Edexcel International AS Chemistry

Your notes

Organic Chemistry: Alcohols

Contents

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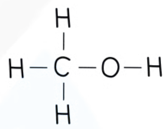
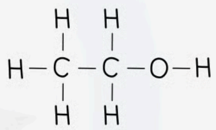
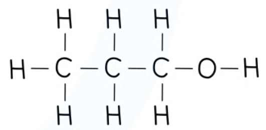
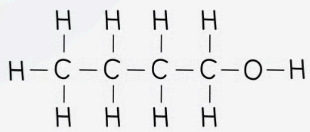
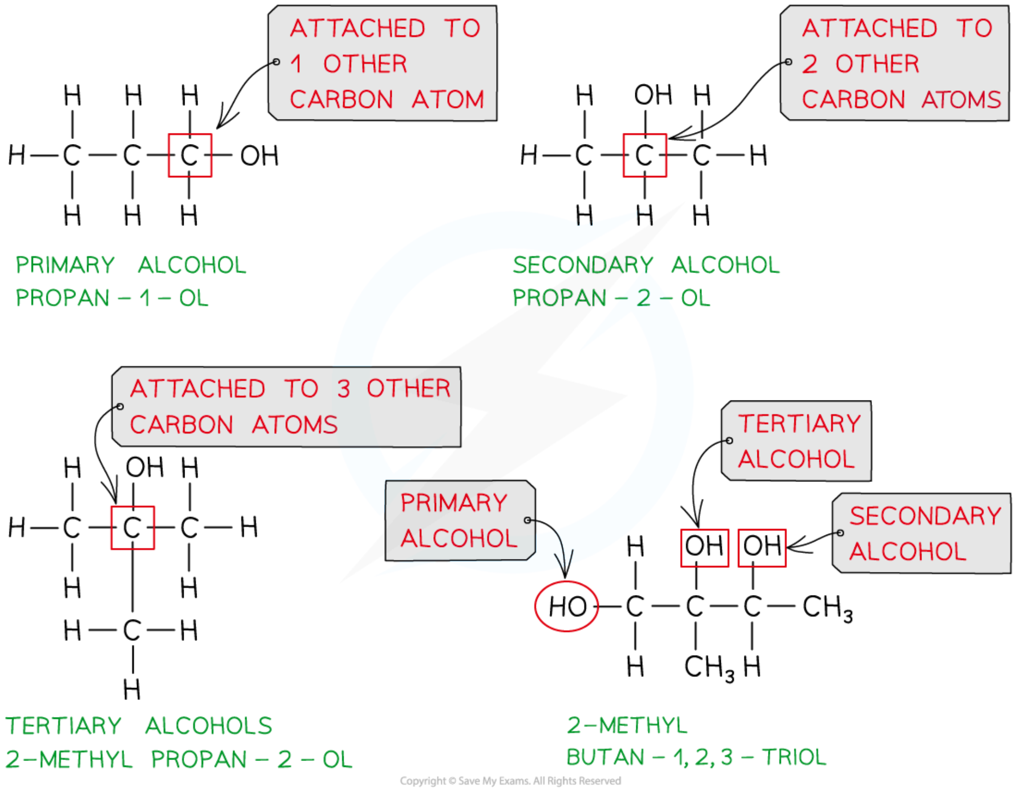
Alcohols – Introduction

- **Alcohols** are a family of molecules that contain the **hydroxyl functional group**, **-OH**
- Their general formula is **$C_nH_{2n+1}OH$**
- The nomenclature of alcohols follows the pattern **alkan + ol**
- If there are two **-OH** groups present the molecule is called a **diol**

The first four Alcohols and their Structures Table

ALCOHOL	STRUCTURAL FORMULA	DISPLAYED FORMULA
METHANOL	CH_3OH	
ETHANOL	CH_3CH_2OH	
PROPANOL	$CH_3CH_2CH_2OH$	
BUTANOL	$CH_3CH_2CH_2CH_2OH$	

- Alcohols are classified as **primary, secondary** or **tertiary** depending on the number of carbons attached to the **functional group** carbon
  - **Primary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **one** other carbon atom (or alkyl group)
  - **Secondary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **two** other carbon atoms (or alkyl groups)
  - **Tertiary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **three** other carbon atoms (or alkyl groups)



Classifying primary, secondary and tertiary alcohols and alcohols with more than one alcohol group

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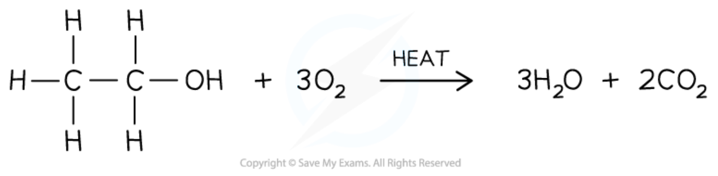
Alcohols – Reactions

Combustion of alcohols

- Alcohols react with oxygen in the air when ignited and undergo **complete combustion** to form carbon dioxide and water

alcohol + oxygen → carbon dioxide + water



Complete combustion of alcohols to produce carbon dioxide and water

Conversions to halogenoalkanes

- These reactions involve replacing the hydroxyl group in an alcohol molecule with a halogen atom(known as halogenation)
- Different methods are required for each halogen

Chlorination

- Phosphorus(V) chloride is added to the alcohol resulting in a vigorous reaction at room temperature
  - This means the mixture doesn't need heating
- This reaction is used as a qualitative test for the presence of the -OH group
  - If you add PCl_5 to an unknown liquid the evolution of steamy fumes (HCl gas) is evidence for the presence of the -OH group
- Two inorganic products are formed: phosphoryl chloride and hydrogen chloride

$$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$$

- Chlorination of tertiary alcohols can be carried out in a different way by mixing (shaking) with hydrochloric acid at room temperature
- An example equation for the reaction of 2–methyl propan–2–ol is:

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

- This reaction does not work for primary and secondary alcohols

Bromination

- This reaction is carried out using a warmed mixture of potassium bromide and 50% concentrated sulfuric acid with the reacting alcohol
- More concentrated sulfuric acid would would oxidise bromide ions to bromine resulting in different products
- The reaction can be written as two equations as the inorganic reactants first react together to form hydrogen bromide and potassium sulfate

$$2KBr + H_2SO_4 \rightarrow K_2SO_4 + 2HBr$$

- The resulting hydrogen bromide then reacts with the alcohol, for example the reaction with butan-1-ol would be as follows:

$$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

Iodination

- This reaction is carried out using a mixture of red phosphorus and iodine with the alcohol whilst heating under reflux
- Similar to bromination, the reaction can be written as two equations as the inorganic reactants first react to form phosphorus(III) iodide

$$2P + 3I_2 \rightarrow 2PI_3$$

- The reaction for the iodination of ethanol would be:

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$

- This reaction results in the formation of phosphorous acid as shown above

Dehydration to Alkenes

- Dehydration is done by heating the alcohol with concentrated phosphoric acid
- The reaction is similar to the elimination reaction of a halogenoalkene
  - The OH group and hydrogen of adjacent carbons are removed forming a C=C bond
- The equation for the dehydration of ethanol would be

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$$

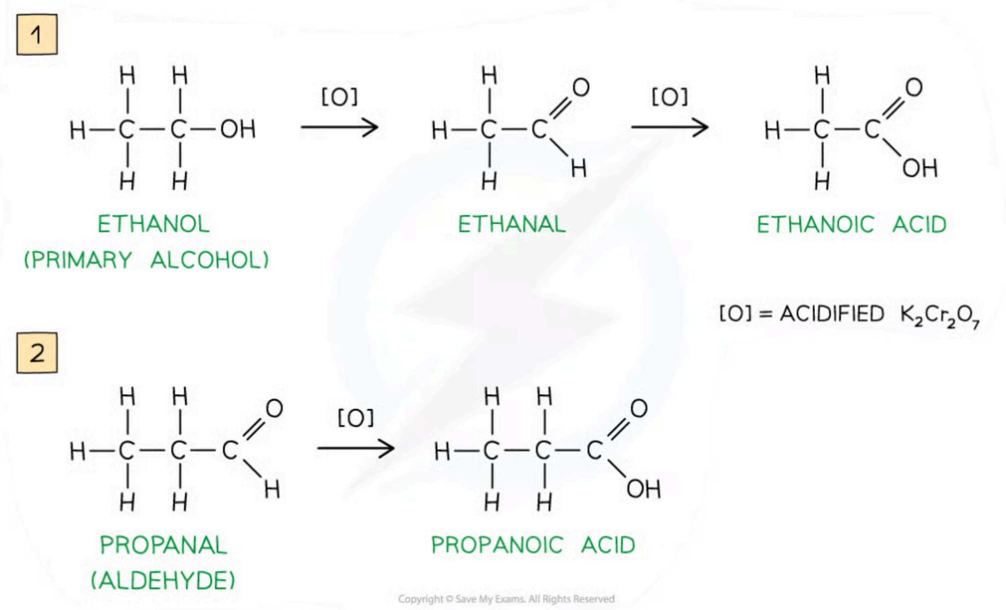
- Phosphoric acid does not appear in the equation as the water formed dilutes the concentrated phosphoric acid

Your notes

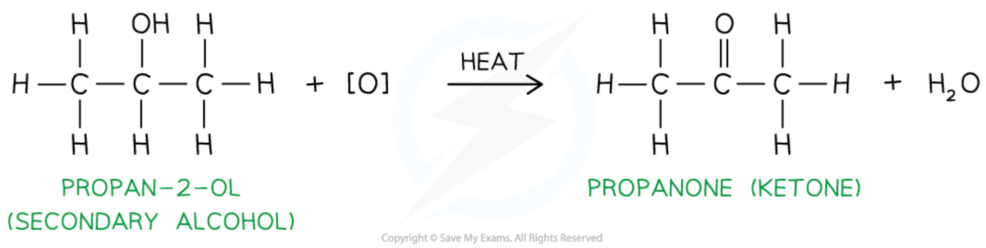
Alcohols – Oxidation

Oxidation of alcohols

- Primary alcohols can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- Secondary alcohols can be oxidised to form **ketones** only
- Tertiary alcohols do not undergo oxidation
- The oxidising agents of alcohols include **acidified $K_2Cr_2O_7$**
- **Acidified potassium dichromate(VI)**, $K_2Cr_2O_7$, is an orange oxidising agent
  - Acidified means that that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
  - For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
  - This reduction requires hydrogen (H^+) ions which are provided by the acidic medium
    - When alcohols are **oxidised** the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
- The primary alcohol is added to the oxidising agent and warmed
- The aldehyde product has a lower boiling point than the alcohol reactant so it can be **distilled off** as soon as it forms
- If the aldehyde is not distilled off, further **refluxing** with excess oxidising agent will oxidise it to a carboxylic acid
- Since ketones cannot be further oxidised, the ketone product does not need to be **distilled off** straight away after it has been formed



Oxidation Stages of Primary Alcohols



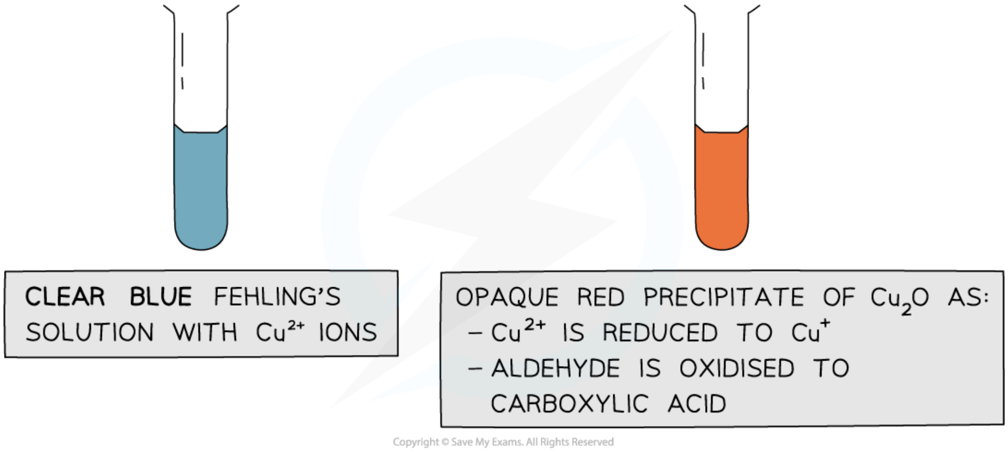
Oxidation of propan-2-ol by acidified $K_2Cr_2O_7$ to form a ketone

- The presence of an aldehyde group (-CHO) in an **unknown compound** can be determined by the **oxidising agents** Fehling's and Tollens' reagents

Fehling's solution

- **Fehling's solution** is an alkaline solution containing copper(II) ions which act as the oxidising agent
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Cu^{2+} ions are reduced to Cu^+ ions
  - In the alkaline conditions, the carboxylic acid formed will be neutralised to a carboxylate ion (the -COOH will lose a proton to become $-COO^-$)
  - The carboxylate ion ($-COO^-$) will form a salt with a positively charged metal ion such as sodium ($-COO^-Na^+$)
- The **clear blue** solution turns **opaque** due to the formation of a **red precipitate**, **copper(I) oxide**

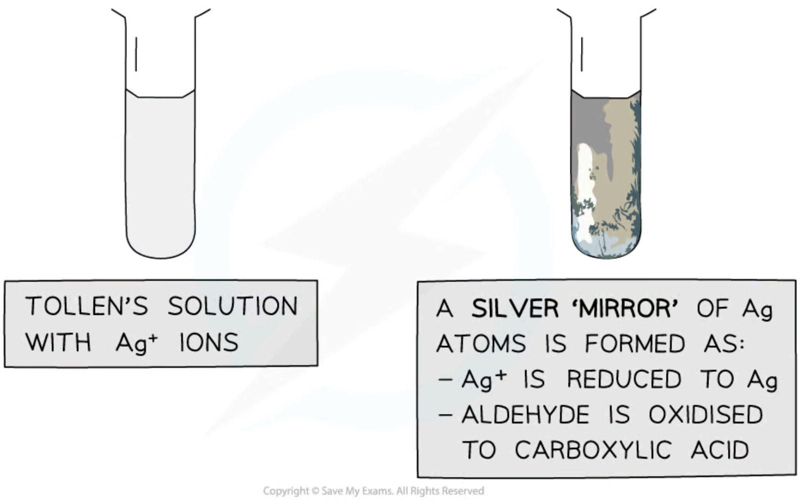
- **Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Fehling's solution



The copper(II) ions in Fehling's solution are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to copper(I) ions in the Cu_2O precipitate

Tollens' reagent

- **Tollens' reagent** is an aqueous alkaline solution of silver nitrate in excess ammonia solution
  - Tollen's reagent is also called **ammoniacal silver nitrate solution**
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Ag^+ ions are reduced to Ag atoms
  - In the alkaline conditions, the carboxylic acid will become a carboxylate ion and form a salt
- The Ag atoms form a silver 'mirror' on the inside of the tube
- **Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Tollens' reagent



The Ag^+ ions in Tollens' reagent are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms

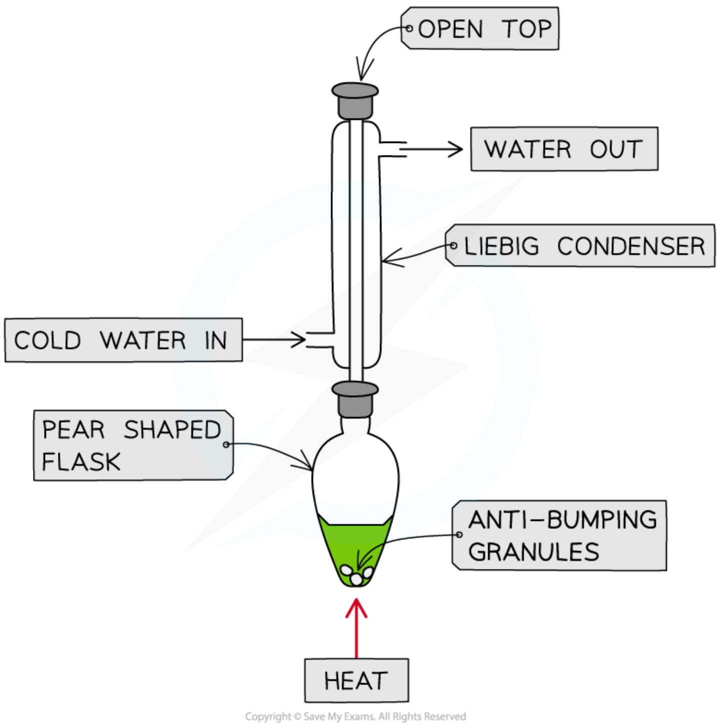
Your notes

Different practical techniques

- Because of the easier oxidation of aldehydes compared to alcohols, two different techniques are used
  - Heating under reflux
  - Distillation with addition

Heating under reflux

- This technique is used when we want full oxidation
  - Producing a carboxylic acid for a primary alcohol
  - Producing a ketone for a secondary alcohol

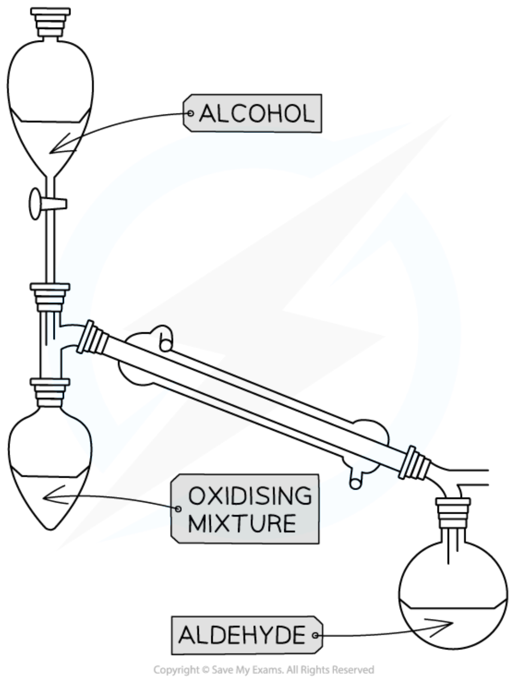


Apparatus set up for heating under reflux

- This set up means any products of oxidation remain in the reaction mixture
- Products which boil off condense in the vertical condenser then return to the heating flask

Distillation with addition

- This technique is used when we do not want to complete oxidation
  - To obtain an aldehyde rather than carboxylic acid for primary alcohol



Apparatus set up for distillation with addition

- Only the oxidising agent is heated whilst the alcohol is slowly added
- When the aldehyde is formed it immediately distils off as it has a much lower boiling point than the alcohol used to make it
- The aldehyde is then collected in the reciever