Formulae

It is important to understand and know when to use the different ways of representing organic molecules. Read the examples carefully so that you are in no doubt.
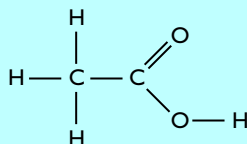
Molecular formula

A molecular formula summarises the numbers and types of atom present in a molecule. The functional group is shown separately from the hydrocarbon chain — for example, C_2H_5OH rather than C_2H_6O.

Structural formula

A structural formula requires the minimum detail to provide an unambiguous structure for a compound. For example, $CH_3CH_2CH_2OH$ is acceptable for propan-1-ol whereas C_3H_7OH is not.

Displayed formula

A displayed formula shows the correct positioning of the atoms and the bonds between them. For example ethanoic acid, which has the structural formula CH_3CO_2H, has the displayed formula:
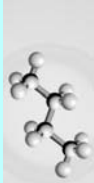

You may be asked for 'partially displayed formulae'. This means that you have to show the positions of atoms and the bonds between them at the site of a reaction.

Skeletal formula

This is a simplified representation of an organic molecule that concentrates on the carbon 'backbone' of a molecule, together with any functional groups. Bonds to hydrogen atoms are *not* normally shown, unless they form part of a functional group. The skeletal formula for butan-2-ol is shown below:
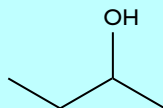

For more complex structures, where the three-dimensional structure of the molecule may be important, a 'partial-skeletal' formula may be used. This shows the geometry of key bonds to hydrogen (and other) atoms in the molecule, as shown below:
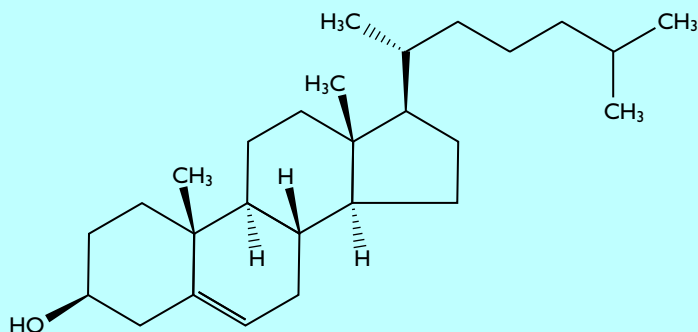
Three-dimensional structures

There are times when you need to be able to show the three-dimensional structures of relatively simple molecules, — for example, showing a pair of optical isomers. The convention of using a solid wedge to represent a bond coming 'out of the paper' and a dashed line for one going 'behind the paper' is used, as shown below:

Mirror plane
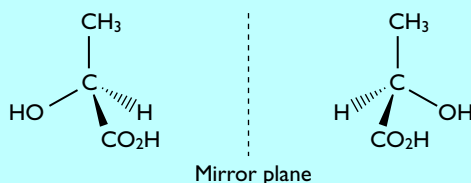
Try this yourself

(30) What is the name of the compound shown in the diagram immediately above?

Names and functional groups

It is important that you know:
- how to name hydrocarbon chains
- how to name the functional groups in organic chemistry
- how to indicate the positions of functional groups in the molecule

There are some simple rules that will help you.

The hydrocarbon chain

The key thing to remember is that the prefix indicates the number of carbon atoms present in the main chain (Table 13.1).
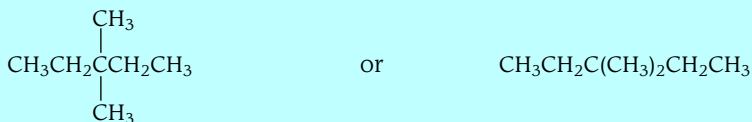
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Table 13.1

Number of carbon atoms	Prefix used
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-

Hydrocarbon molecules do not have only straight chains, they can be branched. For a branched molecule, look at the number of carbon atoms in the branch and count the number of the carbon to which the branch is joined (remember to count from the end that gives the lower number). Some examples are shown below. Remember to use the *longest continuous* carbon chain as the basic hydrocarbon.

So, $CH_3CH_2CH_2CH_2CH_2CH_3$ is hexane.

$CH_3CH_2CHCH_2CH_2CH_3$ or $CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_3$
       |
       CH_2CH_3
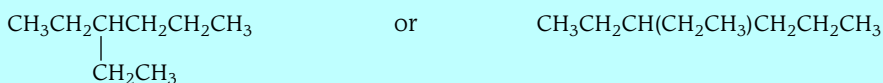
are both 3-ethylhexane (an ethyl group on carbon 3)

      CH_3
      |
$CH_3CH_2CCH_2CH_3$ or $CH_3CH_2C(CH_3)_2CH_2CH_3$
      |
      CH_3

are both 3,3-dimethylpentane (two methyl groups on carbon 3).

Alkanes
Alkanes are a family of hydrocarbons that contain only C—C single bonds and C—H bonds. Alkanes are relatively unreactive, except to combustion and they form the major fuels that we use. All of the examples given above are alkanes.

Alkenes
Alkenes are a family of hydrocarbons that have a reactive functional group, the C=C double bond. The double bond makes alkenes more reactive and they are important organic compounds.

In alkenes, it is the position of the C=C double bond that is indicated. So, $CH_3CH_2CH=CHCH_2CH_3$ is called hex-3-ene and $(CH_3)_2C=CHCH_2CH_3$ is called 2-methylpent-2-ene (the double bond is in the second possible position and there is a methyl group branching from carbon atom 2).

Arenes
Arenes are a family of hydrocarbons that contain a benzene ring made up of six carbons.

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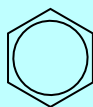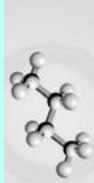
Benzene

In a benzene ring the carbon atoms are numbered clockwise from the uppermost atom. You only need to use this numbering system if there is more than one group attached to the ring.

Tip Arenes are important for the A2 examination. At AS you need to be able to recognise the benzene ring, even though you do not need to know anything about benzene or its compounds.

Other functional groups

Some functional groups are shown in Table 13.2.

Table 13.2

Name of compound	Formula of group
Halogenoalkane/arene	–Hal
Alcohol/phenol	–OH
Aldehyde	–CHO
Ketone	–C=O
Carboxylic acid	$-CO_2H$
Ester	$-CO_2R$ (where R is a hydrocarbon group)
Acyl chloride	–COC*l*
Amine	$-NH_2$
Nitrile	–CN
Amide	$-CONH_2$

Naming compounds is not too difficult. Some examples are shown in Table 13.3.

Table 13.3

Formula	Name of compound
$CH_3CH_2CH_2Br$	1-bromopropane
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2CHO$	Butanal
$(CH_3)_2C=O$	Propanone
$CH_3CH_2CO_2H$	Propanoic acid
$CH_3CH_2CO_2CH_3$	Methyl propanoate
CH_3COCl	Ethanoyl chloride
$CH_3CH_2CH_2CH_2NH_2$	1-aminobutane
$CH_3CH_2CH_2CN$	Propanenitrile
CH_3CONH_2	Ethanamide

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Try this yourself

(31) Name the following compounds:
- **(a)** $CH_3CH_2CH_2CH_2Cl$
- **(b)** $CH_3CHOHCH_3$
- **(c)** $CH_3CH_2CH_2CH_2CH_2CO_2H$
- **(d)** $CH_3CH(CH_3)CH_2CH_2NH_2$

(32) Draw structural formulae for the following compounds:
- **(a)** 2-bromobutane
- **(b)** propanamide
- **(c)** methanal
- **(d)** methyl ethanoate

Organic reactions

It is important to be able to remember, and in some cases to predict, what types of reaction a compound containing a particular functional group will take part in. To do this you need to be aware of both the nature of the functional group and of the possible reactions a given reagent may permit.

Fission of bonds

Organic compounds are held together by covalent bonds, so you no longer need to worry about ionic reactions (except in a few rare cases). In organic molecules, a given bond can split in two ways. In **homolytic** fission one electron goes to each fragment:
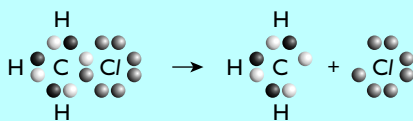
In **heterolytic** fission both electrons go to one fragment and none to the other:
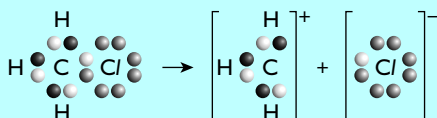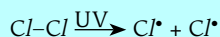

Free radical reactions

Free radicals are usually highly reactive species consisting of an atom or fragment of a molecule with an unpaired electron. In equations, it is usual to show the unpaired electron as a 'dot'. These free radicals may be formed by the action of ultraviolet light (such as in the upper atmosphere) or by the breakdown of a very unstable organic compound.

In general, free radical reactions take place in three distinct steps — initiation, propagation and termination. The reaction you will study is the reaction of methane with chlorine in the presence of ultraviolet light.
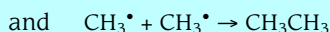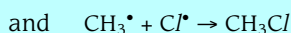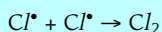
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Step 1: initiation Free radicals are formed by the breaking of a bond by homolytic fission:

$$Cl\text{–}Cl \xrightarrow{\text{UV}} Cl^\bullet + Cl^\bullet$$

Step 2: propagation The free radicals formed begin a chain reaction in which as each free radical is used another is formed:

$$H\text{–}CH_3 + Cl^\bullet \rightarrow CH_3{}^\bullet + HCl$$

and $\quad CH_3{}^\bullet + Cl\text{–}Cl \rightarrow CH_3Cl + Cl^\bullet$
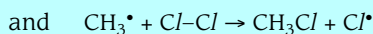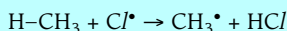
Step 3: termination These are reactions in which free radicals combine and hence end that part of the chain reaction:

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$$

and $\quad CH_3{}^\bullet + Cl^\bullet \rightarrow CH_3Cl$

and $\quad CH_3{}^\bullet + CH_3{}^\bullet \rightarrow CH_3CH_3$

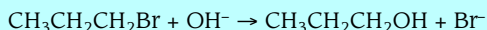## Nucleophilic and electrophilic reactions

Nucleophilic reagents 'like' positive charges and electrophilic reagents 'like' areas of electron density.

> **Tip** Here is a way to remember this — 'nucleo like nucleus, nuclei are positive; electro like electrons, which are negative'.

It follows that the reagents themselves are the opposite of what they seek.

Nucleophiles

Nucleophiles include halide ions, hydroxyl ions, cyanide ions and molecules containing lone pairs, such as water and ammonia, or even ethanol. A typical nucleophilic substitution reaction is:

$$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$$

Electrophiles

Electrophiles are electron-deficient species, generally positively charged ions such as H^+, Cl^+, Br^+, I^+, $NO_2{}^+$, $CH_3{}^+$, CH_3CO^+. An example of an electrophilic addition reaction is:

$$CH_3CH{=}CH_2 \rightarrow HBr \rightarrow CH_3CHBr\ CH_3$$
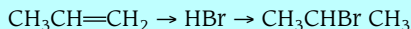
Other types of reaction

Addition

Addition refers to an increase in saturation, in other words adding a molecule to a C$=$C double bond as in the above reaction. The molecule achieves this by interacting with the π-electrons in the double bond (see the structure of ethene on page 126).

Substitution

Substitution refers to the replacement of one group in an organic molecule by another as in nucleophilic substitution on page 140. Both nucleophiles and electrophiles can take part in substitution reactions.

Elimination

An elimination reaction involves the removal of atoms from two adjacent carbon atoms to leave a double bond. It is the reverse of the electrophilic addition reaction on page 135.

Hydrolysis

This is a reaction, usually in aqueous media, between one organic molecule and water or acid or alkali which leads to the formation of at least two products. Two examples are:

$$(CH_3)_3C—Cl + 2H_2O \rightarrow (CH_3)_3C—OH + H_3O^+ + Cl^-$$

$$CH_3CO_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3OH$$
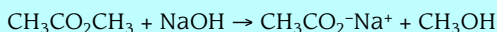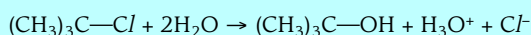
Oxidation

In general, this refers to the oxidation of a C—OH group to form a C=O group in an aldehyde, ketone or carboxylic acid. Such oxidations are often brought about by warming the organic compound with acidified potassium dichromate(VI). This can produce complicated equations, and in organic reactions it is permissible to show the oxidising agent as [O]:

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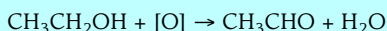
Reduction

This is the opposite of oxidation and, in general, applies to compounds containing a C=O group. Reduction may be brought about by several reducing agents including tin and dilute hydrochloric acid, sodium in ethanol and lithium aluminium hydride. In organic reduction reactions, the reducing agent is usually represented by [H], as shown in the example below:

$$CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$$
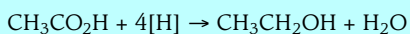
Shapes of molecules

For AS, you need to know the shapes of ethane and ethene. For A2, you also need to know the shape of benzene. Alongside this, you need to be able to work out the shapes of related molecules. The basics of this were covered in Chapter 3, so here are some reminders.

Ethane

An ethane molecule is formed by electrons in hydrogen 1s-orbitals overlapping with electrons in 2sp³-orbitals on the carbon atoms to form molecular orbitals in which
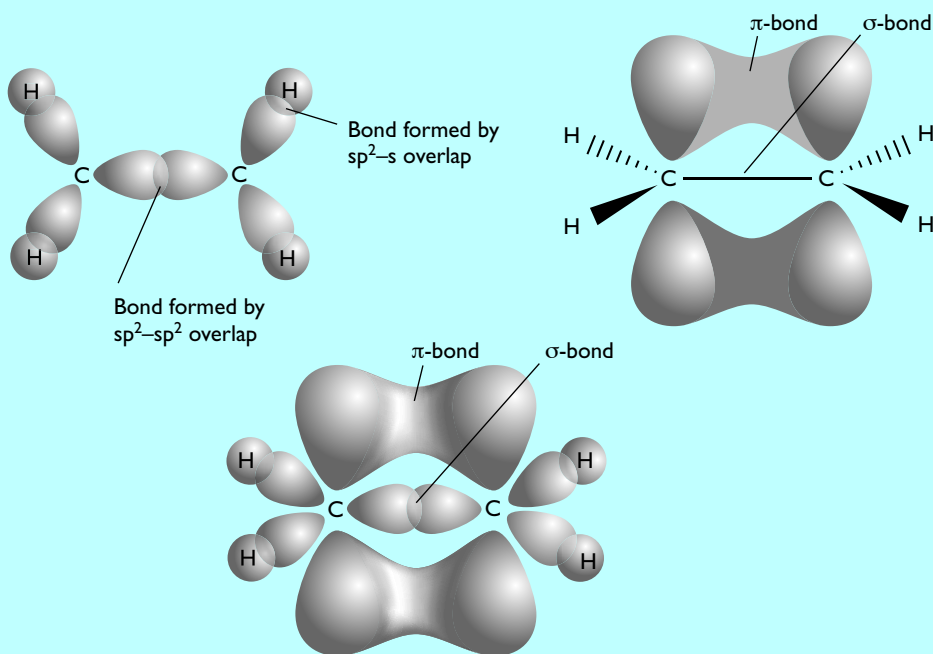
the hydrogen nuclei are embedded. A single C—C σ-bond, formed by the overlapping of one sp³-orbital from each carbon atom, joins the two ends together, but there is no restriction on rotation so the two ends of the molecule can spin relatively freely.


Hydrogen nucleus embedded in new molecular orbital

Sigma (σ) bond
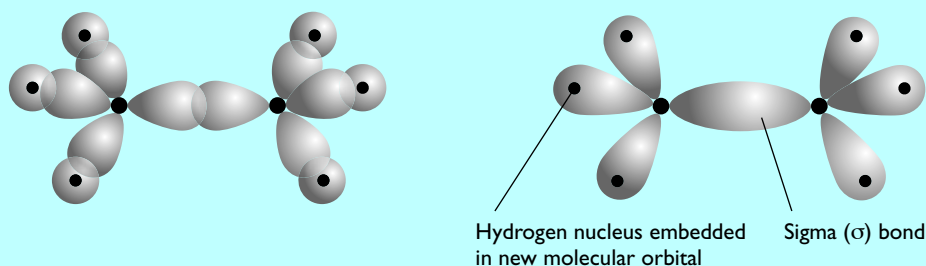
Ethene

In ethene, the carbon atoms form $2sp^2$-hybrid orbitals for three of the electrons, leaving one electron in a 2p-orbital. An ethene molecule is formed by the overlap of two sp²-orbitals on each carbon with two hydrogen 1s-orbitals, with the third sp²-orbital on each carbon atom overlapping to form a σ-bond. The p-orbitals interact to form an additional π-bond which prevents the rotation of the ends of the molecule about the σ-bond:

Bond formed by sp²–s overlap

Bond formed by sp²–sp² overlap

π-bond σ-bond

π-bond σ-bond

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Benzene

A molecule of benzene has six carbons arranged in a hexagonal ring. These carbon atoms have hybridised orbitals in the same manner as ethene. However, in benzene, only one $2sp^2$-orbital is bonded to hydrogen, with the other two sp^2-orbitals being bonded to adjacent carbons. The 2p-orbitals interact around the ring producing a π-electron 'cloud' above and below the plane of the ring.


Sigma bonds
sp^2 hybridized orbitals

6 p_z-orbitals

Delocalised π system
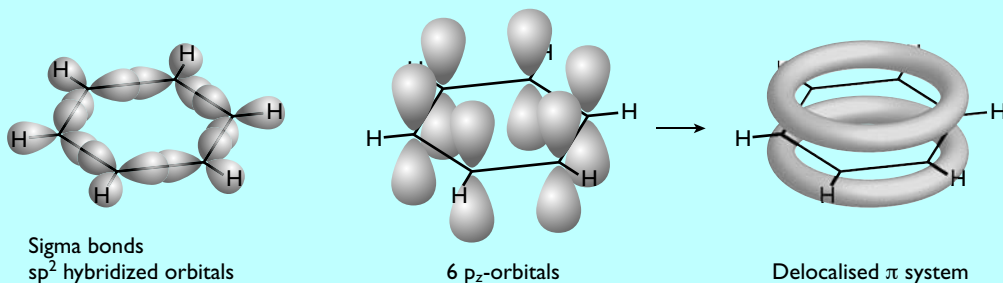
Isomerism

Isomers are compounds that have the same molecular formula (same chemical composition) but different structural formulae. You need to know about three main types of isomerism — structural, geometrical and optical.
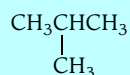
Structural isomerism

Chain isomerism

In **chain isomerism**, the isomers arise due to branching of the carbon chain. So C_4H_{10} can have both a straight chain form and a branched chain form:

$CH_3CH_2CH_2CH_3$ 　　　　　　　　　　CH_3CHCH_3
　　　　　　　　　　　　　　　　　　　　　　$|$
　　　　　　　　　　　　　　　　　　　　　CH_3
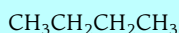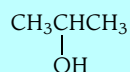
　　　　butane　　　　　　　　　　　2-methylpropane

The compounds have different names based on the system described on page 121. The branched chain is three carbons long and has a methyl group on the second carbon atom.
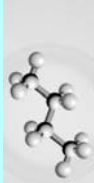
Position isomerism

In **position isomerism**, the carbon chain is fixed, but the position of substituent groups can vary. The alcohols propan-1-ol and propan-2-ol show this:

$CH_3CH_2CH_2OH$ 　　　　　　　　　　CH_3CHCH_3
　　　　　　　　　　　　　　　　　　　　　　$|$
　　　　　　　　　　　　　　　　　　　　　OH
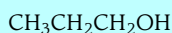
　　　Propan-1-ol　　　　　　　　　　Propan-2-ol

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Changing the position of a group can affect how easily it reacts, as well as its physical properties, such as boiling point. Propan-1-ol has a boiling point of 97 °C whereas propan-2-ol has a boiling point of 82 °C.

Functional group isomerism

In **functional group isomerism** the nature of the functional group within the molecule is different. This is important because it changes the chemical reactions that the molecule undergoes. The formula C_3H_6O can represent three molecules, each with a different functional group:
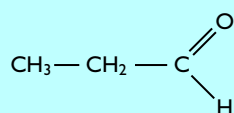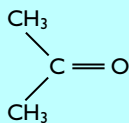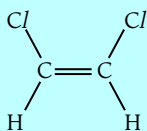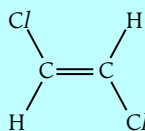

| Propanal | Propanone | 2-propen-1-ol |

Geometric or *cis-trans* isomerism

Geometric isomerism occurs where there is restricted rotation around a bond, such as in alkenes. It also needs two groups, one on each end of the double bond, such as in 1,2-dichloroethene:
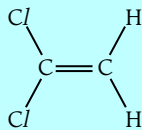

cis-1,2-dichloroethene   *trans*-1,2-dichloroethene

These two forms are different because the double bond prevents the rotation needed to make the two forms identical. Notice that there is another isomer, but this time it is a position isomer, rather than a *cis-trans* isomer.


1,1-dichloroethene

To summarise, in *cis-trans* isomerism:
- there is restricted rotation generally involving a carbon-carbon double bond
- there are two different groups on the left-hand end of the bond and two different groups on the right-hand end

Optical isomerism and chiral centres

The final type of isomerism you need to be able to recognise and explain is **optical isomerism**. This gets its name from the effect an optical isomer has on the plane

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of plane-polarised light. One isomer rotates the polarised light clockwise, and the other isomer rotates it an equal amount anti-clockwise. This occurs when there is a carbon with four different groups attached to it — this is called a **chiral** carbon. An example was shown on page 120 and another example, butan-2-ol, is shown below:

Mirror plane
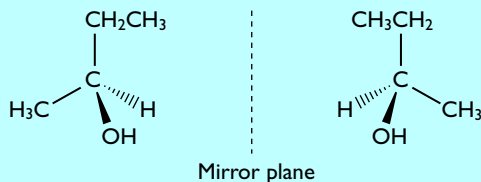
Notice that the two molecules are mirror-images, and that the central carbon atom has four different groups attached. When you draw these structures it is important to check that your diagrams make chemical 'sense'. Take the structure of 2-aminopropanoic acid for example. It is important to show the 'acid' group joined to the central carbon the right way round. (If not, you may be penalised in the exam.) Figure 13.1 shows what you need to do.
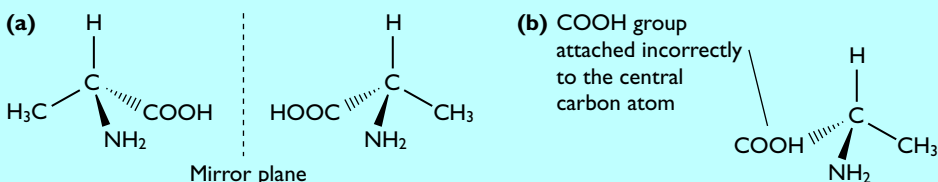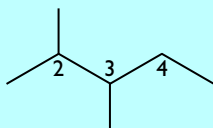

Figure 13.1(a) Optical isomers of 2-aminopropanoic acid
(b) Incorrectly drawn isomer

Identifying chiral carbon atoms can be tricky, particularly in complex or skeletal molecular structures. You have to work out whether or not a given carbon atom has two (or more) identical groups attached to it.

Look at the skeletal structure below:

It contains three non-terminal carbon atoms numbered 2, 3 and 4.

Look at each of these in turn. Carbon 2 has two bonds attached to methyl groups, carbon 4 has two bonds attached to hydrogen atoms (not shown), and carbon 3 is attached to four different groups. Therefore, carbon 3 is chiral.

You may be asked to examine a complex molecule and state the number of chiral carbon atoms (or perhaps circle them). An example of such a molecule, the synthetic form of the hormone testosterone, is shown in Figure 13.2.
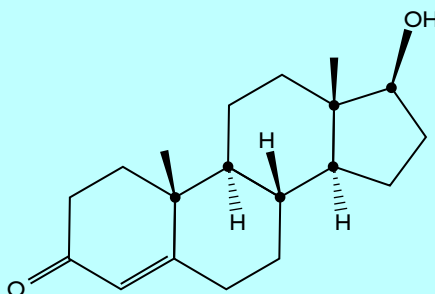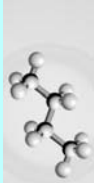
Figure 13.2 Synthetic testosterone

Can you identify the chiral carbon atoms in the structure? There are six, marked ●.

Try this yourself

(33) A compound **P** has the formula C_4H_8O.
- **(a)** Draw a straight-chain structure for **P**.
- **(b)** Does **P** have functional group isomers? If so, draw examples.
- **(c)** How many isomers in total does the straight-chain form of **P** have, incorporating any of the functional groups in Table 13.2?

(34) The compound **Q** has the formula C_4H_7Br and contains a double bond.
- **(a)** How many non-cyclic isomers exist for **Q**?
- **(b)** Draw the *cis-trans* isomers of **Q**.

14 Hydrocarbons

Apart from the section on arenes, all this chapter is needed for the AS examination. Some of the content has been covered previously or you may have studied it at IGCSE.

Alkanes

Combustion

Due to their general lack of reactivity, the single most important use of alkanes is as fuels. You may already know about the importance of crude oil, and the 'cracking' of less useful fractions to form more useful products (this is covered on the next pages).

Ethane is used as an example of an alkane, noting that it has the formula C_2H_6 and that the general formula for alkanes is C_nH_{2n+2}.

Ethane reacts differently with oxygen depending on how much oxygen is available.

Plenty of oxygen: $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Less oxygen: $\qquad$ $2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$

Restricted oxygen: $\qquad$ $2C_2H_6 + 3O_2 \rightarrow 4C + 6H_2O$

Restricting the amount of oxygen reduces the amount by which the carbon in ethane is oxidised until it cannot be oxidised at all. The midway point produces poisonous carbon monoxide, which has been known to kill people using faulty gas heaters.

Crude oil as a source of hydrocarbons

The use of oil as a major fuel is less than 150 years old and results from the revolutions in land and air transport brought about by the development of the internal combustion engine. Crude oil is often talked about as if it is a mixture with fixed composition. However, it can vary enormously in the proportions of the various hydrocarbons that make up the mix. This variation affects how much processing the oil requires to yield useful products.

Not all sources of oil have high proportions of the hydrocarbons that are most in demand. However, chemists have developed ways of converting less useful hydrocarbons into more useful ones. The main process for achieving this is 'cracking' — a large molecule hydrocarbon of limited use is broken into smaller molecule hydrocarbons that are in greater demand.

Some of the most important processes in an oil refinery are shown in Figure 14.1.
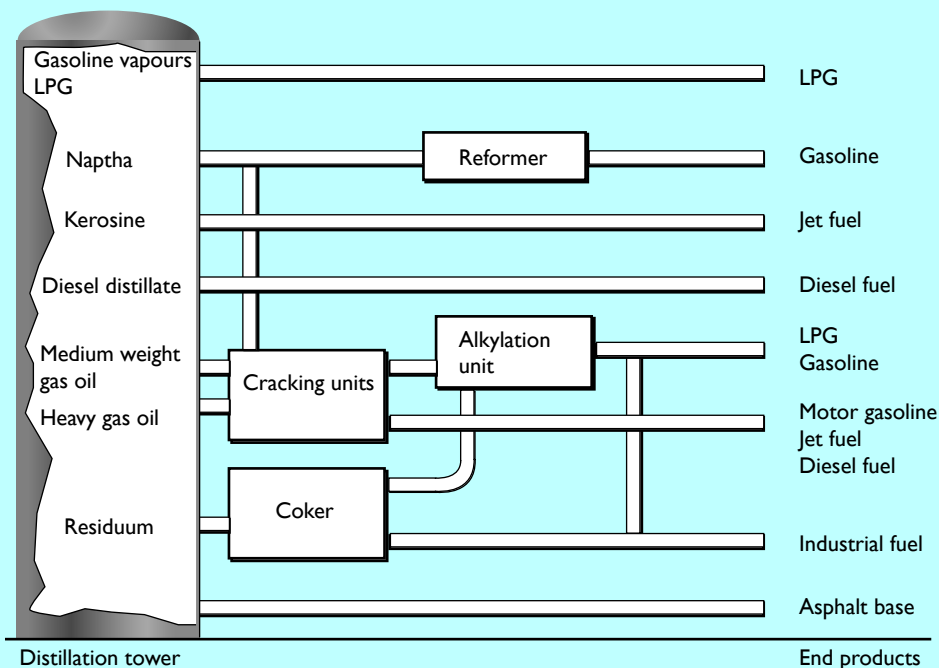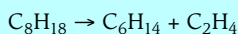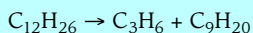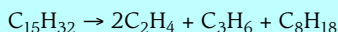

Figure 14.1 Processes in an oil refinery

The cracking process involves using either high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the 'naphtha' fraction or the 'gas oil' fraction from the fractional distillation of crude oil. Although these fractions are obtained as liquids, they have to be vaporised before cracking can occur.
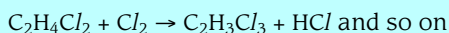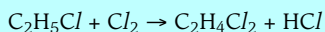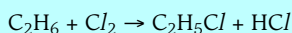
There is no unique reaction in the cracking process. In general, a large hydrocarbon molecule produces one or more smaller alkane molecules and one or more alkene molecules, for example:

$$C_{15}H_{32} \rightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

$$C_{12}H_{26} \rightarrow C_3H_6 + C_9H_{20}$$

$$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$$

The alkanes produced are usually used for motor fuel — either petrol (gasoline) or diesel — while the alkenes formed are used in the polymer industry.

Substitution reactions

Alkanes react with difficulty with both chlorine and bromine. In order to react, alkanes need energy from ultraviolet light (sunlight) and, as you might expect, chlorine reacts more easily than bromine. Taking ethane as the example, the hydrogen atoms are replaced one at a time in substitution reactions:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

$$C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$$

$$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl \text{ and so on}$$

Alkenes

Ethene is used as an example of an alkene, noting that it has the formula C_2H_4 and that the general formula for alkenes is C_nH_{2n}.

Addition reactions

Because alkenes have a double bond, it is reasonable to expect addition reactions to be particularly important.

With hydrogen

Ethene reacts with hydrogen at a temperature of about $150\,°C$ in the presence of finely-divided (powdered) nickel. The hydrogen adds across the double bond forming ethane:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$

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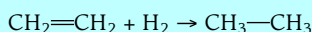
This is not a very useful reaction, but for larger alkenes — such as those found in vegetable oils — the addition of hydrogen across a double bond is more important. These oils are 'hardened', or turned into solid fats, by hydrogenation — a process that is necessary for the manufacture of margarine.

With steam

Water, in the form of steam, can be added across ethene's double bond to form ethanol. This is carried out industrially at a temperature of about $300\,^\circ C$ and a pressure of about $60\,atm$ in the presence of a phosphoric(V) acid catalyst.

For alkenes other than ethene, there is the possibility of adding the hydrogen to two different carbons. In propene, for example, the hydrogen can be added to either the end carbon or to the middle carbon, forming propan-2-ol and propan-1-ol respectively:

$$CH_3{-}CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3 \text{ or } CH_3CH_2CH_2OH$$
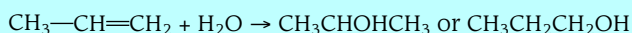
Markovnikoff's rule (worth learning) states that when a molecule of the form HX is added across a double bond, the hydrogen usually becomes attached to the carbon that is already attached to the most hydrogen atoms. This means that in the above reaction, propan-2-ol is favoured.

With hydrogen halides

If a gaseous alkene is bubbled through, or a liquid alkene is shaken with, either a concentrated aqueous solution of hydrogen bromide or hydrogen bromide dissolved in a non-polar solvent, the hydrogen bromide is added across the double bond.

The reaction is similar to the addition of water and follows Markovnikoff's rule:

$$CH_3{-}CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

With halogens

Ethene reacts with halogens by adding across the double bond. Therefore, with bromine at room temperature the reaction forms 1,2-dibromoethane:

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$
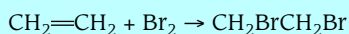
Chlorine, being more reactive, reacts faster than bromine. Iodine reacts more slowly.

The reaction above refers to ethene reacting with the pure halogen. Often, as in testing for alkenes using bromine water, a competing reaction can take place:

$$CH_2{=}CH_2 + Br_2 + H_2O \rightarrow CH_2BrCH_2OH + HBr$$
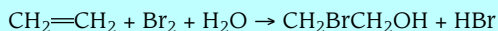
This compound is 1-bromo-2-hydroxyethane (or 2-bromethanol).

Oxidation reactions

Alkenes react with oxidising agents such as acidified manganate(VII) ions. The extent of the reaction, and hence the nature of the products, depends on the concentration of the oxidising agent and the temperature.
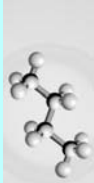
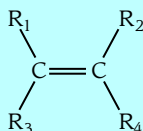### With cold, dilute, acidified manganate(VII) ions

Under these conditions ethene is oxidised to the diol 1,2-dihdroxyethane.

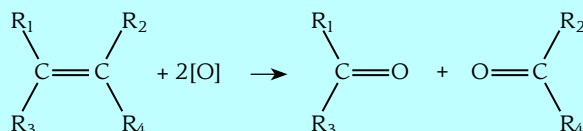$$CH_2{=}CH_2 + [O] + H_2O \rightarrow CH_2OHCH_2OH$$
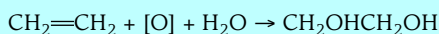
With hot, concentrated, acidified manganate(VII) ions

Acidified manganate(VII) is such a strong oxidising agent that in concentrated solution and with heat the carbon-to-carbon double bond of the alkene is ruptured. You may not think that this is a very useful reaction, but by looking at the products the position of a double bond in an unknown alkene can be determined.
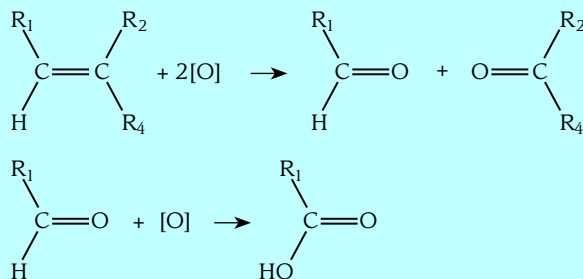
The symbol **R** is used to represent a hydrocarbon group or a hydrogen atom. So, any alkene can be represented by the following formula:
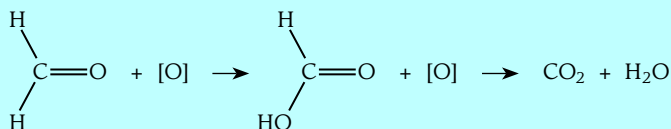
$$
\begin{array}{ccc}
R_1 & & R_2 \\
\diagdown & & \diagup \\
& C{=}C & \\
\diagup & & \diagdown \\
R_3 & & R_4
\end{array}
$$

When the acidified manganate(VII) ions oxidise the alkene, two C=O double bonds are formed:

$$
\begin{array}{ccccc}
R_1 & R_2 & & R_1 & R_2 \\
\diagdown & \diagup & & \diagdown & \diagup \\
C{=}C & +\,2[O] & \rightarrow & C{=}O \;+\; O{=}C \\
\diagup & \diagdown & & \diagup & \diagdown \\
R_3 & R_4 & & R_3 & R_4
\end{array}
$$

A compound that contains a C=O functional group is known as a **carbonyl compound**. A carbonyl compound with two hydrocarbon groups is called a **ketone**. If one of the **R** groups is hydrogen, the carbonyl compound formed is called an **aldehyde** and this can be oxidised further by acidified manganate(VII) to form a **carboxylic acid**:

$$
\begin{array}{ccccc}
R_1 & R_2 & & R_1 & R_2 \\
\diagdown & \diagup & & \diagdown & \diagup \\
C{=}C & +\,2[O] & \rightarrow & C{=}O \;+\; O{=}C \\
\diagup & \diagdown & & \diagup & \diagdown \\
H & R_4 & & H & R_4
\end{array}
$$

$$
\begin{array}{ccccc}
R_1 & & & R_1 & \\
\diagdown & & & \diagdown & \\
C{=}O & +\,[O] & \rightarrow & C{=}O \\
\diagup & & & \diagup & \\
H & & & HO &
\end{array}
$$

There is one further complication that occurs when there are no **R** groups at one end of the double bond. The carboxylic acid formed under those circumstances (methanoic acid) is itself oxidised by the acidified manganate(VII) ions to form carbon dioxide and water:

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$$\begin{array}{c} H \\ \diagdown \\ C{=\!\!=}O \\ \diagup \\ H \end{array} \; + \; [O] \; \longrightarrow \; \begin{array}{c} H \\ \diagdown \\ C{=\!\!=}O \\ \diagup \\ HO \end{array} \; + \; [O] \; \longrightarrow \; CO_2 \; + \; H_2O$$

Here are some simple rules that might help you to work out the structure of the original alkene:

- Think about each end of the double bond separately.
- If there are two hydrocarbon groups at one end of the bond, that part of the molecule will give a ketone.
- If there is one hydrocarbon group and one hydrogen atom at one end of the bond, that part of the molecule will give a carboxylic acid.
- If there are two hydrogen atoms at one end of the bond, that part of the molecule will give carbon dioxide and water.
- Combine the information to work back to the structure of the original alkene.

Polymerisation

Carbon is one of the few elements to form rings and extended chains of atoms. Alkenes can join together to form long chains, or polymers. This does not apply only to hydrocarbon alkenes but also to substituted alkenes such as chloroethene ($CH_2{=\!\!=}CHCl$) which is used to make PVC. Polymerisation is covered in Chapter 19.
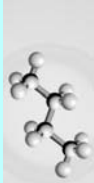
Electrophilic addition

You saw in the previous chapter that halogens behave as electrophiles, and you know that alkenes have a concentration of electrons round the double bond. For the examination, you need to understand the mechanism of electrophilic addition, with the specific example of bromine reacting with ethene. The reaction takes place in two stages.

First, as the bromine molecule approaches the ethene molecule, the π-electrons in ethene induce a dipole on the bromine molecule. A bond is formed between the carbon and the bromine forming a positively charged species called a **carbocation**:
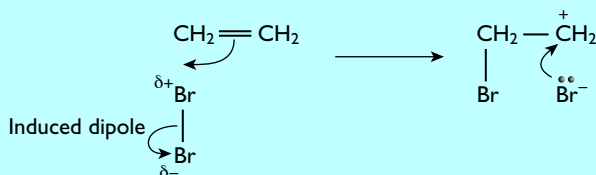
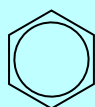Second, the carbocation is attacked rapidly by the remaining Br^- ion to form the dibromide:

135

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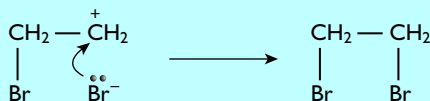
(35) The reaction between bromine and ethene only occurs so 'cleanly' in a non-aqueous solvent. Explain what other product(s) might be formed if the bromine were dissolved in water.

Arenes

You need to know about two arenes — benzene and methylbenzene:


Benzene   Methylbenzene

Although you might not think these molecules are very different, the presence of a side chain in methylbenzene means that it is able to undergo an additional set of reactions compared to benzene.
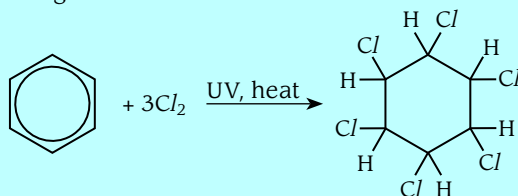
Substitution reactions

Benzene

Benzene reacts at room temperature with chlorine or bromine in the presence of a catalyst. One of the hydrogen atoms in the ring is replaced by a chlorine or bromine atom. A typical catalyst is the aluminium halide of the halogen being substituted, or iron (which reacts with the halogen to form the iron(III) halide which then acts as the catalyst):

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$
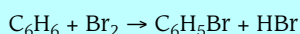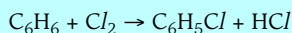
In the presence of ultraviolet light (or sunlight), but without a catalyst, benzene undergoes addition reactions with both chlorine and bromine, with six halogen atoms added to the ring:


As you might expect, the reaction is faster with chlorine than with bromine.

Methylbenzene

With methylbenzene there are two different types of substitution, depending on whether a ring hydrogen or a methyl hydrogen is substituted.

As with benzene, substitution of a ring hydrogen occurs at room temperature in the presence of an aluminium halide or iron catalyst. There is an additional complication of where the halogen atom goes in relation to the methyl group. Methyl groups direct further substitution to the 2- or 4- positions in the ring (the 1-position is that occupied by the methyl group). This reaction with either chlorine or bromine under these conditions results in the formation of a mixture of 2-halo- and 4-halomethylbenzene:
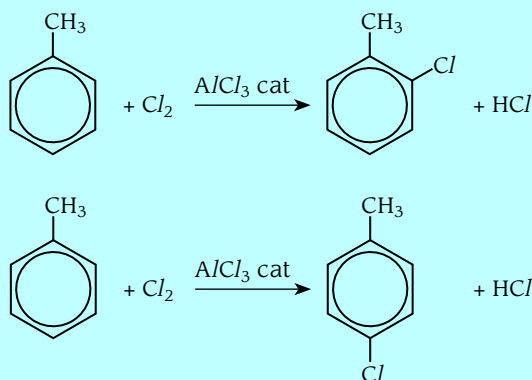
When boiling methylbenzene is reacted with chlorine or bromine in the presence of ultraviolet light, the methyl hydrogen atoms are substituted. Provided sufficient halogen is present, all three hydrogen atoms are eventually substituted:
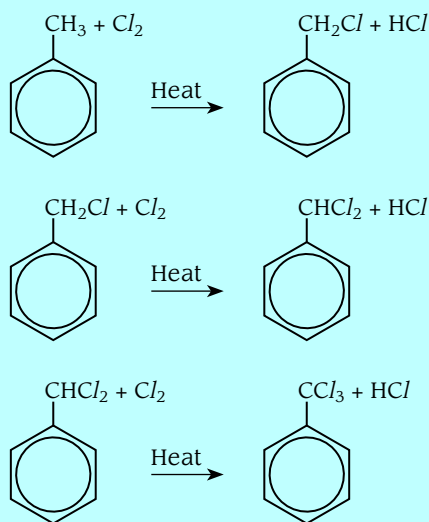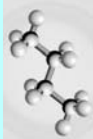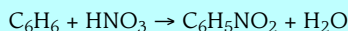
Nitration

This is the only reaction of arenes for which you need to know the mechanism.

Benzene

When benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid at a temperature lower than 50 °C, yellow nitrobenzene is gradually formed. The sulfuric acid acts as a catalyst.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

At higher temperatures, or with prolonged reaction even at 50 °C, further nitration occurs with a second nitro group being substituted into the ring. The second nitro group goes into the 3-position:
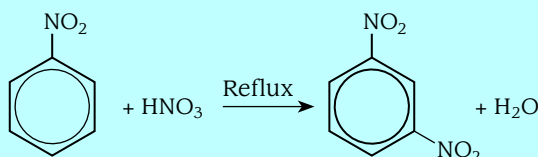

Compare this with the methyl group in methylbenzene (p.137). It *is* possible to get a further nitro group in the 5-position, but the presence of a nitro group 'deactivates' the benzene ring, making it much less likely to react.

The mechanism for the mononitration of benzene is an example of electrophilic substitution. The nitrating mixture of concentrated nitric and concentrated sulfuric acids produces the electrophile — the nitronium ion, NO_2^+:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$
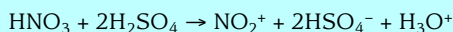
The NO_2^+ ion approaches the delocalised electrons in benzene and two of these form a bond with the positive charge now spread over the rest of the atoms in the ring:
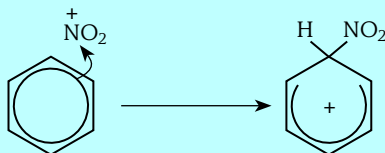

The HSO_4^- ion produced in the nitrating mixture now removes a hydrogen atom, re-forming the sulfuric acid catalyst:

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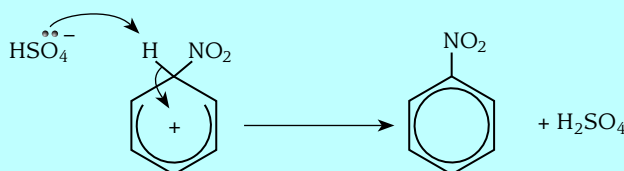
Methylbenzene

In nitration, methylbenzene reacts about 25 times faster than benzene. This means that a lower temperature (around 30 °C rather than 50 °C) has to be used to prevent more than one nitro group being substituted. Apart from that, the reaction is the same and the same nitrating mixture of concentrated sulfuric and nitric acids is used.

As with the halogens, a mixture of the 2- and 4-nitro substituted arenes is formed:
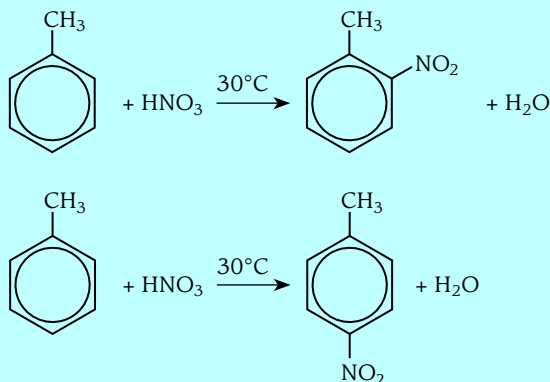
Side-chain oxidation

This applies only to methylbenzene (and other arenes with alkyl side chains). Alkyl groups in alkanes are usually fairly unreactive towards oxidising agents. However, when attached to a benzene ring they are relatively easily oxidised. Heating methylbenzene (or any alkylbenzene) with alkaline potassium manganate(VII) solution, followed by acidification with dilute sulfuric acid, gives benzoic acid:
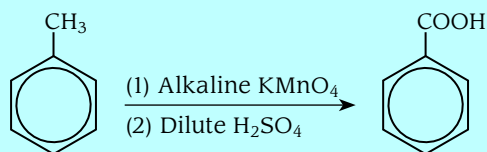
15 Halogen and hydroxy compounds

Most of this chapter, apart from the reactivity of chlorobenzene and the last section on hydroxyl compounds, is needed for the AS examination.

Halogen derivatives

Halogenoalkanes behave differently depending on which other groups are attached to the carbon that the halogen is attached to (you will see this trend with other functional groups).

- If there are only hydrogen atoms attached to the carbon, it is a **primary** (1°) halogenoalkane, for example CH_3CH_2Br.
- If there is one alkyl group attached as well as the halogen, it is a **secondary** (2°) halogenoalkane, for example $(CH_3)_2CHBr$
- If there are *no* hydrogen atoms, only alkyl groups and the halogen, it is a **tertiary** (3°) halogenoalkane, for example $(CH_3)_3CBr$

The C—Hal bond is polar due to the difference in electronegativity between the carbon atom and the halogen atom. Except when bonded to iodine, the carbon atom is relatively positive, making it susceptible to nucleophilic attack by lone pairs of electrons or negative ions.
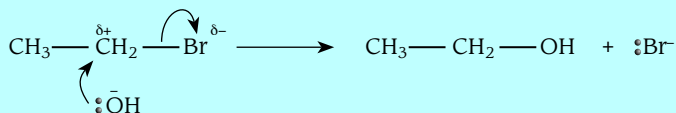
Nucleophilic substitution

Halogenoalkanes undergo a number of nucleophilic substitution reactions. The syllabus requires you to know about three of these using bromoethane as a starting compound. However, you should be able to recognise this type of reaction with different halogenoalkanes and different nucleophilic reagents.

Hydrolysis

When bromoethane, a primary halogenoalkane, is heated under reflux with sodium hydroxide in a solvent of aqueous ethanol, the bromine is substituted by the hydroxyl group and ethanol is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$
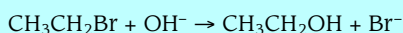
You also need to know the mechanism for this reaction, which can be represented in two ways. The first way is as follows:

$$CH_3 \!-\! \overset{\delta+}{CH_2} \!-\! \overset{\delta-}{Br} \quad \longrightarrow \quad CH_3 \!-\! CH_2 \!-\! OH \ + \ \ddot{:}Br^-$$

$$\ddot{:}\bar{O}H$$

The reaction is described as S_N2, because there are two reactants in the rate-determining or slow step.

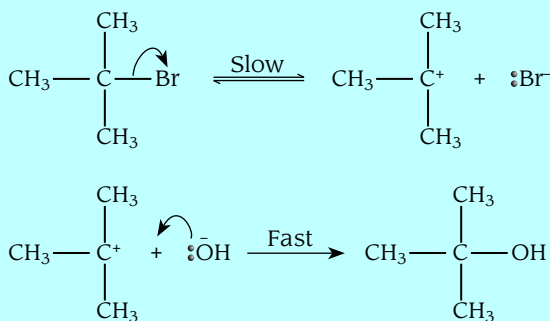> **Tip** Think of S_N2 as 'Substitution Nucleophilic, 2 reactants'.

The other way of representing this reaction is to show it as a two-stage process:

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Transition state
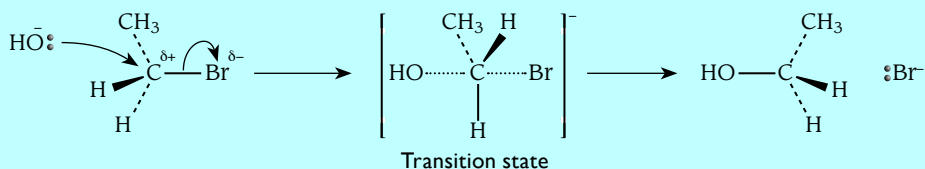
With a tertiary halogenoalkane, the mechanism is still nucleophilic substitution:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$
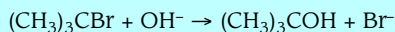
However, in this mechanism, only *one* molecule is present in the rate-determining or slow step. This is an S_N1 mechanism, although there are still two stages:

**Tip** Think of S_N1 as 'Substitution Nucleophilic, 1 reactant'.

For a secondary halogenoalkane, the mechanism is a combination of S_N1 and S_N2.

There is another reaction that can take place when halogenoalkanes react with hydroxide ions. This is covered on page 142.

Formation of nitriles

When a halogenoalkane is heated under reflux with cyanide ions dissolved in ethanol, the cyanide ion is substituted for the halogen and a nitrile is formed:

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$
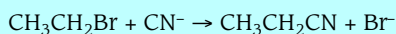
This is an important reaction because a carbon atom has been added to the carbon chain and the nitrile group can be reacted further.

Secondary and tertiary halogenoalkanes react in a similar way, but the mechanism may be different.

Formation of primary amines

When a halogenoalkane is heated with ammonia, a reflux process cannot be used because the ammonia would escape as gas. This reaction has to be carried out in a sealed tube. The reaction takes place in two steps:

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-$$

$$CH_3CH_2NH_3^+Br^- + NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+Br^-$$
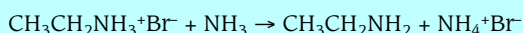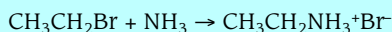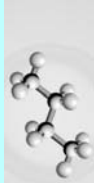
However, in a sealed tube the reaction does not stop with the formation of a primary amine. It continues replacing successive hydrogens on the nitrogen to give secondary and tertiary amines, and finally a quaternary ammonium salt. Note that these reactions are *not* needed for A-level.

Elimination of hydrogen bromide

Under similar conditions to those needed for nucleophilic substitution, it is possible to get an elimination reaction to take place. If, instead of aqueous ethanol, a concentrated hydroxide solution in pure ethanol is used, HBr is eliminated and a double bond is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH{=}CH_2 + H_2O + Br^-$$
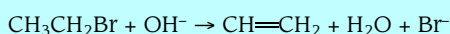
It is important to remember that different halogenoalkanes favour one type of reaction over the other (Table 15.1).

Table 15.1

Halogenoalkane	Reaction favoured
Primary	Mainly substitution
Secondary	Both
Tertiary	Mainly elimination

For a given halogenoalkane, to favour **substitution** use:
- lower temperatures
- more dilute solutions of sodium or potassium hydroxide
- more water in the solvent mixture

To favour **elimination** use:
- higher temperatures
- a concentrated solution of sodium or potassium hydroxide
- pure ethanol as the solvent

Different types of halogenoalkane

So far we have used bromoethane as the example of a halogenoalkane and for most purposes that is fine. However, we must not forget that the different halogens have an effect on the halogenoalkanes they form, not least because of the relative strengths of the C—Hal bond (Table 15.2).

Table 15.2

Bond	Bond energy/kJ mol^{-1}
C—F	467
C—C*l*	338
C—Br	276
C—I	238

For a halogenoalkane to react, the C—Hal bond has to be broken. From Table 15.2 you can see that this is much more difficult for fluoroalkanes than for the other members of the group.

A number of halogenoalkanes have important uses and in looking at these we need to bear this factor in mind.

Uses

The chemical inertness of chlorofluorocarbons (CFCs) has meant that until recently they were used as propellants in aerosols, as refrigerant gases in refrigerators, as 'blowing agents' for making plastic foams (such as expanded polystyrene) and as solvents. There has been considerable recent evidence of their harmful effects on the atmosphere, which has resulted in a large decrease in their use.

CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, ultraviolet light causes carbon-to-chlorine bonds to break forming chlorine free radicals. It is these free radicals that destroy ozone.

It has also been shown that CFCs can cause global warming. One molecule of CCl_3F, for example, has a global warming potential about 5000 times greater than a molecule of carbon dioxide. Fortunately, there is much less of this compound than carbon dioxide in the atmosphere.

The halogen-containing plastics PVC (poly(chloroethene)) and PTFE (poly(tetrafluoro-ethene)) are commercially important. The plastics themselves are not halogenoal-kanes, but they are made from halogenoalkenes.

As well as these major uses, halogenoalkanes are used as flame retardants and as anaesthetics. These uses once again rely on the relative inertness of halogenoalkanes.
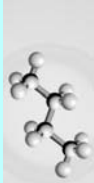
Chlorobenzene is a halogenoarene:
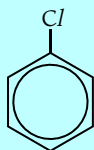
It is much less reactive towards nucleophilic substitution than the halogenoalkanes. The C—Cl bond in the molecule is stronger than you might expect. This is because one of the lone pairs of electrons on the chlorine atom is delocalised with the ring electrons on benzene:

Overlap between lone pair and the ring electrons

Lone pair now delocalised to some extent with the ring electrons

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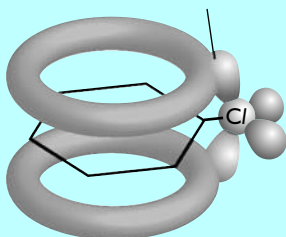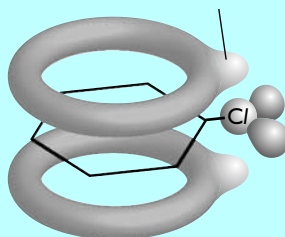
Hydroxy compounds

The first part of this section dealing with alcohols is needed for the AS examination. The second part, dealing with the iodoform reaction, phenol and the relative acidities of water, phenol and ethanol is needed for the A2 examination.
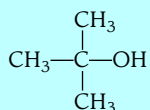
Different types of alcohol

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

Ethanol, CH_3CH_2OH, is a primary alcohol.

Propan-2-ol, $CH_3CHOHCH_3$, is a secondary alcohol.

2-methylpropan-2-ol is a tertiary alcohol:

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$
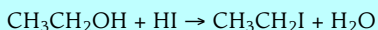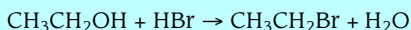
Reactions of alcohols

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:

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
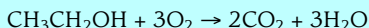
Substitution to form halogenoalkanes

Halogenoalkanes can be hydrolysed to give alcohols, and alcohols can be converted into halogenoalkanes, but by different reagents.
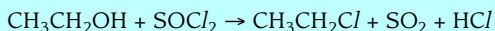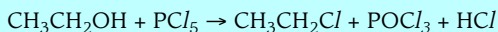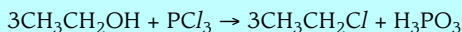
One way of carrying out the substitution is to use the appropriate hydrogen halide. This method works for the bromo- and iodoalkanes if the hydrogen halide is generated in the reaction flask. Sodium bromide with concentrated sulfuric acid can be used for the bromoalkane, but sodium iodide and concentrated phosphoric(V) acid have to be used for the iodoalkane because sulfuric acid would oxidise any HI formed. The equations for the formation of bromoethane and iodoethane are as follows:

$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$

The following method only works with tertiary alcohols, forming the tertiary chloroalkane:

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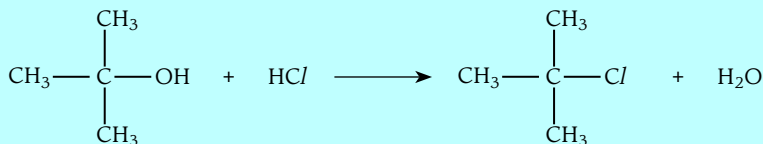
For other chloroalkanes we have to use phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, or thionyl chloride, $SOCl_2$:

$$3CH_3CH_2OH + PCl_3 \rightarrow 3CH_3CH_2Cl + H_3PO_3$$

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

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

Reaction with sodium

When a small piece of sodium is dropped into ethanol it dissolves, producing bubbles of hydrogen gas. It leaves a colourless solution which, if evaporated to dryness, produces a white solid. This white solid is sodium ethoxide, $CH_3CH_2O^-Na^+$:

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2O^-Na^+ + H_2$$
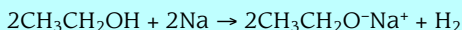
This reaction is sometimes used to dispose of small amounts of old sodium because it is much less violent than reacting sodium with water. It can also be used as a test for an alcohol. The ethoxide ion (like the hydroxide ion) is a strong base and a good nucleophile.
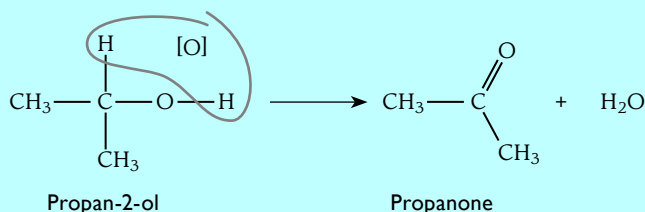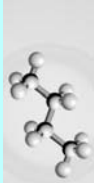
Oxidation reactions

In the presence of an oxidising agent such as acidified dichromate(VI) solution, whether or not an alcohol is oxidised depends on its structure. 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. If this is not removed from the reaction vessel it is further oxidised to a carboxylic acid. The mixture turns from orange to blue-green:
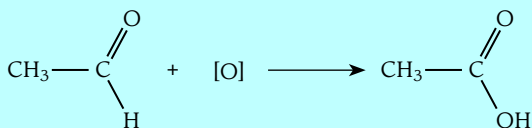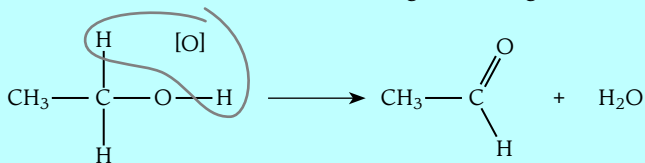

- On refluxing a secondary alcohol with acidified dichromate(VI), a ketone is formed, which is not oxidised further. Again the mixture turns from orange to blue-green:

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Propan-2-ol → Propanone

- With a tertiary alcohol, there are no hydrogen atoms on the carbon atoms that can be oxidised, so there is no reaction.

Tertiary alcohol

There is no hydrogen attached to this carbon for the oxygen to remove.
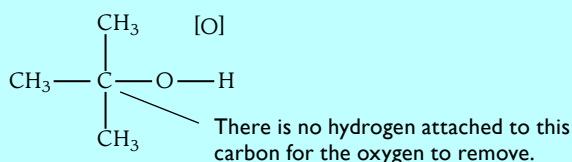
Provided that an aldehyde and a ketone can be distinguished between, these oxidation reactions can be used to detect primary, secondary or tertiary alcohols. There are relatively simple tests for aldehydes that use Fehling's solution or Tollens' reagent (see Chapter 16).

Dehydration
Strong acids such as phosphoric(V) and sulfuric can be used to dehydrate alcohols to form alkenes:
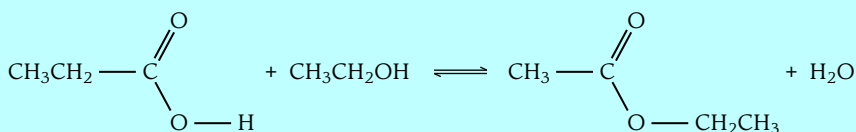
$$CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O$$
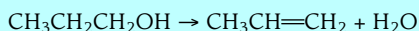
Warming ethanol and passing the vapour over heated aluminium oxide achieves the same reaction:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$$
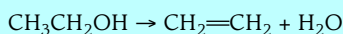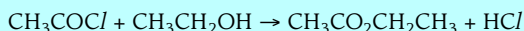
Forming esters
If an alcohol is warmed with an organic acid in the presence of H^+ ions, an ester is formed with the elimination of water:

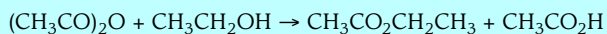This is an equilibrium reaction and it is often quite slow.

The reaction can be speeded up by using another compound containing the $RC{=}O$ group. Suitable compounds include acyl chlorides or acid anhydrides (see Chapter 17).

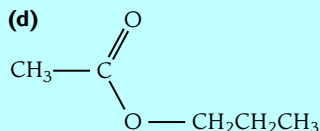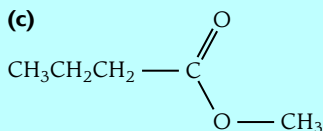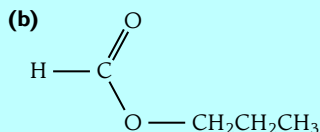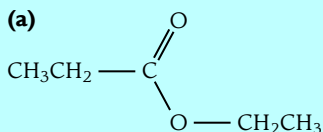With ethanoyl chloride and ethanol, the following reaction occurs:

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + HCl$$

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With ethanoic anhydride and ethanol, this reaction takes place:

$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + CH_3CO_2H$

In 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!).

Try this yourself

(36) Name the four esters whose structures are shown below:

(a)

$CH_3CH_2 - C$ with $=O$ and $O - CH_2CH_3$

(b)

$H - C$ with $=O$ and $O - CH_2CH_2CH_3$

(c)

$CH_3CH_2CH_2 - C$ with $=O$ and $O - CH_3$

**(d)**

$CH_3 - C$ with $=O$ and $O - CH_2CH_2CH_3$

The tri-iodomethane (iodoform) reaction

This reaction is quite specific for a particular structural arrangement in an alcohol. It detects the presence of the $CH_3CH(OH)-$ 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.
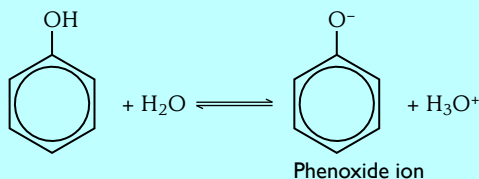
Phenol

Phenol is an aromatic hydroxyl compound:
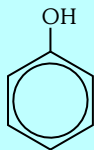
OH on benzene ring

The presence of the benzene ring makes phenol behave differently from alcohols.

Reactions with bases

Phenol is a weakly acidic compound. Its acidity stems from the fact that it ionises in water:

OH-benzene $+ H_2O \rightleftharpoons$ O⁻-benzene $+ H_3O^+$

Phenoxide ion

Because phenol is a very weak acid, the equilibrium lies over to the left. It can lose a proton because the remaining negative charge is delocalised over the benzene ring, making the phenoxide ion more stable. There is evidence for this behaviour because phenol reacts with sodium hydroxide to give a colourless product:


Sodium phenoxide
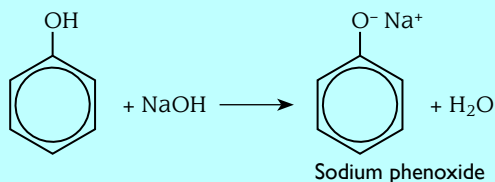
But phenol is neither acidic enough to turn blue litmus paper red, nor to release carbon dioxide from sodium carbonate. It does produce hydrogen when heated with sodium:

Sodium phenoxide
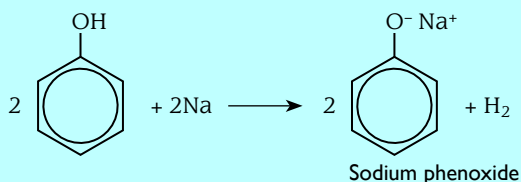
Nitration

Phenol behaves differently from benzene in its reaction with nitric acid. It reacts in the cold with dilute nitric acid, whereas benzene requires a nitrating mixture of concentrated nitric and sulfuric acids. The reason for this is that the presence of the OH group makes the ring much more reactive. It also directs reaction to the 2- and 4-positions on the ring.

With dilute nitric acid, 4-nitrophenol is formed:
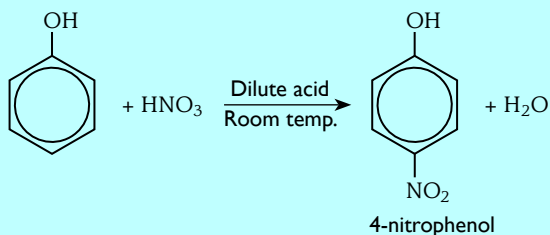
4-nitrophenol

With concentrated nitric acid, 2,4,6-trinitrophenol is formed:

2,4,6-trinitrophenol

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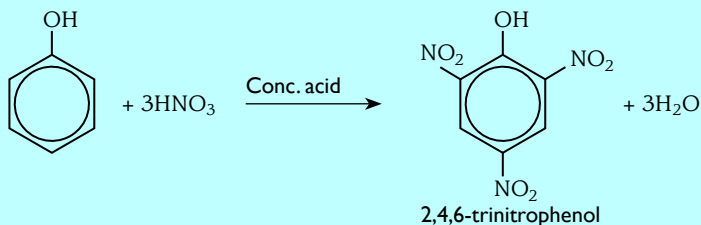
Bromination

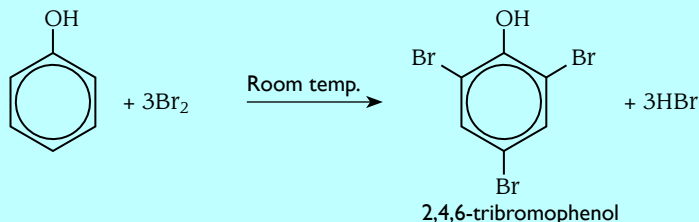When bromine water is added to phenol, there is a similar effect to nitration. The activated ring gives an almost instantaneous white precipitate of 2,4,6-tribromophenol:


2,4,6-tribromophenol

16 Carbonyl compounds

This chapter is needed almost exclusively for the AS examination. Only the very last section is required for the A2 examination. The syllabus treats aldehydes and ketones as two separate classes of organic compound. However, the learning outcomes and this section deal with them together because many of the reactions are similar.

Formation

The oxidation of alcohols by acidified dichromate(VI) was looked at in Chapter 15.

- With a primary alcohol, an aldehyde is first formed. If this is not removed from the reaction vessel, it is further oxidised to give a carboxylic acid:
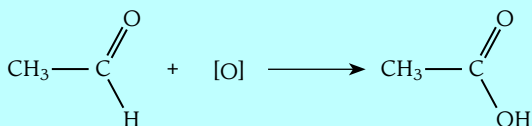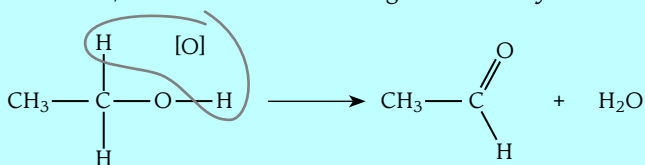
- With a secondary alcohol, a ketone is formed. This is not oxidised further:

Propan-2-ol   Propanone

Reactions
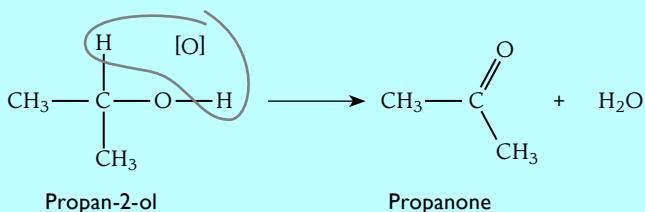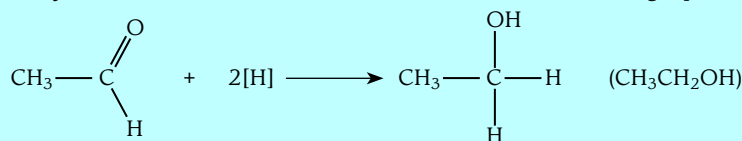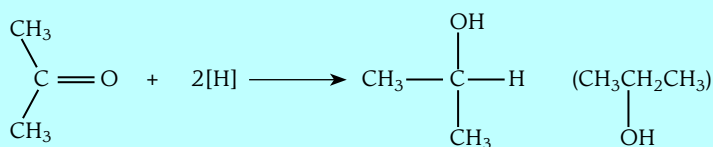
Reduction

This is the reverse of the oxidation reactions used in the preparation of carbonyl compounds. It is carried out using sodium tetrahydridoborate (sodium borohydride), $NaBH_4$.

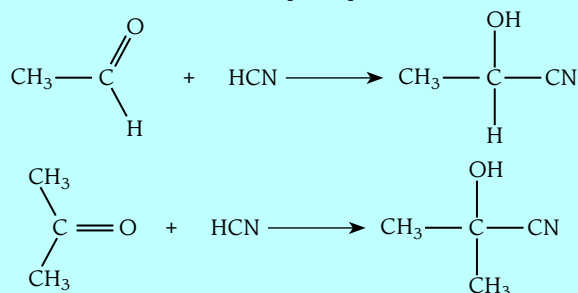With aldehydes such as ethanal the reaction is as follows, forming a primary alcohol:

$$CH_3-C\overset{O}{\underset{H}{\diagdown}} \quad + \quad 2[H] \longrightarrow CH_3-\overset{OH}{\underset{H}{\overset{|}{C}}}-H \quad (CH_3CH_2OH)$$

With ketones such as propanone the reaction is very similar. A secondary alcohol is formed:

$$\overset{CH_3}{\underset{CH_3}{\diagdown}}C=O \quad + \quad 2[H] \longrightarrow CH_3-\overset{OH}{\underset{CH_3}{\overset{|}{C}}}-H \quad (CH_3CH_2CH_3) \quad \underset{OH}{\overset{|}{}}$$

Nucleophilic addition of hydrogen cyanide

In just the same way that alkenes can react by adding a molecule across a C=C double bond, carbonyl compounds can add a molecule across the C=O double bond. At AS you need to know the mechanism for this reaction, using hydrogen cyanide as the nucleophile. You may think that this is a strange reactant, but as we saw earlier it adds a carbon atom to the chain, which is often an important step in a reaction.

The reactions can be summarised in simple equations:

$$CH_3-C\overset{O}{\underset{H}{\diagdown}} \quad + \quad HCN \longrightarrow CH_3-\overset{OH}{\underset{H}{\overset{|}{C}}}-CN$$

$$\overset{CH_3}{\underset{CH_3}{\diagdown}}C=O \quad + \quad HCN \longrightarrow CH_3-\overset{OH}{\underset{CH_3}{\overset{|}{C}}}-CN$$

Hydrogen cyanide itself is not used in the reaction because it is a highly toxic gas. Instead, sodium or potassium cyanide is added to the carbonyl compound followed by a small amount of sulfuric acid. This produces hydrogen cyanide in the reaction vessel but also forms cyanide ions, which are important as you will see when we look at the mechanism.

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The first thing to remember is that the C=O bond is polarised with a partial positive charge on the carbon and a partial negative charge on the oxygen:

$$\overset{\diagdown}{\underset{\diagup}{C}} \overset{\delta+}{=\!=} \overset{\delta-}{O}$$
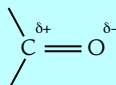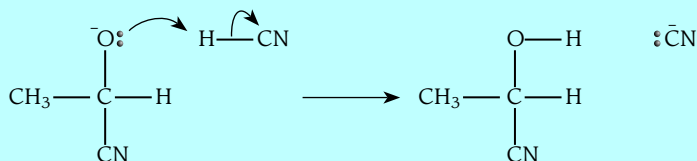
Mechanism of addition of hydrogen cyanide to an aldehyde

The reaction starts with an attack by the nucleophilic cyanide ion on the slightly positive carbon atom:
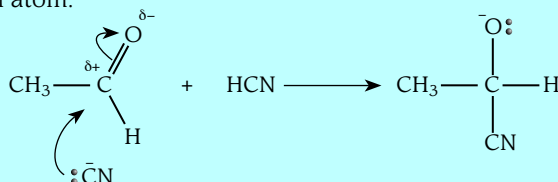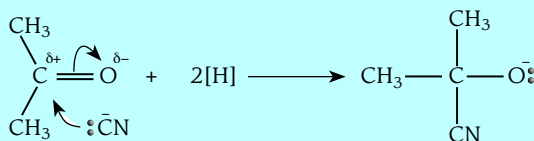

The negative ion formed then picks up a hydrogen ion. It could come from a hydrogen cyanide molecule or from the water or the H_3O^+ ions present in the slightly acidic solution:
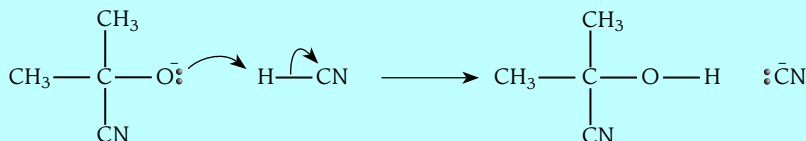

Mechanism of addition of hydrogen cyanide to a ketone

The mechanism for ketones is similar to that for aldehydes. The first stage is a nucleophilic attack by the cyanide ion on the slightly positive carbon atom:

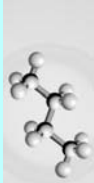The negative ion formed then picks up a hydrogen ion to give the hydroxynitrile (cyanohydrin as it is sometimes called in older textbooks).

Chirality

You may have noticed that the product formed with the aldehyde has four different groups attached to the central carbon. If you remember the section on isomerism in Chapter 13 you will know that this is therefore a **chiral** carbon atom.

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You may also remember that this usually means that the compound exists as a pair of optical isomers that are mirror images of each other. The product of this particular reaction, however, is *not* optically active because ethanal is a planar molecule and the mechanism means that attack by the cyanide ion can occur from both above and below the molecule. This produces a 50:50 mixture of isomers, so the net result is a lack of optical activity.

Reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

This rather complicated sounding reagent is used as a simple test for carbonyl compounds. The reaction is called a 'condensation' or sometimes a 'nucleophilic addition–elimination' reaction.

If a few drops of a suspected carbonyl compound (or a solution of the suspected carbonyl compound in methanol) are added to 2,4-DNPH, a distinct orange or yellow precipitate shows a positive result.
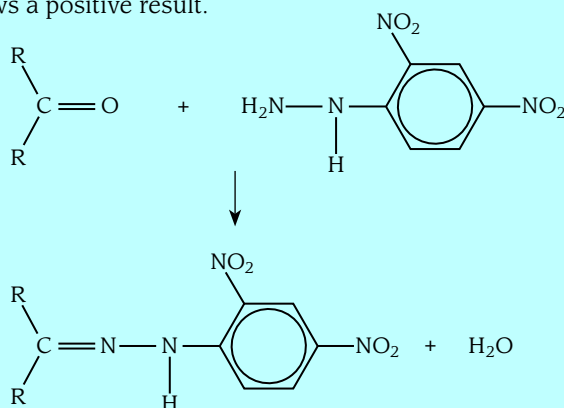
The equation for the reaction is shown above, but it is unlikely that you would be asked to produce this in the examination.

The reaction is rather more useful than just testing for a carbonyl compound. If the precipitate is filtered off, washed and re-crystallised, the melting point of the crystals obtained is characteristic of the particular aldehyde or ketone that reacted, enabling identification to take place.

Distinguishing between aldehydes and ketones

In the section on oxidation reactions of hydroxy compounds in Chapter 15, you saw that primary, secondary and tertiary alcohols can be distinguished between by looking at their oxidation products. These same reactions enable us to distinguish between aldehydes and ketones.

Table 16.1 summarises the behaviour of the two types of carbonyl compound with different reagents.

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Table 16.1

| Reagent	Aldehydes	Ketones
Acidified dichromate(VI)	Orange solution turns blue-green	No change in the orange solution
Fehling's solution	Blue solution produces an orange-red precipitate of copper(I) oxide	No change in the blue solution
Tollens' reagent	Colourless solution produces a grey precipitate of silver, or a silver mirror is formed on the test tube	No change in the colourless solution

Try this yourself

(37) Compound **K** was produced by the oxidation of an alcohol **J** of molecular formula $C_4H_{10}O$. When **K** is reacted with 2,4-DNPH, a yellow-orange precipitate is formed. **K** also reacts with Fehling's solution forming an orange-red precipitate. When treated with alkaline aqueous iodine, no precipitate is formed.

Study the reactions above and use them to deduce the structural formulae of **J** and **K**.

The tri-iodomethane (iodoform) reaction

We saw in Chapter 15 that this reaction is linked to the $CH_3CH(OH)-$ group in alcohols. It can also be used to identify the CH_3CO- group in carbonyl compounds.

In other words, a positive result — the pale yellow precipitate of tri-iodomethane (iodoform) — is given by an aldehyde or ketone containing the group:
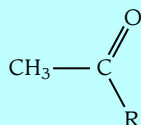
Ethanal is the *only* aldehyde to give a positive reaction. Any methyl ketone will give a positive result.

This bond is broken

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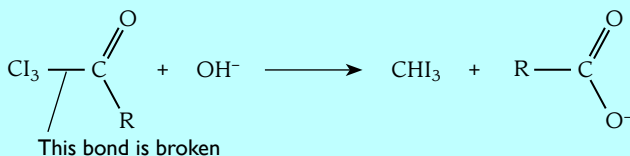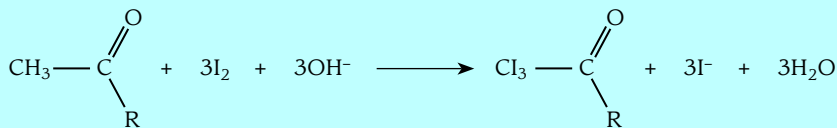
17 Carboxylic acids and their derivatives

This chapter is a mix of material for the AS and A2 examinations. Most of the material on carboxylic acids and esters is for the AS examination; the material related to other derivatives is for A2.
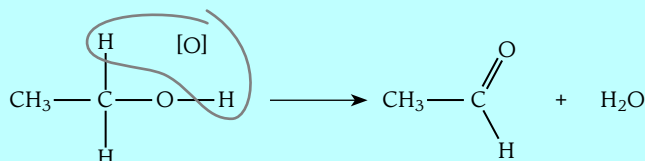
Carboxylic acids

Formation of carboxylic acids

There are three main methods for preparing carboxylic acids (although, strictly, one is a step in another process).
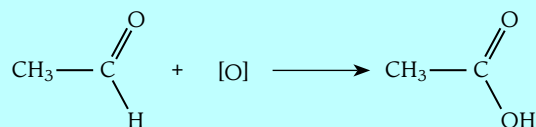
From an alcohol

You will remember from Chapter 15 that a primary alcohol can be oxidised using acidified dichromate(VI) to give an aldehyde and that if this is not distilled off, it is oxidised further to a carboxylic acid, for example:

From an aldehyde

We could start with an aldehyde and oxidise it with acidified dichromate(VI) to form the carboxylic acid, for example:

This is rare, since in order to make an aldehyde we have to start with a primary alcohol.

From a nitrile

You saw in Chapter 15 how nitriles can be produced from halogenoalkanes. They can be hydrolysed to form either carboxylic acids or their salts, depending on whether acid or base is used in the hydrolysis.

If the nitrile is heated under reflux with a dilute acid, such as dilute hydrochloric acid, a carboxylic acid is formed, for example:

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3CO_2H + NH_4^+$$

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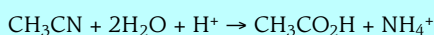
If the nitrile is heated under reflux with an alkali such as sodium hydroxide solution, the sodium salt of the carboxylic acid is formed and ammonia is released, for example:

$$CH_3CN + NaOH + H_2O \rightarrow CH_3CO_2^-Na^+ + NH_3$$
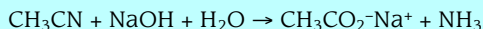
To obtain the carboxylic acid, a strong acid such as hydrochloric acid is added and the carboxylic acid is distilled off.

Reactions of carboxylic acids

Formation of salts

Carboxylic acids are generally relatively weak acids (although there are exceptions). They behave as acids because of their ability to donate protons:

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$$
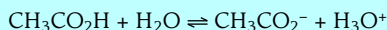
The reaction is reversible with the equilibrium well over to the left. Ethanoic acid is never more than around 1% ionised resulting in solutions with a pH of between 2 and 3.

As a result, carboxylic acids can form salts in a number of ways (although there are some exceptions). Ethanoic acid is used as the example in all the equations shown.
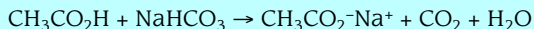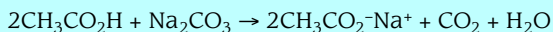
- Aqueous solutions of carboxylic acids react with the more reactive metals such as magnesium to form the salt:

  $$2CH_3CO_2H + Mg \rightarrow (CH_3CO_2^-)_2Mg^{2+} + H_2$$
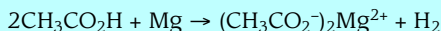
- Aqueous solutions of carboxylic acids react with metal hydroxides such as sodium hydroxide to form the salt:

  $$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$$
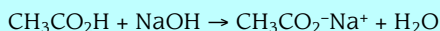
- Aqueous solutions of carboxylic acids react with carbonates and hydrogen carbonates liberating carbon dioxide:

  $$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + CO_2 + H_2O$$

  $$CH_3CO_2H + NaHCO_3 \rightarrow CH_3CO_2^-Na^+ + CO_2 + H_2O$$

  There is very little difference between these reactions and those with other acids. If, however, you chose to use a marble chip as the carbonate, the reaction would be noticeably slower.

- Ethanoic acid reacts with ammonia in just the same way as other acids, forming the ammonium salt:

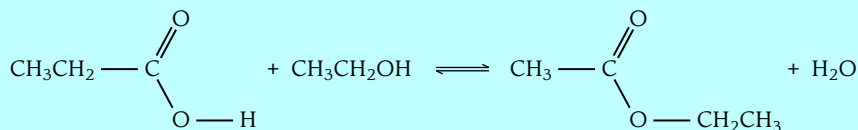 $$CH_3CO_2H + NH_3 \rightarrow CH_3CO_2^-NH_4^+$$
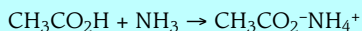
Formation of esters

Making esters from alcohols was covered in Chapter 15, and you learned that a range of reagents can be used to react with the –OH group. Here, we are considering a single reaction — the formation of an ester from a carboxylic acid and an alcohol.

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An ester is formed when a carboxylic acid is heated with an alcohol in the presence of an acid catalyst, usually concentrated sulfuric acid. The reaction is slow and reversible, for example:

$$CH_3CH_2 - \overset{\displaystyle O}{\underset{\displaystyle O - H}{C}} + CH_3CH_2OH \rightleftharpoons CH_3 - \overset{\displaystyle O}{\underset{\displaystyle O - CH_2CH_3}{C}} + H_2O$$
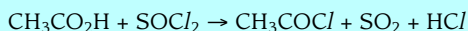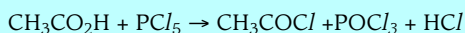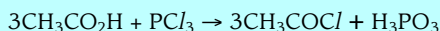
In the laboratory this is achieved by warming the carboxylic acid and alcohol together with a few drops of concentrated sulfuric acid in a water bath for 10–15 minutes and then pouring the contents into a small beaker of cold water. The ester can be detected by its fruity smell. If a sample is required, it can be distilled off from the reaction mixture. Ethyl ethanoate, the most common ester you will come across, can be prepared in this way.

Formation of acyl chlorides

To form an acyl halide from a carboxylic acid, the –OH group in the acid has to be replaced by a –Hal group. You might wonder why this is an important reaction, but acyl chlorides are very reactive and are useful in preparing a range of new materials.

In Chapter 15 we used a group of reagents — phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, and thionyl chloride, $SOCl_2$ — to convert the –OH group of an alcohol to a –Cl group. This same group of reagents can be used to achieve the same outcome here:

$$3CH_3CO_2H + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$CH_3CO_2H + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

$$CH_3CO_2H + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

The third reaction is the 'cleanest' because the by-products are gases.
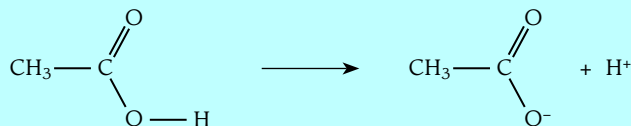
Relative acidity of acids

For the A2 examination it is not enough just to know that carboxylic acids are relatively weak acids because the equilibrium for dissociation lies well to the left. You also need to know what makes some acids stronger or weaker than others.

It helps if you think back to the definition of an acid as a proton donor given in Chapter 7.

> **Tip** It would be a good idea to re-read the section on pK_a and pH on page 73.

Before comparing carboxylic acids, it is useful to look at the ionisation of ethanoic acid in more detail:

$$CH_3 - \overset{\displaystyle O}{\underset{\displaystyle O - H}{C}} \longrightarrow CH_3 - \overset{\displaystyle O}{\underset{\displaystyle O^-}{C}} + H^+$$

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It is helpful to look a little more closely at the ethanoate ion. It has been found that the two carbon–oxygen bond lengths are the same. This means that the usual way of drawing the ion with a C=O and a C—O$^-$ cannot be correct. The representation below is more accurate:

These two bonds are actually identical, so this structure must be wrong.
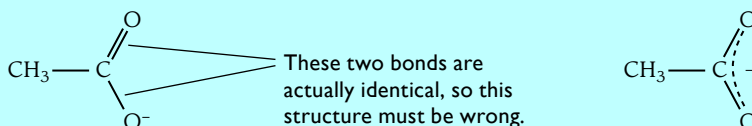
The dashed line represents delocalisation of electrons over the two oxygen atoms and the carbon atom. In general, the more the charge is spread around, the more stable the ion is.

The pK_a values for some carboxylic acids are given in Table 17.1.

Table 17.1

Formula of the acid	pK_a
HCO_2H	3.75
CH_3CO_2H	4.76
$CH_3CH_2CO_2H$	4.87

You might be surprised to see that methanoic acid has a smaller pK_a (stronger acid) than ethanoic acid. Let's think what we know about alkyl groups. They have a tendency to release electrons, which reduces the overall negative charge on the O—C—O group. However, methanoic acid does not have any alkyl groups, so this effect is not present. The addition of an extra CH_2 in propanoic acid makes very little difference to the pK_a.

Now let's see what happens if an **electronegative** atom that pulls electrons away from the O—C—O group is introduced. Chlorine is a good example of an electronegative atom. The pK_a values for ethanoic acid and its chlorinated derivatives are shown in Table 17.2.

Table 17.2

Formula of the acid	pK_a
CH_3CO_2H	4.76
CH_2ClCO_2H	2.86
$CHCl_2CO_2H$	1.29
CCl_3CO_2H	0.65

You can see how the presence of chlorine atoms makes it easier for the hydrogen to be removed.

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content guidance

Acyl chlorides

We saw earlier how to make acyl chlorides from carboxylic acids. Here, their reactions are covered.

Hydrolysis

Acyl halides react quite violently with water, releasing steamy fumes of HCl and forming the appropriate carboxylic acid:
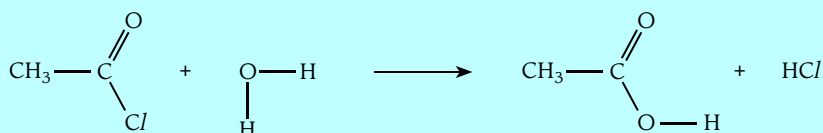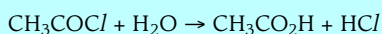

Figure 17.1 The reaction of ethanoyl chloride with water

The equation can also be written as shown below:

$$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$$

However, when studying the reactions of acyl chlorides with alcohols and phenols, it is useful to think about the form shown in Figure 17.1.

The ease with which acyl chlorides react with water is in contrast with the reactivity of alkyl and aryl chlorides. In Chapter 15 you saw that alkyl halides can be hydrolysed by heating under reflux with sodium hydroxide in aqueous ethanol.

Aryl chlorides are very resistant to hydrolysis. Chlorobenzene shows signs of reaction with OH$^-$ only under extreme conditions of around 500 K and approaching 200 atm pressure. One reason for this lack of reaction is repulsion of the OH$^-$ group by the ring electrons. Perhaps a more significant reason is the interaction between one of the lone pairs of electrons on chlorine and the delocalised ring electrons:

Overlap between lone pair and the ring electrons

Lone pair now delocalised to some extent with the ring electrons

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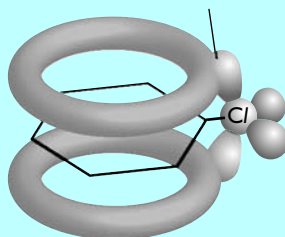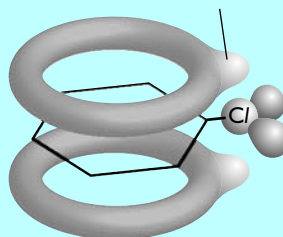
Reaction with alcohols and phenols

With alcohols

The reaction between an acyl chloride and an alcohol is similar to the reaction between an acyl chloride and water, with the release of hydrogen chloride:

$$CH_3-C(=O)Cl \;+\; O-H(CH_2CH_3) \longrightarrow CH_3-C(=O)-O-CH_2CH_3 \;+\; HCl$$
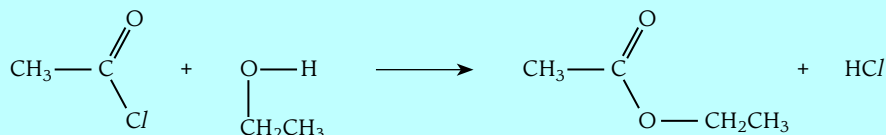
Compare this reaction with the equation shown in Figure 17.1.

From a practical point of view this is a straightforward method for producing an ester because it takes place at room temperature and, because HCl is released, it is not a reversible reaction. This contrasts with the reaction of ethanol with ethanoic acid in the presence of an acid catalyst.

With phenols

In a phenol, the –OH group is attached directly to the benzene ring. The reaction between phenol and ethanoyl chloride is not as vigorous as the reaction with ethanol due to the presence of the benzene ring. Apart from this the reaction is very similar:

$$CH_3-C(=O)Cl \;+\; O-H(C_6H_5) \longrightarrow CH_3-C(=O)-O-C_6H_5 \;+\; HCl$$
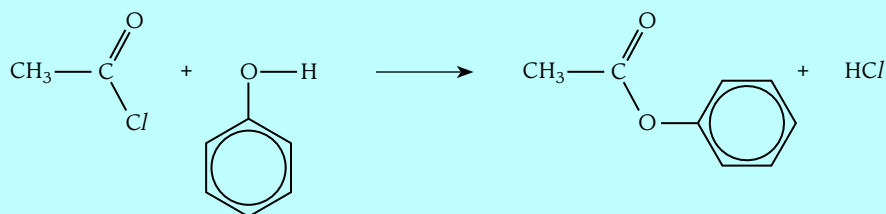
The product is called phenyl ethanoate (remember alcohol/phenol part first, then the carboxylic acid part). The reaction is called **acylation**.
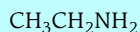
Reaction with primary amines

A primary amine is an ammonia molecule in which one of the hydrogen atoms has been replaced by an alkyl group:

$$NH_3 \qquad CH_3NH_2 \qquad CH_3CH_2NH_2 \qquad C_6H_5NH_2$$

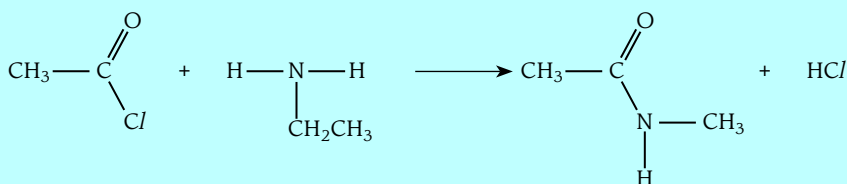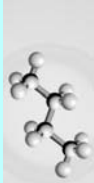Ammonia   Methylamine   Ethylamine   Phenylamine

Primary amines react with acyl chlorides by substitution, replacing the chlorine atom and joining via the nitrogen atom, for example:

The product is an **N-substituted amide**.

Esters

Most of this section is needed for AS; only polyesters are required for A2.

Hydrolysis

You will remember that to form an ester, an alcohol (or phenol) is reacted with a carboxylic acid and water is formed as a by-product. Hydrolysis is the reverse of this process and can be achieved in either of two ways.

Acid hydrolysis

In acid hydrolysis, the ester is heated under reflux with either dilute hydrochloric or dilute sulfuric acid:

$$CH_3CO_2CH_2CH_3 + H_2O \rightleftharpoons CH_3CO_2H + CH_3CH_2OH$$

As in the formation of an ester, the reaction is reversible. We try to make the reaction as complete as possible by having an excess of water present.

Base hydrolysis

Base hydrolysis is the more usual way of hydrolysing esters because the reaction goes to completion, rather than forming an equilibrium mixture:

$$CH_3CO_2CH_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3CH_2OH$$
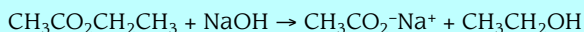
Although this forms the sodium salt of the carboxylic acid, it is still relatively easy to separate the products. First, the alcohol is distilled off and then an excess of a strong acid (dilute hydrochloric or dilute sulfuric acid) is added. This forms the carboxylic acid which is only slightly ionised and can be distilled off.

Commercial uses

Perfumes and flavours

Esters can be formed from a large number of combinations of alcohols with carboxylic acids. They are distributed widely in nature and are responsible for many of the smells and flavours associated with fruits and flowers. This has led to the development of artificial esters for the food industry — for example for ice cream — and for products that need a nice smell, such as detergents and air fresheners. Figure 17.2 shows some of the esters that are used.
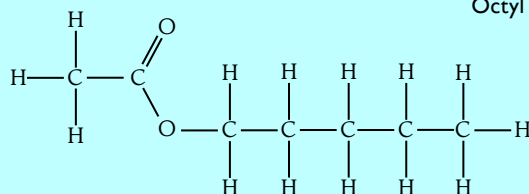
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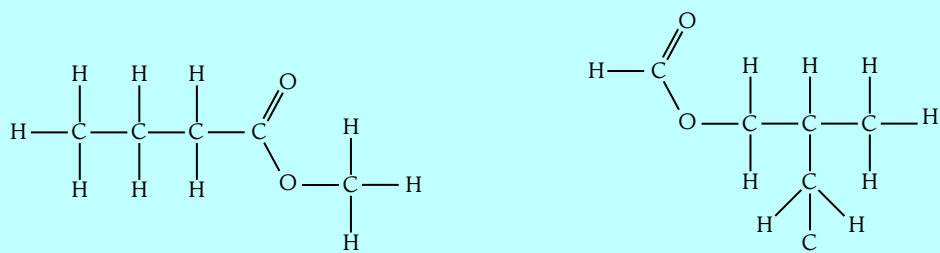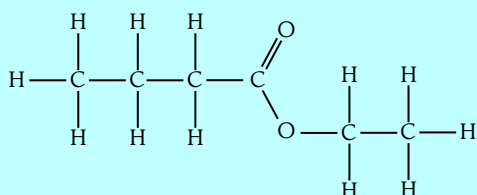
Methyl butanoate (apple)
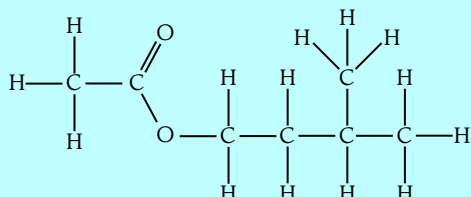
Methylpropyl methanoate (raspberry)
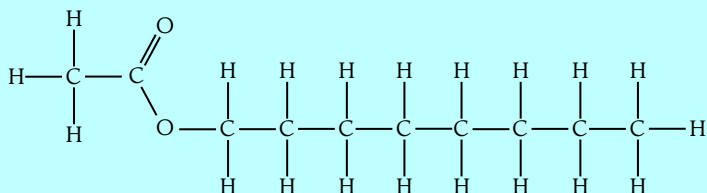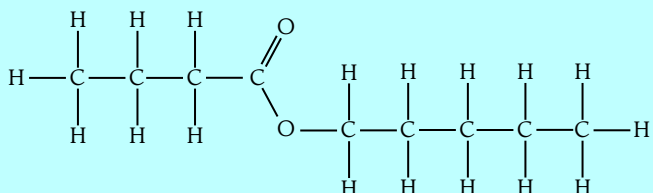
Octyl ethanoate (orange)

Pentyl ethanoate (pear)

Ethyl butanoate (pineapple)

3-methylbutyl ethanoate (banana)

Pentyl butanoate (apricot, strawberry)

Figure 17.2 Esters used in industry

Natural esters are still used in perfumes.

Margarine production

Most oils and fats are esters of long-chain carboxylic acids with the alcohol glycerol $(CH_2OHCHOHCH_2OH)$. Oils often contain carboxylic acids in which the chain has one or more C=C double bonds present. Fats contain mainly carboxylic acids with saturated chains (containing only C—C single bonds) (see Figure 17.3).

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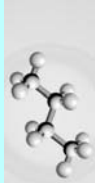
It is this that makes the oils liquid and the fats low-melting solids. These esters are often referred to as glycerides because the common name for the alcohol is glycerol.
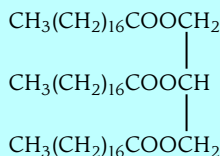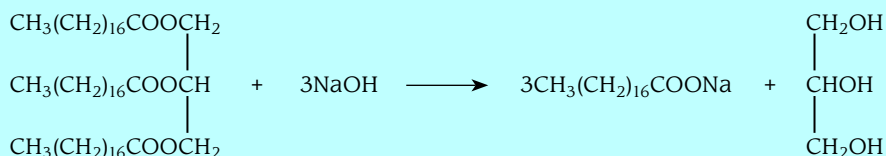
$$CH_3(CH_2)_{16}COOCH_2$$
$$|$$
$$CH_3(CH_2)_{16}COOCH$$
$$|$$
$$CH_3(CH_2)_{16}COOCH_2$$

Figure 17.3 A molecule of a fat

In order to make margarine, the vegetable oils have to have some of the double bonds removed. This is achieved by reacting the oils with hydrogen in the presence of a nickel catalyst.

Consumption of saturated fats has been linked to heart disease, so it is important that these do not form a large part of the human diet. Saturated fats are more common in animal fat than in vegetable oils.

Soap making

Animal fats and vegetable oils have been the raw materials for making soaps and some detergents for hundreds of years. The large molecule esters found in oils and fats are heated with concentrated sodium hydroxide solution and undergo base hydrolysis. The sodium salt of the carboxylic acid is formed (and acts as the soap or detergent) along with the alcohol 1,2,3-trihydroxypropane (glycerol):

$$CH_3(CH_2)_{16}COOCH_2 \qquad\qquad CH_2OH$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH_3(CH_2)_{16}COOCH \quad + \quad 3NaOH \quad \longrightarrow \quad 3CH_3(CH_2)_{16}COONa \quad + \quad CHOH$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$CH_3(CH_2)_{16}COOCH_2 \qquad\qquad CH_2OH$$

Solvents

The smaller molecule esters are important solvents in, for example, the decaffeination of tea and coffee, and in paints and varnishes (such as nail varnish remover).

Polyesters

A **polyester** is a polymer or chain made up of repeating units joined by an ester linkage. Polymerisation was covered briefly in Chapter 14 where we covered poly-alkenes. The polymerisation is different here because two different molecules are needed, rather than just one.

The most important commercial polyester is known as Terylene® and is produced by reacting a dicarboxylic acid with a dialcohol:

HOOC —⬡— COOH   HO —— CH_2CH_2 —— OH

Benzene-1,4-dicarboxylic acid   **Ethane-1,2-diol**

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