen iodide** reacts with alcohols. Typically the alcohol is treated with **potassium iodide** and **phosphoric(V) acid**. Phosphoric(V) acid is used in this reaction instead of **sulfuric acid** as sulfuric acid will readily **oxidise the iodide ions** to iodine.
$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$$

Reactions with Phosphorus Halides

Alcohols react with **phosphorus(III) halides** to produce halogenoalkanes:

$$3CH_3CH_2OH + PCl_3 \rightarrow 3CH_3CH_2Cl + H_3PO_3$$
$$3CH_3OH + PBr_3 \rightarrow 3CH_3Br + H_3PO_3$$
$$3CH_3CH_2CH_2OH + PI_3 \rightarrow 3CH_3CH_2CH_2I + H_3PO_3$$

Phosphorus(V) chloride will react violently with alcohols to produce steamy fumes of hydrogen chloride.

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + HCl + POCl_3$$

Reaction with Sulfur Dichloride Oxide

Sulfur dichloride oxide reacts with alcohols at room temperature to produce **chloroalkanes**.

$$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$$

Reaction with Sodium

When sodium reacts with an alcohol, a salt and bubbles of **hydrogen gas** are produced.

Ethanol and Sodium

When **ethanol** reacts with **sodium**, sodium ethoxide and hydrogen gas are produced. This equation can be applied to other alcohols by substituting R for CH_3CH_2 (where R is any group):

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$$

Sodium ethoxide (CH_3CH_2ONa) is an **ionic** compound because the positive sodium ion (Na^+) is attracted to the negative ethoxide ion ($CH_3CH_2O^-$).

This reaction can be used to remove alcohol groups from a compound or to safely dispose of small amounts of sodium (as sodium reacts explosively with water).

Oxidation to Carbonyl Compounds and Carboxylic Acids

Alcohols undergo **oxidation** when reacted with **potassium or sodium dichromate(VI)**. During this reaction, the **orange** potassium dichromate(VI) turns **green**.The products of this reaction varies depending on the **classification of the alcohol** (primary, secondary or tertiary). When writing an equation, **[O]** is used to denote the oxidising agent.

Primary Alcohols

Primary alcohols can be **partially oxidised** to **aldehydes**.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

With **further oxidation**, **aldehydes** become **carboxylic acids**.

$$CH_3CHO + [O] \rightarrow CH_3COOH + H_2O$$

The full oxidation reaction can be written as:

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + 2H_2O$$

Secondary Alcohols

Secondary alcohols are oxidised to **ketones**. No further oxidation can take place.

$$CH_3C(OH)HCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$

Tertiary Alcohols

Tertiary alcohols do not easily undergo oxidation.

Dehydration to Alkenes

Alcohols can be dehydrated to form **alkenes**. This can be carried out using **aluminium oxide** or an **acid** as a **catalyst**.

Dehydration of Ethanol using Aluminium Oxide

If **ethanol vapour** is passed over an aluminium oxide catalyst, the ethanol is **cracked**, producing ethene and water.

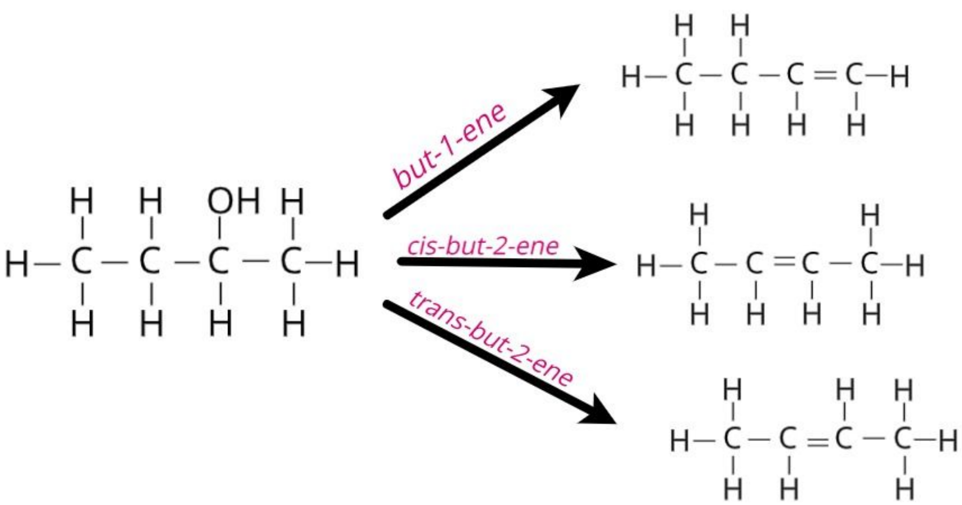
$$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$$

Dehydration of Ethanol using Acid Catalyst

Concentrated sulfuric or phosphoric acid can be used as acid catalysts to produce ethene from ethanol. When ethanol is heated with excess sulfuric acid (a strong oxidising agent), the alcohol is further oxidised to carbon dioxide and the acid is reduced to sulfur dioxide. These **gases must be removed** from the reaction. Phosphoric acid is often used in place of concentrated sulfuric acid because it is a weaker oxidising agent meaning the reaction is safer.

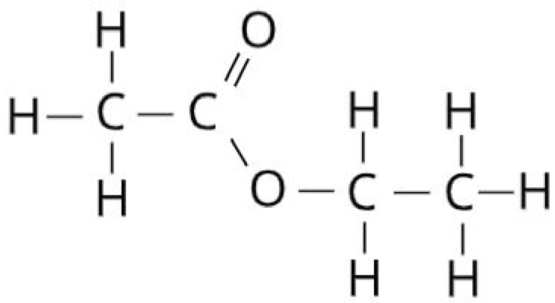
$$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$$

If an alcohol is unsymmetrical, a **variety of products** will be produced from dehydration. For example, dehydration of **butan-2-ol** will produce but-2-ene, cis-but-1-ene and trans-but-1-ene.



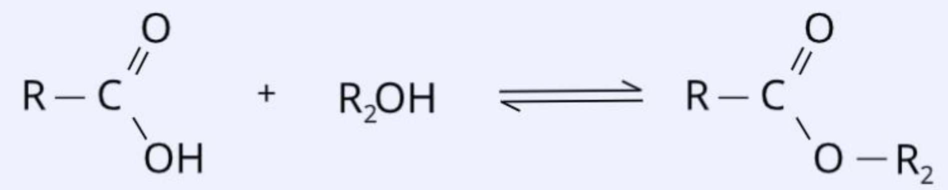
Formation of Esters by Esterification with Carboxylic Acids

Esters can be formed when an **alcohol** and a **carboxylic acid** are heated together in the presence of an acid catalyst (commonly sulfuric acid). The process is known as esterification.

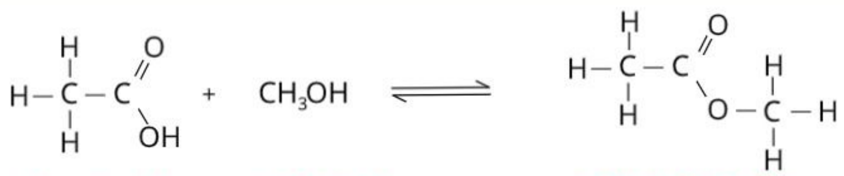


The diagram on the left shows an ester. The **left side** of this compound is derived from the **carboxylic acid** and the **right side** from the **alcohol**. This ester was formed from ethanoic acid and ethanol and it is called **ethyl ethanoate**. 'Ethyl' comes from the alcohol and 'ethanoate' from the carboxylic acid.

GENERAL EQUATION



E.g.



ethanoic acid *methanol* *methyl ethanoate*