# **AS Level**Organic chemistry

# 16 Alcohols

#### Functional group:

The —OH (hydroxyl) group occurs in many organic compounds. In addition to the alcohols, it forms all or part of the functional group in sugars, phenols and carboxylic acids. In this topic we look at the reactions of the hydroxyl group when it is the only functional group in the molecule, in the alcohols. The hydrogen atom attached to oxygen is slightly acidic, and the  $\delta$ + nature of the carbon atom makes it susceptible to nucleophilic substitution reactions. Primary and secondary alcohols also undergo oxidation.

#### Learning outcomes

By the end of this topic you should be able to:

- 14.1a) interpret and use the general, structural, displayed and skeletal formulae of the alcohols (including primary, secondary and tertiary)
- 17.1a) recall the chemistry of alcohols, exemplified by ethanol in the following reactions: combustion, substitution to give halogenoalkanes, reaction with sodium, oxidation to carbonyl compounds and carboxylic acids, dehydration to alkenes, formation of esters by esterification with carboxylic acids (part, see also Topic 26)
- 17.1b) classify hydroxy compounds into primary, secondary and tertiary alcohols, and suggest characteristic distinguishing reactions, e.g. mild oxidation
- **17.1c)** deduce the presence of a CH<sub>3</sub>CH(OH)— group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane.

# 16.1 Introduction

The **alcohols** form a homologous series with the general formula  $C_nH_{2n+1}OH$ . They occupy a central position in organic functional group chemistry: they can be readily converted to aldehydes and carboxylic acids by oxidation, and can be formed from them by reduction; and they can be converted to and from halogenoalkanes by nucleophilic substitution.

Alcohols are useful solvents themselves, but they are also key intermediates in the production of esters, which are important solvents for the paints and plastics industries.

The polar —OH group readily forms hydrogen bonds to similar groups in other molecules. This accounts for the following major differences between the alcohols and the corresponding alkanes.

 The lower alcohols (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and some isomers of C<sub>4</sub>) are totally miscible with water, owing to hydrogen bonding between the alcohol molecules and water molecules (see Figure 16.1). As the length of the alkyl chain increases, van der Waals' attractions predominate between the molecules of the alcohol, and so the miscibility with water decreases.

Figure 16.2 Intermolecular hydrogen bonding in ethanol

 The boiling points of the alcohols are all much higher than the corresponding (isoelectronic) alkanes, owing to strong intermolecular hydrogen bonding (see Figure 16.2).

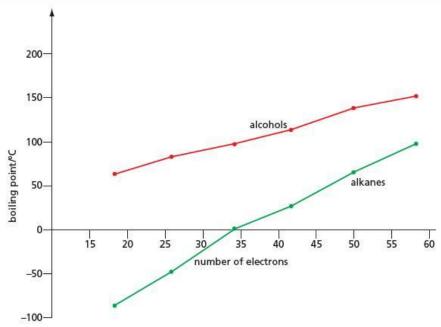
$$CH_{2}$$
  $CH_{3}$   $CH_{2}$   $CH_{3}$   $CH_{2}$   $CH_{2}$   $CH_{3}$   $CH_{4}$   $CH_{5}$   $C$ 

Table 16.1 and Figure 16.3 show this large difference. As is usual in homologous series, the boiling points increase as the number of carbon atoms increases, owing to increased van der Waals' attractions between the longer alkyl chains. The enhancement of boiling point due to hydrogen bonding also decreases, as the longer chains become more alkane-like.

**Table 16.1** Boiling points of some alcohols and alkanes

Number of electrons in the molecule	Alkane		Alcohol		Enhancement
	Formula	Bolling point/°C	Formula	Boiling point/°C	of boiling point/°C
18	C <sub>2</sub> H <sub>6</sub>	-88	CH₃OH	65	153
26	C₃H <sub>8</sub>	-42	C <sub>2</sub> H <sub>5</sub> OH	78	120
34	C <sub>4</sub> H <sub>10</sub>	0	C <sub>3</sub> H <sub>7</sub> OH	97	97
42	C <sub>5</sub> H <sub>12</sub>	36	C <sub>4</sub> H <sub>9</sub> OH	118	82
50	C <sub>6</sub> H <sub>14</sub>	69	C <sub>5</sub> H <sub>11</sub> OH	138	69
58	C <sub>7</sub> H <sub>16</sub>	98	C <sub>6</sub> H <sub>13</sub> OH	157	59

Figure 16.3 Boiling points of some alcohols and alkanes



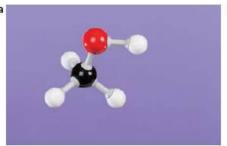
The electron pairs around the oxygen atom in alcohols are arranged in a similar way to those around the oxygen atom in the water molecule, as both have two lone pairs of electrons (see Figure 16.4).

Figure 16.4 The oxygen atom in an alcohol has two lone pairs of electrons.

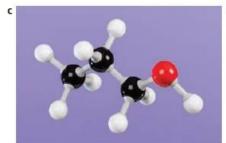
## 16.2 Isomerism and nomenclature

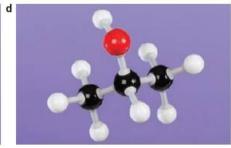
As was mentioned in section 12.5, the alcohols are named by adding the suffix '-ol' to the alkane stem of the compound. The longest carbon chain that contains the —OH group is chosen as the stem. A numeral precedes the '-ol' to describe the position of the —OH group along the chain.

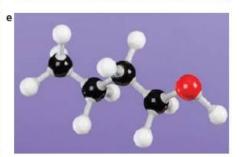
Figure 16.5 Molecular models of a methanol, **a b** ethanol, **c** propan-1-ol, **d** propan-2-ol and **e** butan-1-ol











#### Worked example

Name the following compounds.

- a CH3-CH(OH)-CH2-CH3
- b CH₂=CH—CH₂OH
- CH3-CH2-CH(CH3)-CH2OH

#### Answer

- a The longest (and only) carbon chain contains four carbon atoms. The —OH is on the second atom, so the alcohol is butan-2-ol.
- b The three-carbon base is propene. Taking the —OH group to be on position 1, the name is thus prop-2-en-1-ol.
- The longest chain contains four carbon atoms, with a methyl group on position 2 and the —OH group on position 1. The compound is 2-methylbutan-1-ol.

Alcohols show chain, positional and optical isomerism (see section 12.6).

Alcohols are classed as primary, secondary or tertiary, depending on the number of alkyl groups that are attached to the carbon atom joined to the -OH group. Of the five isomers with the formula  $C_4H_9OH$ , two (A and B below) are primary alcohols, two (C and D) are secondary alcohols, and one (E) is a tertiary alcohol.

#### Now try this

- 1 Describe the type of isomerism shown by the following pairs of alcohols, whose structures are shown.
- a A and B b B and E
- CA and Cd Cand D
- 2 Name the five alcohols whose structures are shown. (Note: alcohols C and D will have the same name.)

# CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH A B CH<sub>3</sub>CH<sub>2</sub> CH<sub>3</sub> CH<sub>3</sub>CH<sub>2</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> HO H H OH H<sub>3</sub>C OH C D E

#### The ethers

**Ethers** are isomers of alcohols, but they do not contain the —OH group and so have none of the reactions of alcohols, and do not form intermolecular hydrogen bonds.

Hence they are fairly inert compounds with boiling points lower than those of the isomeric alcohols. For example:

They are quite good at dissolving organic compounds, and so are often used as solvents.

## 16.3 Reactions of alcohols

#### 1 Combustion

All alcohols burn well in air, but only the combustion of ethanol is of everyday importance:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

The use of ethanol as a fuel has been mentioned in section 13.4.

For its uses as a fuel, and as a common solvent, ethanol is marketed as 'methylated' or 'rectified' spirit. This contains about 90% ethanol, together with 5% water, 5% methanol, and pyridine. The poisonous methanol is added to make it undrinkable, and hence exempt from the large excise duty that spirits attract. The pyridine gives it a bitter taste, which makes it unpalatable.

The other reactions of alcohols can be divided into three groups:

- · reactions involving the breaking of the O-H bond
- reactions involving the breaking of the C—O bond
- $\bullet$  reactions of the  $\begin{array}{c} H \\ \text{OH} \end{array}$  group (tertiary alcohols cannot show this group of reactions).

# 2 Reactions involving the breaking of the O—H bond

#### With sodium metal

The hydroxyl hydrogen in alcohols is slightly acidic, just like the hydrogen atoms in water, but the alcohols ionise to a lesser extent:

$$H - O - H \rightleftharpoons H - O^- + H^+$$
  $K_w = 1.0 \times 10^{-14} \, \text{mol}^2 \, \text{dm}^{-6}$   $K - O - H \rightleftharpoons R - O^- + H^+$   $K = 1.0 \times 10^{-16} \, \text{mol}^2 \, \text{dm}^{-6}$ 

Alcohols liberate hydrogen gas when treated with sodium metal:

$$CH_3CH_2OH + Na \rightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

The reaction is less vigorous than that between sodium and water. The product is called sodium ethoxide (compare sodium hydroxide, from water). This is a white solid, which is soluble in ethanol and in water (to give a strongly alkaline solution).

All compounds containing —OH groups liberate hydrogen gas when treated with sodium. The fizzing that ensues is a good test for the presence of an —OH group (as long as water is absent).

They can be obtained by reacting alcohols with carboxylic acids or with acyl chlorides (see Topics 18 and 26).

alcohol + carboxylic acid → ester + water

For example:

$$\begin{array}{c|c} O & heat with & O \\ \parallel & & \parallel \\ CH_3CH_2OH + CH_3C - OH \xrightarrow{as catalyst} & CH_3 - C - O - CH_2CH_3 + H_2O \end{array}$$

It has been found that the oxygen in the water comes from the carboxylic acid, and the —O— in the ester comes from the alcohol. The methods of ester preparation will be dealt with in detail in Topics 18 and 26.

Esters are useful solvents, and several are also used, in small quantities, as flavouring agents in fruit drinks and sweets.

# 3 Reactions involving the breaking of the C—O bond

Although the C—O bond is polarised C<sup>84</sup>–O<sup>8</sup>, it is a strong bond, and does not easily break heterolytically:

$$-C -OH \rightarrow -C^{+} + -OH$$

If, however, the oxygen is protonated, or bonded to a sulfur or phosphorus atom, the C—O bond is much more easily broken. As a result, alcohols undergo several **nucleophilic substitution** reactions.

#### Reaction with hydrochloric acid

Tertiary alcohols react easily with concentrated hydrochloric acid on shaking at room temperature. The reaction proceeds via the  $S_{\rm N}1$  mechanism (see section 15.3):

Secondary and primary alcohols also react with concentrated hydrochloric acid, but at a slower rate. Anhydrous zinc chloride needs to be added as a catalyst, and the mixture requires heating:

$$CH_3CH_2OH + HCI \xrightarrow{ZnCl_2, heat} CH_3CH_2CI + H_2O$$

This reaction is the basis of the **Lucas test** to distinguish between primary, secondary and tertiary alcohols (see Table 16.2). It relies on the fact that alcohols are soluble in the reagent (concentrated HCl and ZnCl<sub>2</sub>) whereas chloroalkanes are not, and therefore produce a cloudiness in the solution.

Type of alcohol	Observation on adding conc. HCl + ZnCl <sub>2</sub>	
R₃COH (tertiary)	immediate cloudiness appears in the solution	
R₂CHOH (secondary)	cloudiness apparent within 5 minutes	
RCH <sub>2</sub> OH (primary)	no cloudiness apparent unless warmed	

Table 16.2 The Lucas test

#### Reaction with phosphorus(V) chloride or sulfur dichloride oxide

Both of these reagents convert alcohols into chloroalkanes (see section 15.5), and in both cases hydrogen chloride is evolved. This fizzing with PCl<sub>5</sub>, and the production of misty fumes, can be used as a test for the presence of an alcohol (as long as water is absent). Both reactions occur on gently warming the reagents.

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$
  
 $CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$ 

#### Reaction with hydrogen bromide

Alcohols can be converted into bromoalkanes by reaction with either concentrated hydrobromic acid or a mixture of sodium bromide, concentrated sulfuric acid and water (50%). These react to give hydrogen bromide:

$$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$$

$$CH_{3}-CH_{2}-O$$

$$H$$

$$CH_{3}-CH_{2}-O$$

$$H$$

$$CH_{3}-CH_{2}-O$$

$$H$$

$$CH_{3}-CH_{2}-Br + H_{2}O$$

$$CH_{3}-CH_{2}-Br + H_{2}O$$

#### Reaction with red phosphorus and bromine or iodine

These halogens react with phosphorus to give the phosphorus trihalides:

$$2P + 3Br_2 \rightarrow 2PBr_3$$
  
 $2P + 3I_2 \rightarrow 2PI_3$ 

The phosphorus trihalides, for example phosphorus triiodide, then react with alcohols as follows:

#### Reaction with concentrated sulfuric acid

Ethanol and concentrated sulfuric acid react together to give the compound ethyl hydrogensulfate:

$$CH_3-CH_2-OH+H-O-S-O-H \rightleftharpoons O$$

$$CH_3-CH_2-O-S-O-H+H_2O$$

The ethyl hydrogensulfate can then undergo an elimination reaction to form ethene:

H
$$CH_2$$
 $CH_2$ 
 $CH_2$ 

As the sulfuric acid is regenerated on elimination, it is essentially a catalyst for the conversion of the alcohol to the alkene:

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

Concentrated phosphoric acid also acts as a catalyst for the reaction. This is often preferred because, unlike sulfuric acid, it is not also an oxidising agent, and so the formation of by-products is minimised.

$$CH_3CH_2OH \xrightarrow{\text{heat with } H_3PO_4} CH_2 = CH_2 + H_2O$$

A third method of dehydration is to pass the vapour of the alcohol over strongly heated aluminium oxide:

$$CH_3CH_2OH \xrightarrow{Al_2O_3 \text{ at } 350^{\circ}C} CH_2 = CH_2 + H_2O$$

Tertiary alcohols dehydrate very easily on warming with an acid. The reaction goes via the carbocation, which then loses a proton:

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ H \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ H \\ CH_{3} \\ \end{array} \begin{array}{c} H \\ CH_{2} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{2} \\ CH_{3} \\ CH_{4} \\ CH_{4} \\ CH_{5} \\ CH_{$$

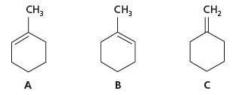
#### Worked example

Dehydrating longer-chain alcohols can give a mixture of alkenes. Suggest structures for the alkenes possible from the dehydration of the alcohol 1-methylcyclohexanol:

Which alkene will be the most stable?

#### Answei

The H and the OH of the water which is eliminated come from adjacent carbon atoms, forming the C=C bond between them. There are three possibilities:



**A** and **B** are identical (rotating **A** by 180° around a vertical axis produces **B**), so there are *two* possible alkenes. Alkene **A/B** is the most stable because it has three alkyl groups around the double bond, whereas alkene **C** has only two (see also section 14.5).

#### Now try this

Draw all the possible alkenes that could be obtained by the dehydration of 3-methylhexan-3-ol. Which is likely to be the *least* stable of these alkenes?

### 4 Reactions of the >CH(OH) group

#### Oxidation

Primary and secondary alcohols are easily oxidised by heating with an acidified solution of potassium dichromate(VI). The orange dichromate(VI) ions are reduced to green chromium(III) ions. Tertiary alcohols, however, are not easily oxidised.

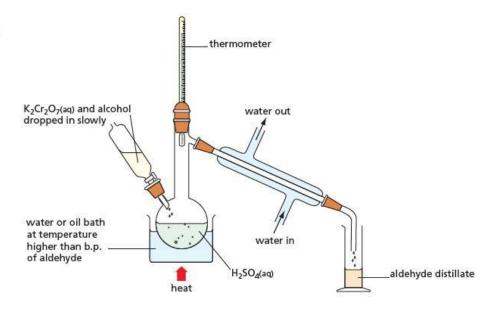
Secondary alcohols are oxidised to ketones (see Topic 17):

$$\begin{array}{cccc} CH_3 & OH & & CH_3 \\ C & & \xrightarrow{K_2Cr_2O_7 + H_2SO_4 \text{ (aq)}} & CH_3 \\ CH_3 & H & & CH_3 \\ & & & & CH_3 \\ & & & & & \\ & & & & & \\ \end{array}$$

Primary alcohols are oxidised to aldehydes, which, in turn, are even more easily oxidised to carboxylic acids:

As soon as any aldehyde is formed it can be oxidised further by the oxidising agent, to the carboxylic acid, and so special techniques are needed to stop the oxidation at the aldehyde stage. One such method makes use of the lower volatility of the alcohol (due to hydrogen bonding) compared with the aldehyde. The reaction mixture is warmed to a temperature that is above the boiling point of the aldehyde, but below that of the alcohol. The aldehyde is allowed to distil out as soon as it is formed, thus avoiding any further contact with the oxidising agent (see Figure 16.6).

Figure 16.6 Apparatus for distilling off the aldehyde as it is formed by the oxidation of an alcohol



Using an excess of oxidising agent, on the other hand, and heating the reaction under reflux to prevent any escape of the aldehyde before distillation, allows the alcohol to be oxidised all the way to the carboxylic acid.

This oxidation reaction can be used to distinguish between primary, secondary and tertiary alcohols (see Table 16.3).

**Table 16.3** The use of potassium dichromate(VI) and sulfuric acid to distinguish between primary, secondary and tertiary alcohols

Type of alcohol		Observation on warming with reagent	Effect of distillate on universal Indicator	
R₃C—OH	(tertiary)	stays orange	neutral (stays green)  – only water is produced	
R₂CH—OH	(secondary)	turns green	neutral (stays green) – ketone is produced	
RCH₂—OH	(primary)	turns green	acidic (goes red)  – carboxylic acid is produced	

#### 5 The tri-iodomethane (iodoform) reaction

Alcohols that contain the group CH<sub>3</sub>CH(OH)—, that is, those that have a methyl group and a hydrogen atom on the same carbon atom that bears the OH group, can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound CH<sub>3</sub>C(O)—. This can then undergo the tri-iodomethane reaction:

$$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}_3 \xrightarrow{\text{I}_2+\text{OH}^-(\text{aq})} \\ \text{CH}_3\text{CH}_2-\text{C} \xrightarrow{\text{CH}_3} & \text{CH}_3\text{CH}_2-\text{C} \xrightarrow{\text{O}} \\ \text{CH}_3 & \text{CH}_3\text{CH}_2-\text{C} \xrightarrow{\text{O}} \end{array}$$



Figure 16.7 The tri-iodomethane reaction

The result is shown in Figure 16.7.

Except for ethanol, all the alcohols that undergo this reaction are secondary alcohols, with the OH group on the second carbon atom of the chain, that is, they are alkan-2-ols. The exception, ethanol, is the only primary alcohol to give the **pale yellow precipitate** of tri-iodomethane (iodoform) with alkaline aqueous iodine:

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{I_2 + \text{OH}^-(\text{aq})} \left[ \text{CH}_3\text{CHO} \right] \longrightarrow \text{CHI}_3(s) + \text{HCO}_2^-(\text{aq})$$

The tri-iodomethane (iodoform) reaction is thus a very specific test for the CH<sub>3</sub>CH(OH)— group (or the CH<sub>3</sub>C=O group).

#### Worked example

Which of these alcohols will undergo the iodoform reaction?

$$\rightarrow$$
 OH  $\rightarrow$  OH  $\rightarrow$  OH  $\rightarrow$  OH  $\rightarrow$  OH

#### Answer

Only alcohols  $\bf A$  and  $\bf D$  contain the grouping  $CH_3CH(OH)$ —, so these are the only two to give iodoform.  $\bf B$  is a tertiary alcohol, whilst  $\bf C$  is a primary alcohol.

#### Now try this

P, Q and R are three isomeric alcohols with the formula C<sub>5</sub>H<sub>11</sub>OH. All are oxidised by potassium dichromate(VI) and aqueous sulfuric acid, but only P gives an acidic distillate. When treated with alkaline aqueous iodine, Q gives a pale yellow precipitate, but P and R do not react. What are the structures of P, Q and R?

# 16.4 Preparing alcohols

As we would expect from their central position in organic synthesis, alcohols can be prepared by a variety of different methods.

# 1 From halogenoalkanes, by nucleophilic substitution

See section 15.3 for details of this reaction.

#### 2 From alkenes, by hydration

See section 14.3 for details. This is the preferred method of making ethanol industrially:

$$CH_2 = CH_2 + H_2O \xrightarrow{pass \text{ vapours over a catalyst of}} CH_3CH_2OH$$

$$\xrightarrow{\text{H}_3PO_4 \text{ at } 300^{\circ}\text{C and } 70 \text{ atm}} CH_3CH_2OH$$

The hydration can also be carried out in the laboratory by absorbing the alkene in concentrated sulfuric acid, and then diluting with water:

$$CH_2$$
= $CH_2 + H_2SO_4 \rightarrow CH_3CH_2$ - $OSO_3H$   
 $CH_3CH_2$ - $OSO_3H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$ 

#### 3 From aldehydes or ketones, by reduction

See section 17.3 for details. There are three common methods of reducing carbonyl compounds.

By hydrogen on a nickel catalyst:

$$CH_3CH_2CHO \xrightarrow{H_2+Ni} CH_3CH_2CH_2OH$$

• By sodium tetrahydridoborate(III) (sodium borohydride) in alkaline methanol:

$$CH_3CH_2COCH_3 \xrightarrow[\text{in methanol}]{NaBH_4 + OH} CH_3CH_2CH(OH)CH_3$$

By lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether:

Lithium tetrahydridoaluminate(III) is a dangerous reagent, producing heat and hydrogen gas (which usually catches fire) with any water, and ether is a hazardous solvent being very volatile and flammable. Hence this method is usually avoided.

#### 4 Preparing ethanol by fermentation

In many parts of the world, the fermentation of sugar or starch is only used to produce flavoured aqueous solutions of ethanol for drinks. But in some countries, for example Brazil, where petroleum is scarce and expensive, ethanol produced by fermentation is used as a fuel for vehicles. The ethanol can be used either alone or as a 25% mixture with petrol. This could become increasingly important for the rest of the world, once oil reserves become depleted.

Yeasts are micro-organisms of the genus *Saccharomyces*. They contain enzymes that not only break glucose down into ethanol and carbon dioxide, but also break down starch or sucrose (from cane or beet sugar) into glucose. They can therefore convert a variety of raw materials into ethanol:

$$\begin{array}{c} (C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{yeast}} nC_6H_{12}O_6 \\ \text{starch} & \text{glucose} \end{array}$$
 
$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{sucrose} & \text{glucose} & \text{fructose} \end{array}$$
 
$$\begin{array}{c} C_6H_{12}O_6 \xrightarrow{} C_6H_{12}O_6 \\ \text{fructose} & \text{glucose} \end{array}$$

and finally:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$
  
glucose ethanol carbon dioxide

The conditions required for successful fermentation are:

- yeast
- water
- yeast nutrients (ammonium phosphate is often used)
- warmth (a temperature of 30 °C is ideal)
- absence of air (with oxygen present, the ethanol can be partially oxidised to ethanoic acid, or completely oxidised to carbon dioxide).

The reaction is carried out in aqueous solution. Assuming enough glucose is present, it stops when the ethanol concentration reaches about 15%. Above this concentration, the yeast cells become dehydrated, and the yeast dies. After filtering off the dead yeast cells, the solution is fractionally distilled. The distillate consists of 95% ethanol and 5% water. If required, the remaining 5% water can be removed chemically, by adding either quicklime (calcium oxide):

$$CaO + H_2O \rightarrow Ca(OH)_2$$

or metallic magnesium:

$$Mg + 2H_2O \rightarrow Mg(OH)_2(s) + H_2(g)$$

Figure 16.8 a An electron micrograph of yeast cells. b Ethanol can be used on its own or as an additive to petrol to power vehicles. c Wine production







For most chemical and industrial purposes, however, 95% ethanol is perfectly acceptable.

Apart from the economic advantage of this method of producing alcohol (and hence fuel), the use of ethanol as a fuel has an environmental advantage. As was mentioned in section 13.4, fermentation-ethanol is a renewable fuel. It returns to the atmosphere exactly the same number of molecules of  ${\rm CO_2}$  as were used in its production by photosynthesis and fermentation:

$$6CO_2 + 6H_2O \xrightarrow{photosynthesis} C_6H_{12}O_6 + 6O_2$$
 (1)

$$C_6H_{12}O_6 \xrightarrow{\text{fermentation}} 2C_2H_5OH + 2CO_2$$
 (2)

$$2C_2H_5OH + 6O_2 \xrightarrow{\text{combustion}} 6H_2O + 4CO_2$$
 (3)

The carbon dioxide balance is therefore maintained. Indeed, if we add together the three equations (1), (2) and (3) we find no net change in *any* substance. We have obtained the energy we require entirely from the Sun, indirectly through the intermediates glucose and ethanol.

#### Summary

- Alcohols can be prepared from halogenoalkanes, alkenes and carbonyl compounds.
- An important source of ethanol is the fermentation of starch or sucrose by yeast.
- Alcohols are important intermediates in organic synthesis and are useful solvents.
- All alcohols burn to give carbon dioxide and water. The lower members are used as additives in petrol.
- Alcohols can react generally in three different ways: by breaking the O—H bond, by breaking the C—O bond, and by breaking the C—H bond next to the —OH group.
- Two good tests for the —OH group are the effervescence of HCl when reacted with PCl<sub>5</sub>, or the effervescence of H<sub>2</sub> when reacted with sodium metal.
- Primary, secondary and tertiary alcohols can be distinguished either by their different oxidation products with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub> or by using the Lucas reagent (concentrated HCl and ZnCl<sub>2</sub>).
- The iodoform reaction is a test for the presence of the groups CH<sub>3</sub>CO— or CH<sub>3</sub>CH(OH)— in a molecule. The products are iodoform and a sodium carboxylate with one fewer carbon atoms than the original alcohol or ketone.

#### Key reactions you should know

(R, R' = primary, secondary or tertiary alkyl unless otherwise stated.)

Combustion:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Redox:

$$R - OH + Na \rightarrow R - O^{-}Na^{+} + \frac{1}{2}H_{2}$$

Esterification:

R—OH + 
$$HO_2$$
CR′  $\xrightarrow{\text{heat with conc. } H_2SO_4}$  R—OCOR′ +  $H_2O$ 

Nucleophilic substitutions:

$$R$$
—OH + HCl(conc.)  $\rightarrow$  R—CI + H<sub>2</sub>O (best with R = tertiary alkyl)

$$R - OH + HBr \xrightarrow{\qquad \qquad heat \ with \ NaBr \ + \ H_2SO_4/H_2O} R - Br + H_2O$$

Eliminations:

$$R-CH_2-CH_2OH \xrightarrow{Al_2O_3 \text{ at } 350^{\circ}C} R-CH=CH_2+H_2CH_2$$

$$R-CH_2-CH_2OH \xrightarrow{H_2SO_4 \text{ at } 180^{\circ}C} R-CH=CH_2 + H_2O$$

Oxidations:

RCH<sub>2</sub>OH 
$$\xrightarrow{\text{heat with Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4(\text{aq})}} \text{R}\text{--CH}\text{--O} \rightarrow \text{RCO}_2\text{H}$$

$$\xrightarrow{\text{heat with Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4(\text{aq})}} \text{R}_2\text{C}\text{--O}$$

$$\begin{array}{c} \text{heat with Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4\text{(aq)} \\ \hline \\ \text{R}_3\text{COH} & \longrightarrow \text{no reaction} \end{array}$$

# Examination practice questions

Please see the data section of the CD for any  $A_r$  values you may need.

1 The structural formulae of six different compounds, A – F, are given below. Each compound contains four carbon atoms in its molecule.

- a i What is the empirical formula of compound E?
  - ii Draw the skeletal formula of compound D.
  - iii Structural formulae do not show all of the isomers that may exist for a given molecular formula. Which two compounds each show different types of isomerism and what type of isomerism does each compound show? Identify each compound by its letter. [4]
- b Compound D may be converted into compound C.
  - i What type of reaction is this?
  - ii What reagent would you use for this reaction?

- iii What is formed when compound E undergoes the same reaction using an excess of the same reagent? [3]
- Compound A may be converted into compound B in a two-stage reaction.

$$\begin{array}{c} \text{stage I} & \text{stage II} \\ \text{CH}_3\text{CH} = \text{CHCH}_3 \xrightarrow{} \text{intermediate} \xrightarrow{} \text{CH}_3\text{CH}_2\text{COCH}_3 \end{array}$$

- i What is the structural formula of the intermediate compound formed in this sequence?
- ii Outline how stage I may be carried out to give this intermediate compound.
- iii What reagent would be used for stage II? [4]
- d Compounds **D** and **F** are isomers. What type of isomerism do they show? [1]

  [Cambridge International AS & A Level Chemistry 9701,
  Paper 21 Q4 November 2009]

2 The alcohols are an example of an homologous series. The table shows the boiling points for the first four members of straight-chain alcohols.

Alcohol	Structural formula	Boiling point/°C	
methanol	CH₃OH	65	
ethanol	CH₃CH₂OH	78	
propan-1-ol	CH₃CH₂CH₂OH	97	
butan-1-ol CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH		118	

- a i What is the general formula of a member of the alcohol homologous series?[1]
  - ii Deduce the molecular formula of the alcohol that has 13 carbon atoms per molecule. [1]
- b Alcohols contain the hydroxyl functional group.
  What is meant by the term functional group? [2]
- c i At room temperature and pressure, the first four members of the alcohol homologous series are liquids whereas the first four members of the alkanes homologous series are gases. Explain this difference.[3]
  - ii Methylpropan-1-ol and butan-1-ol are structural isomers. Methylpropan-1-ol has a lower boiling point than butan-1-ol. Suggest why.

- d Alcohols, such as methanol, can be used as fuels.
  - i Write equations for the complete and incomplete combustion of methanol. [2]
  - ii Suggest what conditions might lead to incomplete combustion of methanol. [1]
  - iii In addition to its use as a fuel, methanol can be used as a solvent and as a petrol additive to improve combustion.
    - State another large-scale use of methanol.
- e Butan-1-ol can be oxidised by heating under reflux with excess acidified potassium dichromate(VI).
  Write an equation for the reaction that takes place.
  Use [O] to represent the oxidising agent. [2]
- f Butan-1-ol is one of the structural isomers of  $C_4H_{10}O$ .
  - i Write the name and draw the structure of the structural isomer of C<sub>4</sub>H<sub>10</sub>O that is a tertiary alcohol.[2]
  - ii Draw the structure of the structural isomer of C<sub>4</sub>H<sub>10</sub>O that can be oxidised to form butanone. [1]

[OCR Chemistry A Unit F322 Q2 May 2011]

[1]