

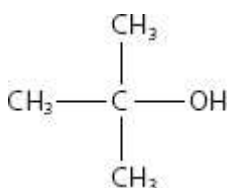
# 16 Hydroxy compounds

As with the halogen compounds, the aliphatic hydroxy compounds are covered in this chapter for AS Level but aromatic hydroxy compounds and phenols are revisited for A Level in [Chapter 32](#).

## Different types of alcohols

In just the same way as with primary, secondary and tertiary halogenoalkanes, there are primary, secondary and tertiary alcohols:

- ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is a primary alcohol
- propan-2-ol,  $\text{CH}_3\text{CHOHCH}_3$ , is a secondary alcohol
- 2-methylpropan-2-ol ([Figure 16.1](#)) is a tertiary alcohol



**Figure 16.1**

Mild oxidation, for example with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , gives a colour change from orange to green and can be used to distinguish the types of alcohol.

### NOW TEST YOURSELF

**1** Draw skeletal structures for these alcohols:

- a** butan-2-ol
- b** 2-methylpropan-1-ol
- c** 2-methylpropan-2-ol
- d** cyclohexanol

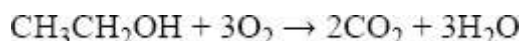
**2** For your structures in question 1, label each alcohol as primary, secondary or tertiary.

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# Reactions of alcohols

## Combustion

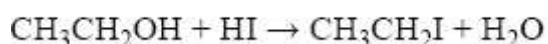
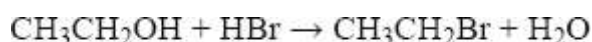
Like most organic compounds, alcohols are flammable. You may remember this from using a spirit burner. The equation for the complete combustion of ethanol is:



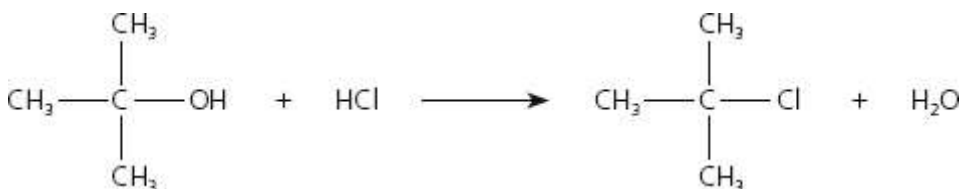
## Substitution to form halogenoalkanes

- Halogenoalkanes can be hydrolysed to make alcohols, and alcohols can be converted into halogenoalkanes – but using different reagents.
- One way of carrying out the substitution is to use the appropriate hydrogen halide. This method works for the bromoalkanes and iodoalkanes if the hydrogen halide is generated in the reaction flask.
- Sodium bromide with concentrated sulfuric acid can be used for the bromoalkane, but sodium iodide and concentrated phosphoric(v) acid have to be used for the iodoalkane because sulfuric acid would oxidise any hydrogen iodide formed.

The equations for the formation of bromoethane and iodoethane are:

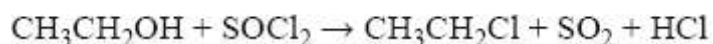
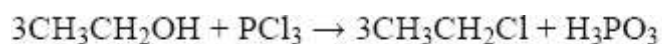


The method shown in [Figure 16.2](#) only works with tertiary alcohols, forming the tertiary chloroalkane.



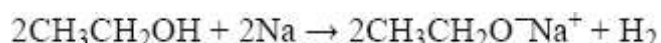
**Figure 16.2**

For other chloroalkanes you have to use phosphorus trichloride,  $\text{PCl}_3$ , phosphorus pentachloride,  $\text{PCl}_5$ , or thionyl chloride,  $\text{SOCl}_2$ :



## Reaction with sodium

When a small piece of sodium is dropped into ethanol it dissolves and reacts, producing bubbles of hydrogen gas. It leaves a colourless solution that produces a white solid, if evaporated to dryness. This white solid is sodium ethoxide,  $\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+$ :



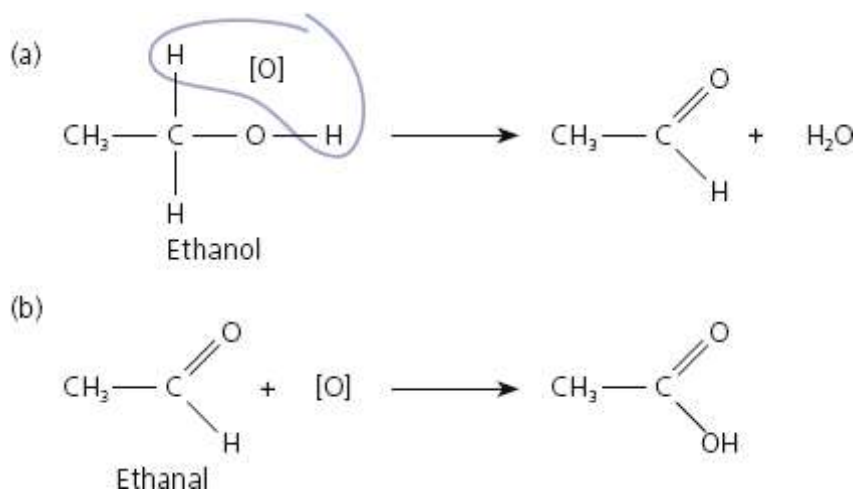
This reaction is sometimes used to dispose of small amounts of ‘old’ sodium because it is much less violent than reacting sodium with water.

This reaction can also be used as a test for an alcohol. The ethoxide ion (like the hydroxide ion) is a strong base and a good nucleophile.

## Oxidation reactions

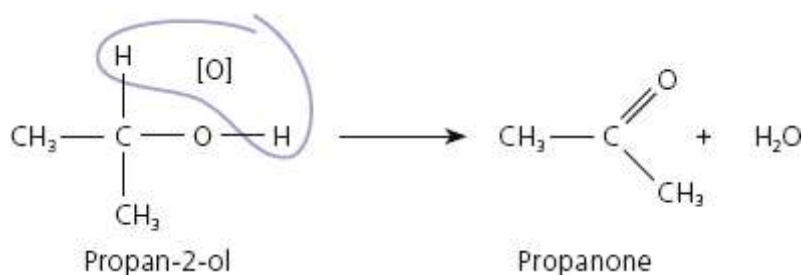
Whether or not an alcohol can be oxidised depends on its structure. On addition to an oxidising agent such as acidified dichromate(VI) solution, a positive test for oxidation is that the dichromate(VI) solution turns from orange to blue-green.

- On warming a primary alcohol with acidified dichromate(VI), an aldehyde is first formed ([Figure 16.3\(a\)](#)).
- If this is not removed from the reaction vessel it is further oxidised to a carboxylic acid ([Figure 16.3\(b\)](#)). The mixture turns from orange to blue-green.



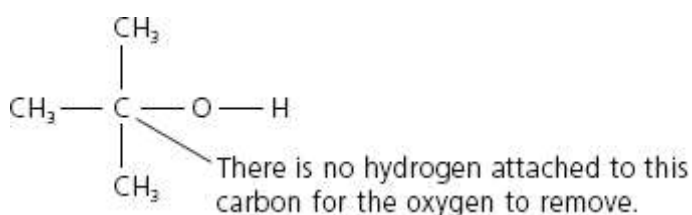
**Figure 16.3** Oxidation of a primary alcohol

- On refluxing a secondary alcohol with acidified dichromate(VI), a ketone is formed ([Figure 16.4](#)), which is not oxidised further. Again, the mixture turns from orange to blue-green.



**Figure 16.4** Oxidation of a secondary alcohol

- With a tertiary alcohol ([Figure 16.5](#)), there are no hydrogen atoms on the carbon atoms that can be oxidised, so there is no reaction.



**Figure 16.5**

Provided that we can distinguish between an aldehyde and a ketone, these oxidation reactions can be used to detect primary, secondary or tertiary alcohols. There are relatively simple tests for aldehydes that use Fehling's solution or Tollens' reagent (see [Chapter 17](#)).

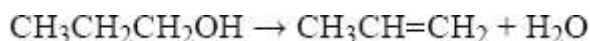
## NOW TEST YOURSELF

**3** Draw skeletal structures for the products, if any, of reacting these alcohols with acidified dichromate(vi):

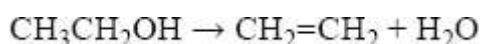
- a** butan-2-ol
- b** 2-methylpropan-1-ol
- c** 2-methylpropan-2-ol

## Dehydration

Strong acids such as phosphoric(v) and sulfuric can be used to dehydrate alcohols to form alkenes:

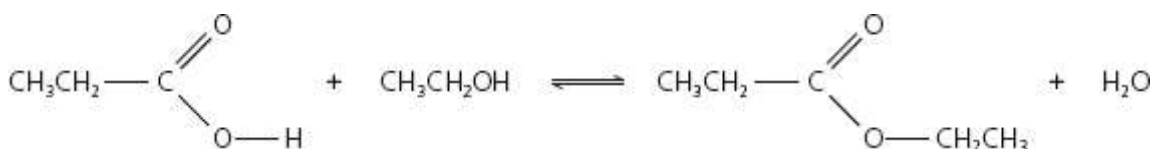


Warming ethanol and passing the vapour over heated aluminium oxide achieves the same reaction:



## Forming esters

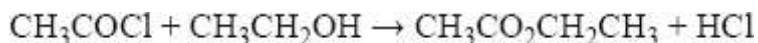
If an alcohol is warmed with an organic acid in the presence of  $\text{H}^+$  ions, an ester is formed with the elimination of water ([Figure 16.6](#)).



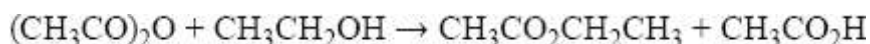
**Figure 16.6**

This is an equilibrium reaction and is often quite slow. The reaction can be speeded up by using another compound containing the  $\text{RC}=\text{O}$  group. Suitable compounds include acyl chlorides (see [Chapter 33](#)) or acid anhydrides.

With ethanoyl chloride and ethanol, this reaction occurs:



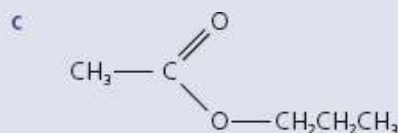
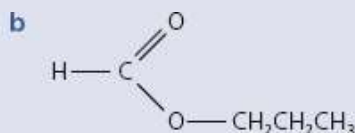
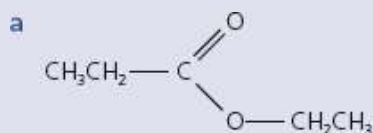
With ethanoic anhydride and ethanol, this reaction takes place:



When naming esters the convention is to give the fragment of the alcohol first and then the anion name of the acid. So the esters shown above are all ethyl ethanoate (rather strangely, they are usually drawn with the acid fragment first).

## NOW TEST YOURSELF

4 Name the four esters whose structures are shown below.

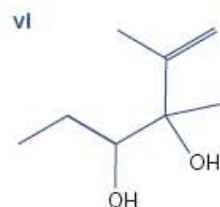
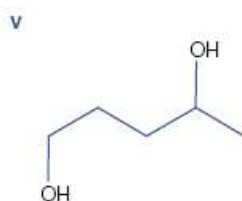
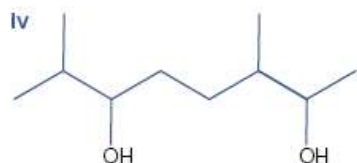
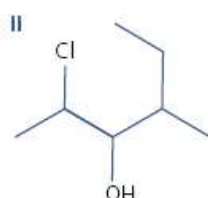


## The tri-iodomethane (iodoform) reaction

This reaction is quite specific for a particular structural arrangement in an alcohol. It detects the presence of the  $\text{CH}_3\text{CH}(\text{OH})-$  group. The test is carried out by adding iodine solution to the alcohol and then adding just enough sodium hydroxide to remove the colour of the iodine. On standing, or more usually on warming, a pale-yellow precipitate of tri-iodomethane is formed if the group is present.

## REVISION ACTIVITY

a Classify the following as primary, secondary or tertiary alcohols.



b How does reaction with acidified potassium dichromate(vi) enable you to decide whether an unknown alcohol has a primary, secondary or tertiary structure?

## END OF CHAPTER CHECK

By now you should be able to:

- recall the reactants and conditions by which alcohols can be produced
- classify alcohols as primary, secondary or tertiary and state characteristic distinguishing reactions, e.g. mild oxidation with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$
- describe reactions with oxygen, sodium metal, oxidation with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  or acidified  $\text{KMnO}_4$
- describe substitution to form halogenoalkanes, dehydration to form alkenes, esterification
- deduce the presence of a  $\text{CH}_3\text{CH}(\text{OH})-$  group in an alcohol by its reaction with alkaline  $\text{I}_2(\text{aq})$
- explain the acidity of alcohols compared with water