

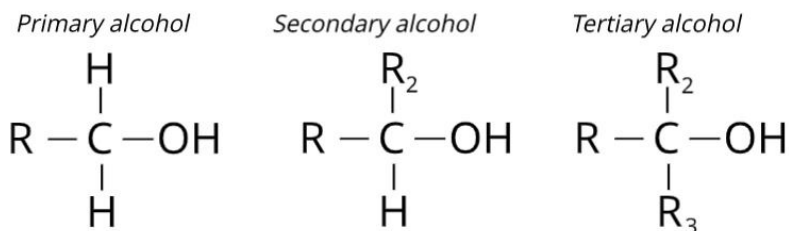
CIE Chemistry A Level

17 : Hydroxy Compounds Notes



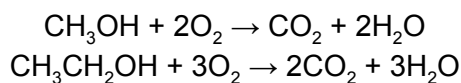
Alcohols

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

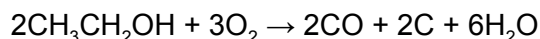


Combustion

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**.



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:

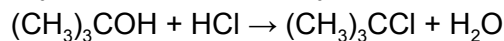


Substitution to halogenoalkanes

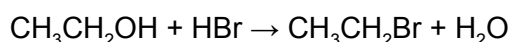
Alcohols can react with **halides** to form halogenoalkanes. During this substitution reaction, the hydroxyl group is replaced by a halogen atom.

Reactions with hydrogen halides

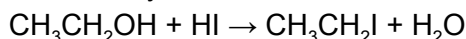
- **Primary** and **secondary** alcohols react **very, very slowly** with **hydrogen chloride**, HCl. **Tertiary** alcohols react rapidly with concentrated hydrochloric acid at room temperature:



- **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:

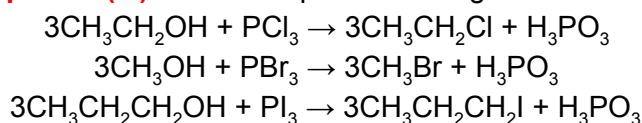


- **Hydrogen iodide** reacts with alcohols. Typically the alcohol is treated with **potassium iodide** and **phosphoric(V) acid**. Phosphoric(V) acid is used in this reaction instead of **sulfuric acid** as sulfuric acid will readily **oxidise the iodide ions** to iodine.

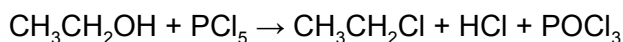


Reactions with phosphorus halides

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

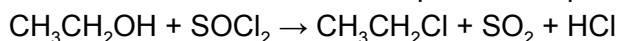


Phosphorus(V) chloride will react violently with alcohols to produce steamy fumes of hydrogen chloride.



Reaction with sulfur dichloride oxide

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

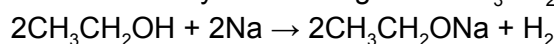


Reaction with sodium

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):



Sodium ethoxide ($\text{CH}_3\text{CH}_2\text{ONa}$) is an **ionic** compound because the positive sodium ion (Na^+) is attracted to the negative ethoxide ion ($\text{CH}_3\text{CH}_2\text{O}^-$).

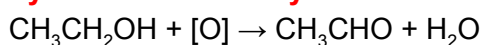
This reaction can be used to remove alcohol groups from a compound or to safely dispose of small amounts of sodium (as sodium reacts explosively with water).

Oxidation to carbonyl compounds and carboxylic acids

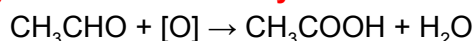
Alcohols undergo **oxidation** when reacted with **potassium or sodium dichromate(VI)**. During this reaction, the **orange** potassium dichromate(VI) turns **green**. The products of this reaction varies depending on the **classification of the alcohol** (primary, secondary or tertiary). When writing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

Primary alcohols

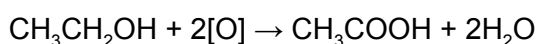
Primary alcohols can be **partially oxidised** to **aldehydes**.



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

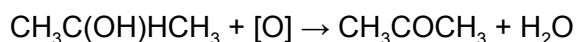


The full oxidation reaction can be written as:



Secondary alcohols

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



Tertiary alcohols

Tertiary alcohols do not undergo oxidation.

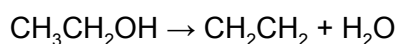


Dehydration to alkenes

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

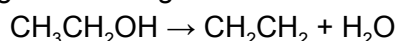
Dehydration of ethanol using aluminium oxide

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

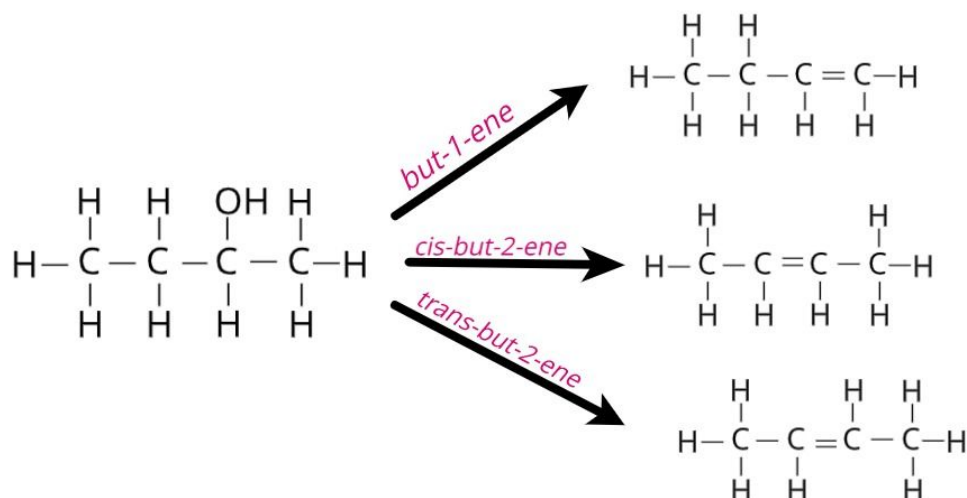


Dehydration of ethanol using acid catalyst

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.

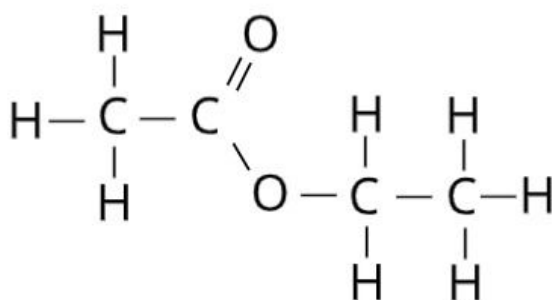


If an alcohol is unsymmetrical, a **variety of products** will be produced from dehydration. For example, dehydration of **butan-2-ol** will produce but-2-ene, cis-but-1-ene and trans-but-1-ene.



Formation of esters by esterification with carboxylic acids

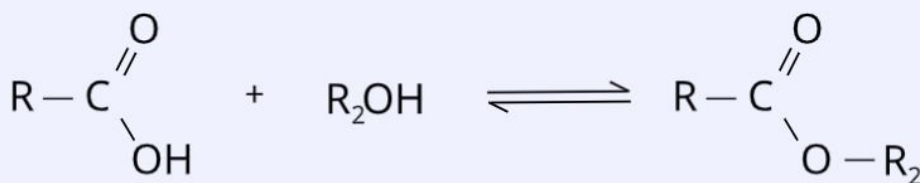
Esters can be formed when an **alcohol** and a **carboxylic acid** are heated together in the presence of an acid catalyst (commonly sulfuric acid). The process is known as esterification.



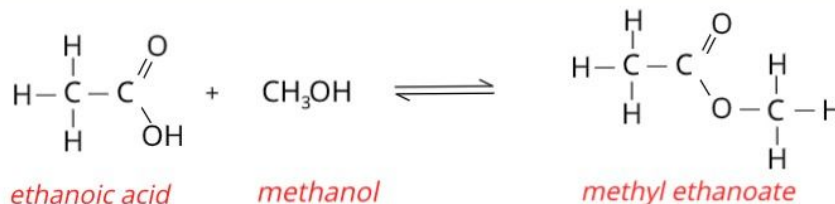
The diagram on the left shows an ester. The **left side** of this compound is derived from the **carboxylic acid** and the **right side** from the **alcohol**. This ester was formed from ethanoic acid and ethanol and it is called **ethyl ethanoate**. 'Ethyl' comes from the alcohol and 'ethanoate' from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



GENERAL EQUATION

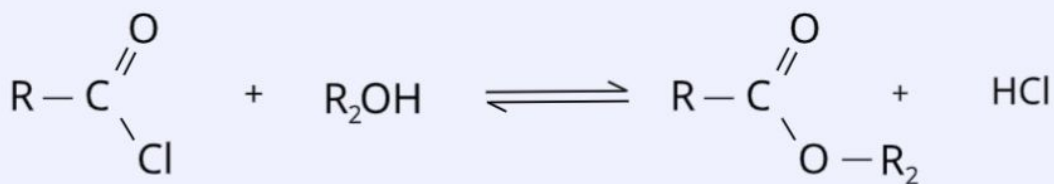


E.g.

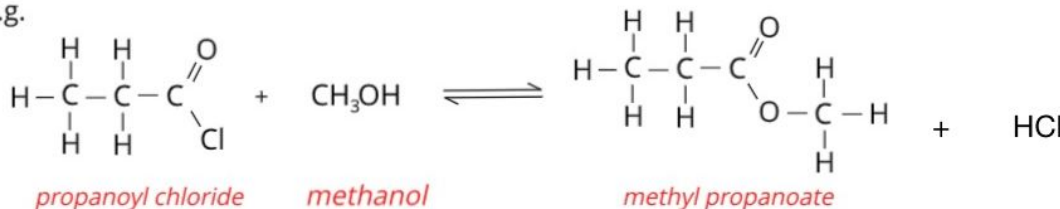

Formation of esters by acylation with acyl chlorides (A Level only)

Esters can also be produced from **alcohols** and **acyl chlorides**. Alcohol react vigorously with acyl chlorides, releasing steamy fumes of hydrochloric acid

GENERAL EQUATION

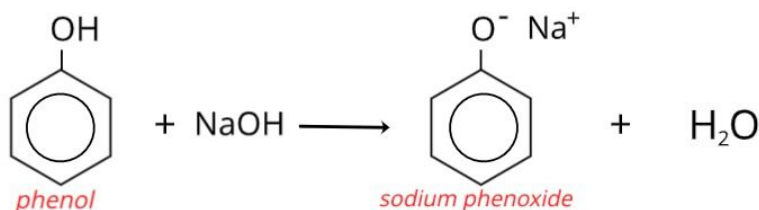


E.g.

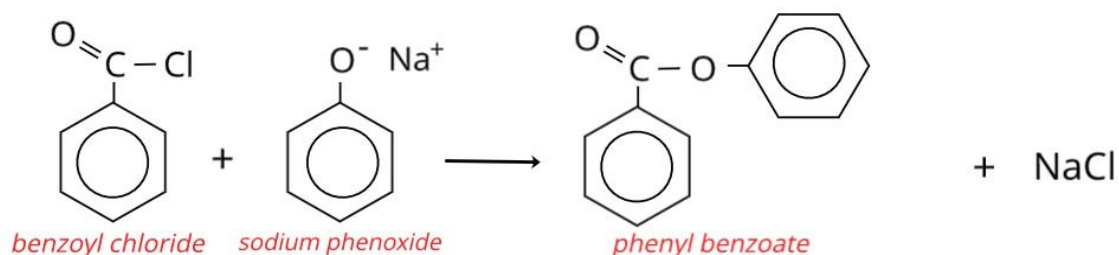


Phenyl benzoate:

Benzoyl chloride is very **unreactive** because the $-\text{COCl}$ group is directly attached to a **stable benzene ring**. To produce the ester phenyl benzoate, phenol is first converted into an ionic compound by **dissolving it in sodium hydroxide**. This produces the **phenoxide** ion:



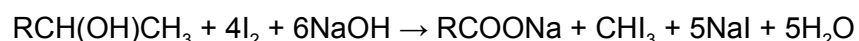
The **phenoxide ion** is **more reactive** than the phenol so this ion can react with benzoyl chloride to produce phenyl benzoate (see the following page).



Deducing the presence of CH₃CH(OH)- group in an alcohol

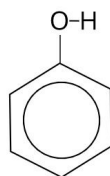
The presence of a CH₃CH(OH)- group can be detected in an alcohol using **alkaline aqueous iodine**, I₂.

Iodine is added to the alcohol, followed by **sodium hydroxide**. If the CH₃CH(OH)- group is present, a **yellow precipitate** of **tri-iodomethane**, CHI₃, will be produced.



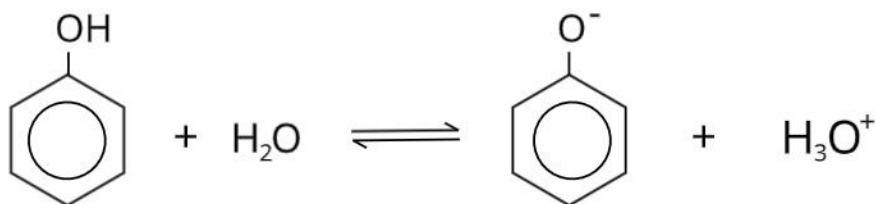
Phenol (A Level only)

Phenol is an aromatic hydrocarbon consisting of one alcohol group bonded to the benzene ring:



Reactions with bases

Phenol is a **weak acid**. A hydrogen ion can be removed from the hydroxyl group and transferred to a base. The position of **equilibrium** for the reaction below lies far to the left which means that phenol is a weak acid.

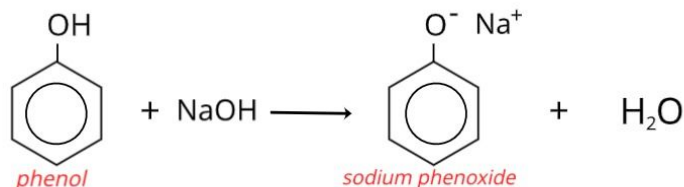


Phenol is able to donate a hydrogen ion because the **phenoxide ion** is **relatively stable**. The **lone pair** on the oxygen atom is delocalised into the **pi system** which is above and below the benzene ring. This means that the **negative charge is dispersed** among the carbon atoms so the compound is more stable.



Reaction with sodium hydroxide

When phenol reacts with sodium hydroxide, colourless **sodium phenoxide** is formed.

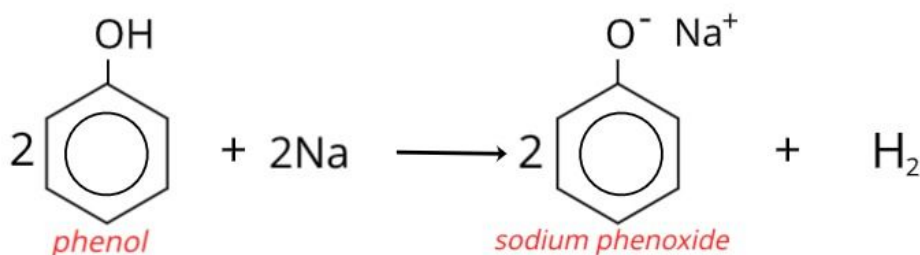


Reaction with sodium carbonate

Phenol isn't acidic enough to react with sodium carbonate.

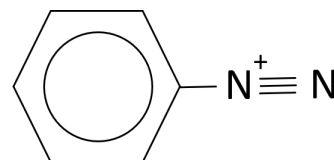
Reactions with sodium

Phenol reacts with metals in the same way that most acids. **Hydrogen gas** and a salt are produced. The reaction occurs **slower** than comparable acid-metal reactions because phenol is a **weak acid**.

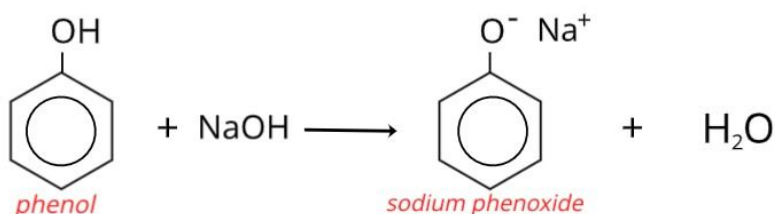


Reactions with diazonium salts

Diazonium salts contain the diazonium ion, R-N_2^+ (where R is any organic group). In the case of the following example, we will be looking at the diazonium ion when it is attached to a **benzene ring**.

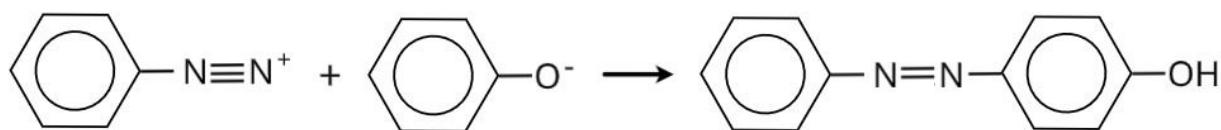


Before a diazonium salt is reacted with phenol, phenol is dissolved in **sodium hydroxide** to give the **phenoxide ion**:



Cold **benzenediazonium chloride** is then added to the **sodium phenoxide** solution. The diazonium and phenoxide ions react together to form an **azo compound**. An azo compound contains two benzene rings that are joined together with a nitrogen bridge. The product can be identified as a **yellow solution** or **precipitate**.





Nitration and bromination of the aromatic ring

Phenol is **more reactive than benzene** because it contains an -OH functional group. The lone pair on the oxygen atom is delocalised into the **pi system**. This **increases the electron density**, making phenol more likely to be **attacked by electrophiles**.

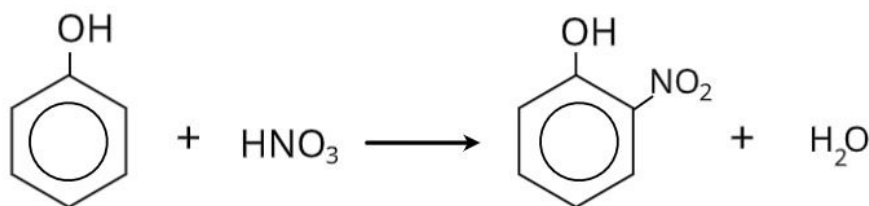
The effect of the OH group is sometimes referred to as the **2,4-directing effect**. This is because the incoming groups tend to bond to the second and fourth carbons from the hydroxyl group.

Nitration

Phenol reacts with dilute and concentrated nitric acid:

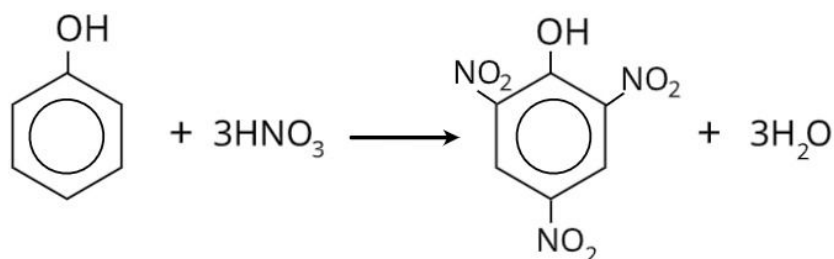
- **Dilute** nitric acid

The 2,4-directing effect of the hydroxyl group causes a mixture of **2-nitrophenol** and **4-nitrophenol** to be produced. The reaction for 2-nitrophenol is shown below.



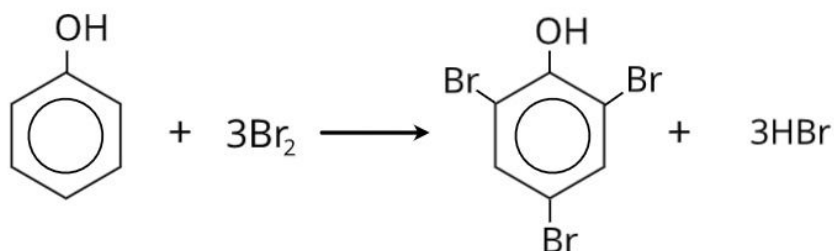
- **Concentrated** nitric acid

The compound **2,4,6-trinitrophenol** is formed.



Bromination

When bromine water is added to a solution of phenol, the orange bromine water is decolourised. **2,4,6-tribromophenol (white precipitate)** and hydrogen bromide are formed.



Relative acidities of water, phenol and ethanol

The relative acidities are as follows: **phenol > water > ethanol**

- Phenol is the **most acidic** because the **phenoxide ion** (formed when phenol donates a proton) is **relatively stable**. The **lone pair** on the oxygen atom is **delocalised** into the pi system meaning the negative charge is dispersed among the carbon atoms. This means that phenol is **more likely to donate a hydrogen ion** than water or ethanol.
- Ethanol and water have similar acidities but **ethanol is the least acidic**. This is because of the **positive inductive effect**. The alkyl group in the **ethoxide ion** “**pushes**” **electrons** away from itself, towards the oxygen. This **increases the electron density of the oxygen**, making it more likely to bond to a hydrogen ion and reform ethanol.

