

10 Organic chemistry

Learning objectives

- Understand that the alkanes are a family of hydrocarbons
- Distinguish between the different types of formulas (empirical, molecular, structural)
- Understand the difference between a full and a condensed structural formula



Most of the world's oil reserves are controlled by just a few countries.

Indeed it is estimated that more than 80% of the world's oil reserves are controlled by OPEC. The control of oil has already been the source of conflicts between countries – like the 1990 Gulf War – and is likely to be even more of a political issue in the future as oil reserves dwindle.

Empirical and molecular formulas are discussed more fully in Topic 1.

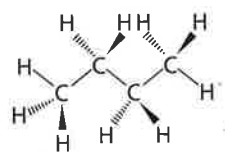


Figure 10.1 The full structural formula of butane showing the tetrahedral arrangement around the carbon atoms.

10.1 Fundamentals of organic chemistry

10.1.1 Introduction to organic chemistry

Organic chemistry is the study of carbon compounds, and specifically compounds containing the C–H bond. The chemistry of carbon is more extensive than that of any other element and there are more compounds of carbon than of all other elements put together. There are so many carbon compounds because of the fact that carbon atoms can join together to form chains and rings – a property called **catenation**.

The source of many carbon compounds is crude oil (petroleum) and many substances can be separated from this complex mixture using fractional distillation. These molecules form the basis of organic synthesis reactions, in which ever-more-complex molecules are made to be used as medicines, cosmetics, polymers etc.

Alkanes

The alkanes are a family of hydrocarbons. The first six members are shown in Table 10.1.

These compounds are all straight-chain alkanes, and the molecular formula of all alkanes can be represented by the general formula C_nH_{2n+2} . For instance eicosane, the alkane with 20 carbon atoms, has $(20 \times 2) + 2$, i.e. 42 hydrogen atoms and its molecular formula is $C_{20}H_{42}$.

Hydrocarbon: a compound containing only carbon and hydrogen.

Empirical formula: the simplest whole number ratio of the elements present in a compound.

Molecular formula: the total number of atoms of each element present in a molecule of the compound. A molecular formula is an integer multiple of the empirical formula.

A full structural formula, also called a displayed or graphic formula, shows all the atoms and bonds in a molecule. Although we draw the full structural formula with 90° bond angles, it must be remembered that with four electron pairs around each carbon atom, the shape is tetrahedral around each one and butane should be more correctly drawn as shown in Figure 10.1. However, this form is significantly less convenient to draw.

A condensed structural formula is the simplest representation that shows how the atoms are joined together in a molecule.

Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
methane	CH_4	CH_4	CH_4	<pre> H H-C-H H </pre>
ethane	C_2H_6	CH_3	CH_3CH_3	<pre> H H H-C-C-H H H </pre>
propane	C_3H_8	C_3H_8	$CH_3CH_2CH_3$	<pre> H H H H-C-C-C-H H H H </pre>
butane	C_4H_{10}	C_2H_5	$CH_3CH_2CH_2CH_3$	<pre> H H H H H-C-C-C-C-H H H H H </pre>
pentane	C_5H_{12}	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	<pre> H H H H H H-C-C-C-C-C-H H H H H H </pre>
hexane	C_6H_{14}	C_3H_7	$CH_3CH_2CH_2CH_2CH_2CH_3$	<pre> H H H H H H H-C-C-C-C-C-C-H H H H H H H </pre>

Table 10.1 The first six straight-chain alkanes.

$CH_3CH_2CH_2CH_3$ is a condensed structural formula for butane because it is an unambiguous representation of the structure of the molecule but C_4H_{10} is not a structural formula because it could represent either of the molecules shown in Figure 10.2.

Molecules can also be represented using skeletal formulas like the one shown in Figure 10.3. Skeletal formulas are very convenient and are widely used for drawing more complex molecules.

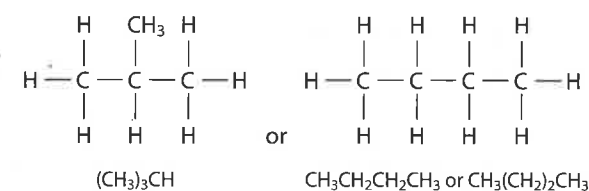


Figure 10.2 Same molecular formula (C_4H_{10}), different structural formulas.

Exam tip

Skeletal formulas should not be used in examinations unless specifically requested.



Figure 10.3 The skeletal formula of butane.



Different ways of representing the structures of molecules have been shown here. Why is one way sometimes preferred to another? What is the relationship between ease of use and sophistication? Which is probably the most accurate way of representing a molecule? Which is the most useful if we need to draw a reaction scheme?



Figure 10.4 Computer-generated images: **a** a stick model, **b** a ball and stick model and **c** a space-filling model.

Some other ways of representing the structure of butane are shown in Figure 10.4.

10.1.2 Homologous series

The alkanes represent a homologous series.

Learning objectives

- Understand what is meant by a homologous series
- Understand what is meant by a functional group
- Identify functional groups in molecules
- Understand that compounds containing a benzene ring are described as aromatic
- Explain trends in boiling points within homologous series

Chemical properties: how a substance reacts.

Note that the diagrams in Figure 10.5 do not show the full structural formulas because the O–H bonds are not shown. However, it is a structural formula type that is often drawn to represent molecules.

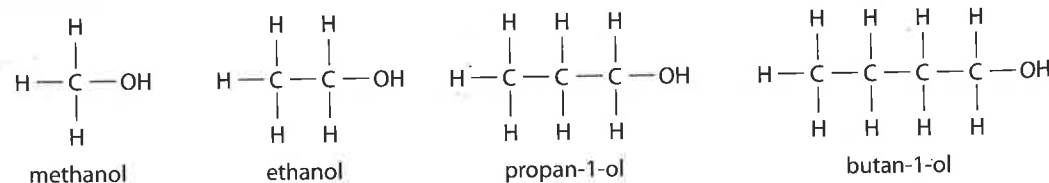


Figure 10.5 The first four members of the alcohol series.

A **homologous series** is a series of compounds that have the same functional group. Each member differs from the next by a common structural unit (usually $-\text{CH}_2-$).

A **functional group** is the atom or group of atoms in a molecule that gives it its characteristic chemical properties – this is the reactive part of a molecule.

Although there is not really a functional group in alkanes, because only single C–C and C–H bonds are present, examples of functional groups in other homologous series are C=C in alkenes and –OH in alcohols.

The features of a homologous series are:

- they can usually be described by a general molecular formula – e.g. $\text{C}_n\text{H}_{2n+2}$ for alkanes (non-cyclic) and C_nH_{2n} for alkenes
- members of the series have similar chemical properties
- members of the series show a gradation in physical properties such as boiling point.

Other homologous series

Table 10.2 shows the functional groups you are likely to meet during the IB Chemistry course.

Each of the functional groups in Table 10.2 could form the basis of a homologous series. For example, the first four members of the alcohol series, in which the –OH group is on the first carbon, are shown in Figure 10.5.

Homologous series / class name	Functional group	Functional group name	Example	General name	Name
alkane		alkyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkane	butane
alkene	C=C	alkenyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alk-x-ene (or x-alkene)	but-1-ene (or 1-butene)
alkynes	$\text{C}\equiv\text{C}$	alkynyl	$\begin{array}{cccc} & & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}\equiv\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ & & \text{H} & \text{H} \end{array}$	alk-x-yne (or x-alkyne)	but-1-yne (or 1-butyne)
alcohol	–OH	hydroxyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkan-x-ol (or x-alkanol)	propan-1-ol (or 1-propanol)
ether	$\text{C}-\text{O}-\text{C}$	ether	$\begin{array}{cccc} \text{H} & & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alkoxyalkane	methoxyethane
aldehyde	$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{H} \end{array}$	carbonyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{O} & \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & & \end{array}$	alkanal	propanal
ketone	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \end{array}$		$\begin{array}{ccccccc} \text{H} & \text{O} & \text{H} & \text{H} & \text{H} & & \\ & & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & & \\ \text{H} & & \text{H} & \text{H} & \text{H} & & \end{array}$	alkan-x-one (or x-alkanone)	pentan-2-one (or 2-pentanone)
carboxylic acid	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \backslash \\ \text{O}-\text{H} \end{array}$	carboxyl	$\begin{array}{cccc} \text{H} & \text{H} & \text{O} & \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\ & & & \\ \text{H} & & & \end{array}$	alkanoic acid	propanoic acid
halogenoalkane	–X X = Cl/Br/I	halo (chloro, bromo, iodo)	$\begin{array}{cccc} \text{H} & \text{Br} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	x-haloalkane	2-bromobutane
amine	$\begin{array}{c} -\text{NH}_2 \\ -\text{NHR} \\ -\text{NR}_2 \end{array}$	amino	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{N}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	alkylamine or x-aminoalkane or alkan-x-amine (or x-alkanamine)	propylamine or 1-aminopropane or propan-1-amine (or 1-propanamine)
ester	$\text{C}-\text{O}-\text{C}(=\text{O})$	ester	$\begin{array}{cccc} \text{H} & \text{O} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$	alkyl alkanoate	methyl propanoate
nitrile	–C≡N	nitrile	$\begin{array}{ccc} \text{H} & \text{H} & \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}\equiv\text{N} \\ & & \\ \text{H} & & \end{array}$	alkanenitrile (C of C≡N included in chain)	propanenitrile
amide	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \\ \text{NH}_2 \end{array}$	carboxamide	$\begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{NH}_2 \\ & & \\ \text{H} & & \end{array}$	alkanamide	propanamide

Table 10.2 Functional groups that you are likely to meet. 'R' can be used to represent an alkyl group – so a general carboxylic acid may be represented as 'RCOOH' and an aldehyde as 'RCHO'. 'R' is occasionally also used to represent a phenyl group ($-\text{C}_6\text{H}_5$).

Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
ethene	C ₂ H ₄	CH ₂	CH ₂ CH ₂	
prop-1-ene	C ₃ H ₆	CH ₂	CH ₂ CHCH ₃	
but-1-ene	C ₄ H ₈	CH ₂	CH ₂ CHCH ₂ CH ₃	
pent-1-ene	C ₅ H ₁₀	CH ₂	CH ₂ CHCH ₂ CH ₂ CH ₃	
hex-1-ene	C ₆ H ₁₂	CH ₂	CH ₂ CHCH ₂ CH ₂ CH ₂ CH ₃	

Table 10.3 The first five members of the alkene homologous series.

Amines are strong-smelling substances (said to smell like fish) and some of the trivial (non-systematic) names for them reflect this. Cadaverine (1,5-diaminopentane) and putrescine (1,4-diaminobutane) are produced in rotting flesh.

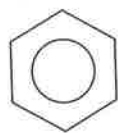


Figure 10.6 A common representation of a molecule of benzene.

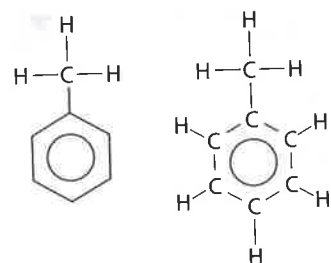


Figure 10.7 Representations of methylbenzene.

There are three different functional groups for amines in Table 10.2 because amines are classified as primary, secondary or tertiary – see Section 10.1.6.

The first five members of the alkene homologous series, in which the C=C is between carbon 1 and carbon 2, are shown in Table 10.3.

Compounds containing a benzene ring

Benzene has the molecular formula C₆H₆ and its molecules have a planar, hexagonal ring of six carbon atoms with one hydrogen atom joined to each. It is usually represented by the skeletal formula shown in Figure 10.6.

Compounds that contain a benzene ring are described as **aromatic** – compounds without benzene rings are called **aliphatic**. The functional group in aromatic compounds is the benzene ring because it performs characteristic chemical reactions.

When determining molecular formulas or condensed structural formulas for compounds that contain benzene rings, it must be remembered that there is a carbon atom and, if there is nothing else attached, a hydrogen atom at each vertex. So, for example, methylbenzene has the molecular formula C₇H₈ and can be represented in different ways (Figure 10.7).

The condensed structural formula of methylbenzene can be written as C₆H₅CH₃. The C₆H₅ group in methylbenzene and other aromatic compounds is often called a phenyl group.

Boiling point and homologous series

As the number of carbon atoms in a molecule in any homologous series increases, the boiling point increases.

The boiling point of straight-chain alkanes increases when a methylene (–CH₂–) group is added, because the strength of the London forces between molecules increases as the relative molecular mass (number of electrons in the molecule) of the alkanes increases. A similar trend is seen in the boiling points of other homologous series.

Figure 10.8 compares the boiling points of alcohols (with the –OH group on the first carbon atom) with the boiling points of alkanes. It can be seen that both series show the same trend – the boiling point increases as the number of carbon atoms increases. However, the alcohol with one carbon atom (*M_r* 32.05) has a higher boiling point than the alkane with five carbon atoms (*M_r* 72.17). It is important to realise that comparisons based on the relative molecular mass (and hence strength of London forces) can be made *within* a particular homologous series but not *between* homologous series. The boiling points of the alcohols are higher because of hydrogen bonding between alcohol molecules.

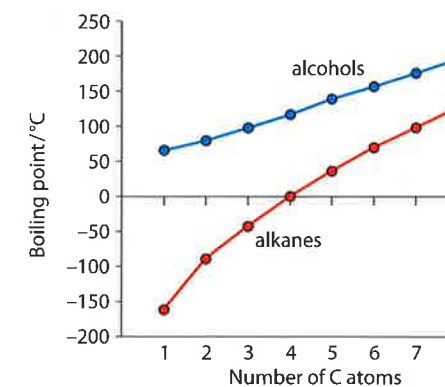


Figure 10.8 The boiling points of some alkanes and alcohols.

Boiling points of alcohols and ethers

Alcohols have higher boiling points than ethers and are more soluble in water because alcohol molecules can form hydrogen bonds to each other and also to water molecules. Ethers have no hydrogen atoms bonded to oxygen atoms and so cannot form hydrogen bonds – Figure 10.9.

Ethanol is soluble in water in all proportions – this is because the –OH group allows it to hydrogen bond with water. However, the solubility decreases as the length of the hydrocarbon chain increases (see page 157) so that pentan-1-ol and hexan-1-ol are only sparingly soluble in water.

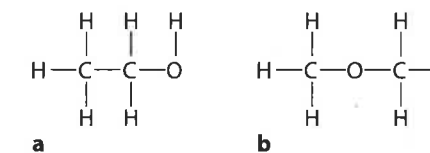


Figure 10.9 The structures of: **a** ethanol (an alcohol) and **b** methoxymethane (an ether).

Nature of science

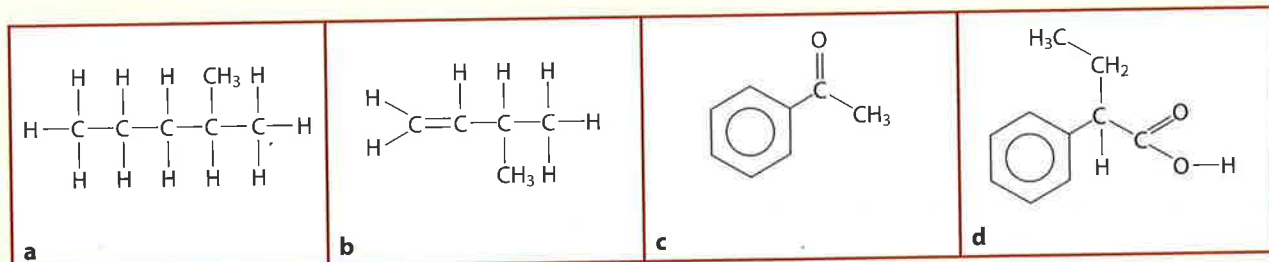
Scientists share a common language in the form of mathematics and also in terms of organic structures. Organic structures drawn in skeletal form would be recognised and understood by any organic chemist anywhere in the world.

There are certain areas of scientific research which are more controversial and involve significant ethical implications. Organic chemists make a large range of substances and amongst these would be pesticides, drugs and food additives. These are all substances that are almost certainly being produced because a need exists and there is the potential to make money but they could also have an adverse effect on the environment and human health. Scientists, however, also have to earn a living and, if working for a large company (which is likely to be driven solely by the desire to make money) may not have the choice to follow their own interests and conscience when selecting projects. Regulatory authorities have to consider the risks and benefits of new substances before licensing them for use.

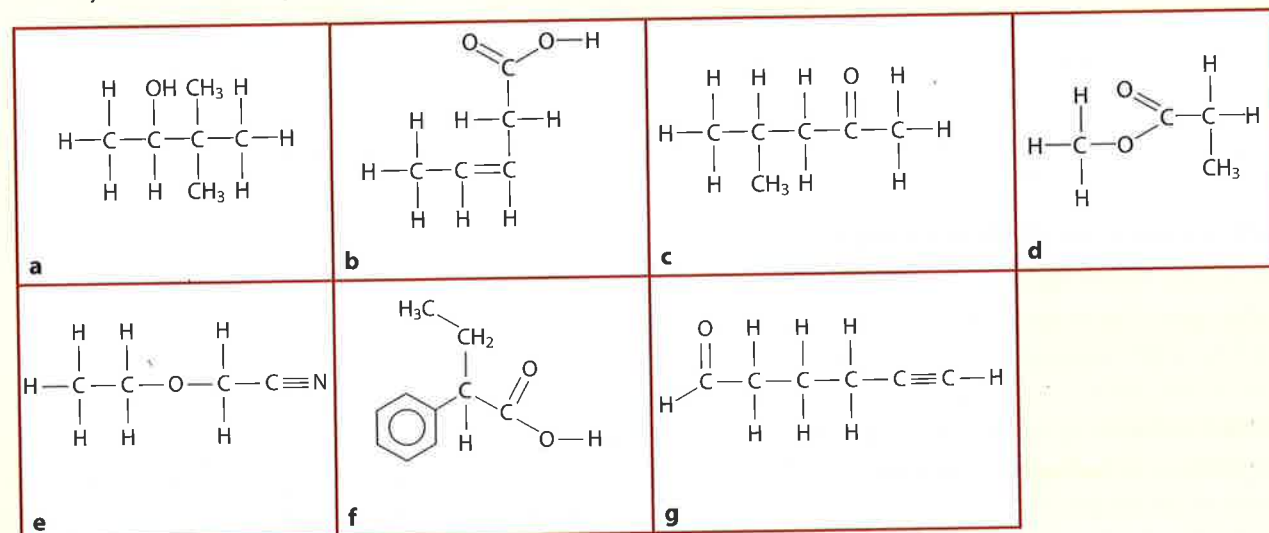
The role of serendipity in scientific discovery is discussed on page 483.

? Test yourself

- 1 What is the molecular formula of the alkane with 15 carbon atoms?
- 2 Give the molecular formula and empirical formula of each of the following:



- 3 Identify the functional group(s) in each of the following molecules.



Learning objectives

- Use IUPAC rules to name alkanes, alkenes and alkynes
- Distinguish between saturated and unsaturated compounds

Carbon atoms	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-

Table 10.4 Prefixes indicating the number of carbon atoms in the longest continuous carbon chain.

10.1.3 Naming hydrocarbons

Naming alkanes

Organic molecules are named according to the International Union of Pure and Applied Chemistry (IUPAC) system. Although older, non-systematic names are still in use in some situations, molecules should, wherever possible, be named according to the following systematic set of rules.

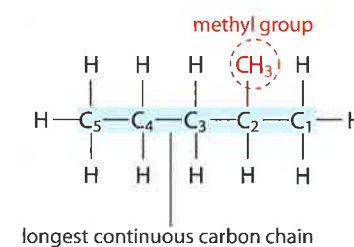
- 1 Find the longest *continuous* carbon chain in the molecule.
- 2 Choose the prefix from Table 10.4 corresponding to the number of carbon atoms in the longest continuous carbon chain and add the ending 'ane' to indicate an alkane.
- 3 Look for substituent groups (alkyl groups) – the names for these are shown in Table 10.5.

- 4 Number the positions of the substituent groups using the combination that has the lowest individual numbers (not the sum).
- 5 Choose a prefix from Table 10.6 to indicate the number of each substituent present.
- 6 Arrange the names of the substituent groups in alphabetical order (ignoring the prefix used in step 5).

Examples

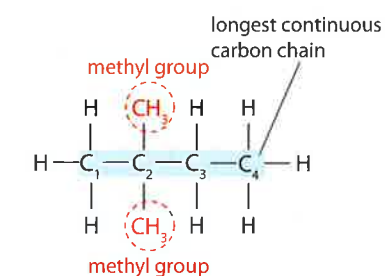
2-methylpentane

The longest continuous carbon chain has five carbon atoms, and this gives the basic name 'pentane'. A methyl group is present in the molecule, and this is on carbon number 2 if we start numbering from the right-hand carbon atom. If we had started numbering from the left-hand carbon atom, we would have a methyl group on carbon 4, which is a higher number than the 2 obtained if we number from the other side – therefore '4' is not used.



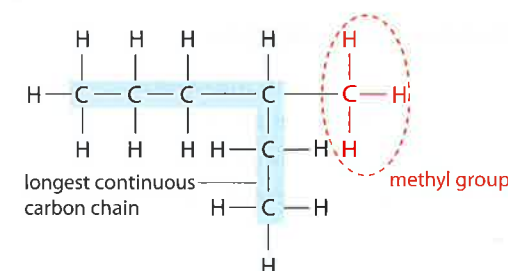
2,2-dimethylbutane

The longest continuous carbon chain is of four carbon atoms, and this gives rise to the 'butane' part of the name. There are two methyl groups, so we use 'dimethyl'. These methyl groups are both on carbon 2 (this time we count from the left-hand side to generate the lowest numbers) and so we have '2,2-dimethyl' – both 2s are needed.



3-methylhexane

The longest continuous carbon chain may not always be shown as a horizontal, straight line of carbon atoms, as in this molecule:



-CH ₃	methyl
-C ₂ H ₅	ethyl
-C ₃ H ₇	propyl

Table 10.5 The names of substituent groups.

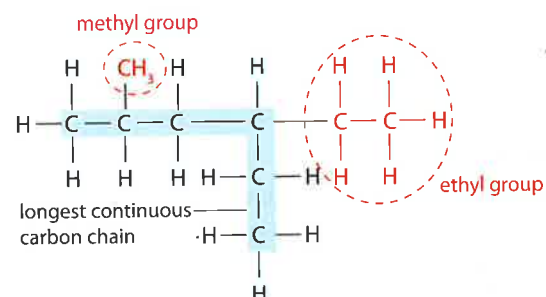
Number of identical substituents	Prefix
2	di-
3	tri-
4	tetra-

Table 10.6 Prefixes indicating the number of identical substituents.

When naming molecules we use commas between numbers, and dashes between numbers and letters.

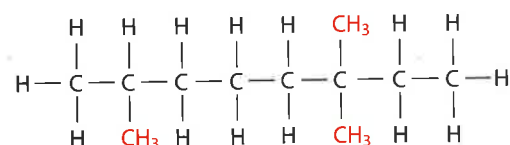
4-ethyl-2-methylhexane

This combination of numbers gives the lowest number possible – the alternative name would be 3-ethyl-5-methylhexane, but 2 is lower than 3. The substituent (alkyl) groups are arranged in alphabetical order.



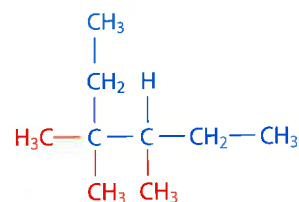
2,6,6-trimethyloctane

If we numbered the carbon atoms from the other direction, we would have obtained the name 3,3,7-trimethyloctane. Although the sum of the numbers in this name is lower, the lowest number here is higher than the lowest number in the accepted name, and so this name is not used.



3,3,4-trimethylhexane

If the first number is the same after numbering from both directions then the second number is investigated and the name is chosen to give the lower number at the first position at which the names differ. The molecule shown below could be named 3,3,4-trimethylhexane or 3,4,4-trimethylhexane, depending on the side we start counting from. Both names start with 3 but they differ at the second digit, and so the name 3,3,4-trimethylhexane is chosen because it gives the lower number at the second position.



Naming alkenes and alkynes

The names of alkenes are of the form **alk-x-ene** (*x*-alkene is also acceptable). The number, *x*, indicates the position of the double bond. If there is a double bond between carbon 1 and carbon 2, the lower number is taken to generate a '-1-ene'. If there are alkyl groups present in the

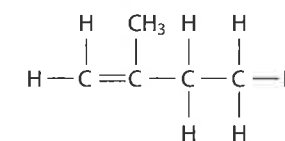
molecule, the numbering is chosen to give the double bond the lowest possible number.

Alkynes are named in exactly the same way except the suffix **-yne** is used.

Examples

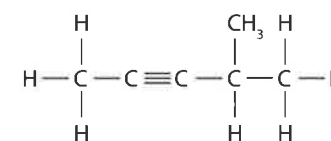
2-methylbut-1-ene

The molecule has four carbon atoms in the longest continuous carbon chain and produces the stem 'but-'. A double bond between carbon 1 and carbon 2 gives us '-1-ene' and the methyl group on carbon 2 produces '2-methyl'.



4-methylpent-2-yne

This alkyne could have been named 2-methylpent-3-yne, but the lowest possible number is given to the triple bond component – so it is more correctly named 4-methylpent-2-yne.



When more than one C=C bond is present in a molecule, the naming changes slightly – an extra 'a' is added to the stem. The alkene in Figure 10.10a is called hexa-1,3-diene and that in b is called hexa-1,3,5-triene.

Saturated and unsaturated compounds

Alkenes and alkynes are called **unsaturated compounds** because they contain C=C bonds or C≡C bonds (Figure 10.11). Alkanes and other compounds not containing multiple bonds are described as **saturated**.

Benzene is also described as an unsaturated hydrocarbon as the structure could be drawn with three C=C bonds.

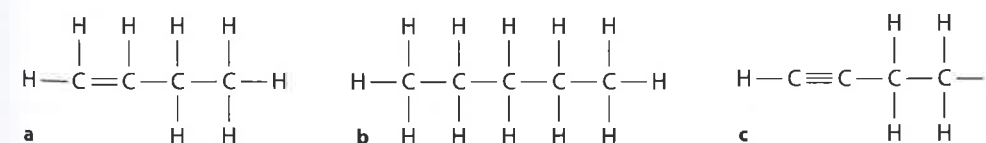
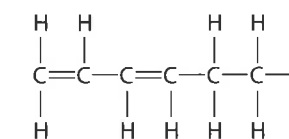
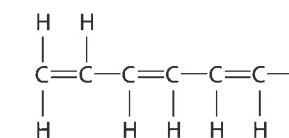


Figure 10.11 Hydrocarbons: a unsaturated; b saturated; c unsaturated.



a



b

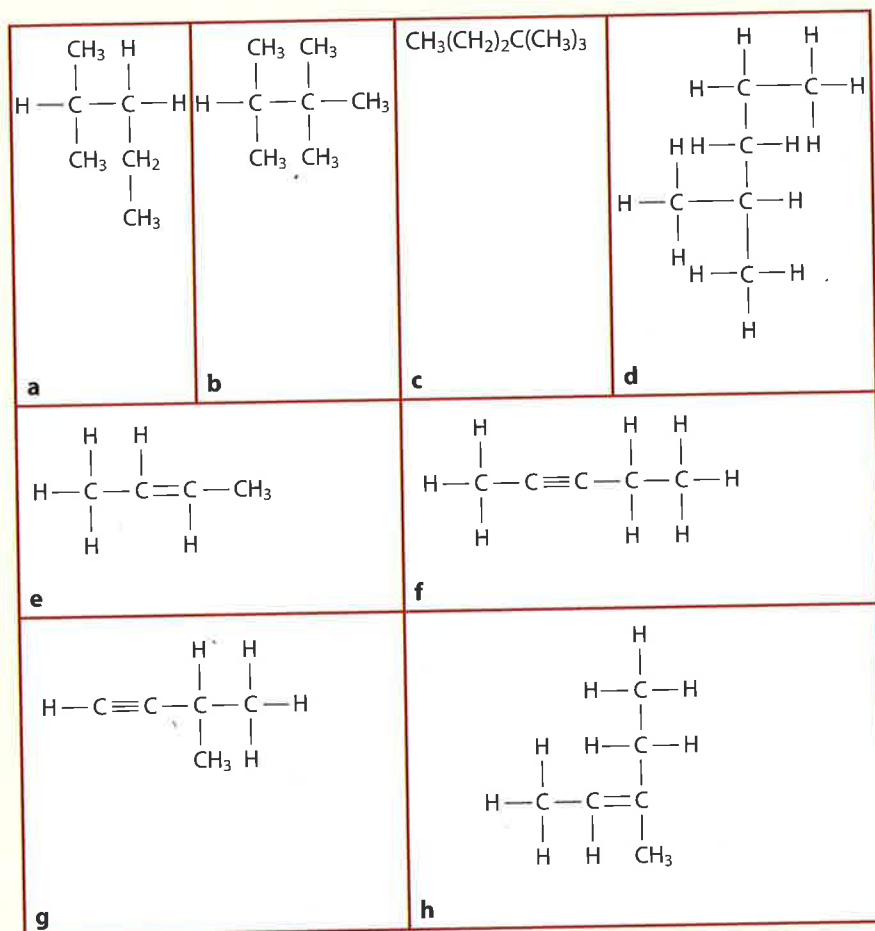
Figure 10.10 Compounds containing more than one C=C bond; a hexa-1,3-diene; b hexa-1,3,5-triene.

Exam tip

You should be able to name alkanes with up to a maximum of six C atoms in the longest carbon chain. Some of the examples here are for a bit of extra practice and to illustrate all the rules.

? Test yourself

4 Name the following molecules:



5 Draw the following molecules:

- 3-methylhexane
- 2,2,3-trimethylpentane
- 2,4-dimethylhexane
- 2,3-dimethylbut-1-ene

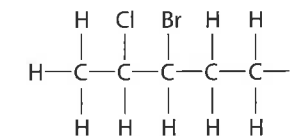
6 Give the correct name for each of the following:

- 1,2-dimethylbutane
- 1,2,3-trimethylpropane
- 1-methyl-2,2-dimethylpropane

Where more than one substituent is present, they are arranged in alphabetical order using the numbering system that gives the lowest possible number for any substituent. Where two or more substituents would have the same numbers when numbering from either side, the one that comes first in the alphabet (ignoring di-, tri- etc.) is allocated the lowest position number.

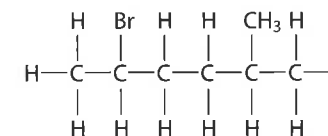
3-bromo-2-chloropentane

The two possible names for this are 3-bromo-2-chloropentane and 3-bromo-4-chloropentane. The first name gives the lowest individual number (2), and so the name is 3-bromo-2-chloropentane.



2-bromo-5-methylhexane

There are two substituents on the chain – a bromo group and a methyl group. The two possible names are 2-bromo-5-methylhexane and 5-bromo-2-methylhexane. Both names contain the same numbers, and so the name is chosen according to position in the alphabet. 'Bromo' comes before 'methyl' in the alphabet, and so the numbering is chosen to give the lower number to the 'bromo', which leads to the name 2-bromo-5-methylhexane.



Some more examples of halogenoalkane names are given in Table 10.8.

$\begin{array}{c} \text{H} \quad \text{Br} \quad \text{Cl} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{Br} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
2-bromo-3-chlorobutane	2-chloro-3-methylpentane	3-bromo-2-methylpentane
$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{Cl} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{H} \\ \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{Cl} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{Cl} \quad \text{Br} \quad \text{H} \\ \quad \quad \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$
2-chloro-4-methylpentane	1,1,1,2-tetrachloropropane	2-bromo-1,1-dichloropropane

Table 10.8 Examples of halogenoalkanes.

Learning objective

- Use IUPAC rules to name halogenoalkanes

10.1.4 Naming halogenoalkanes

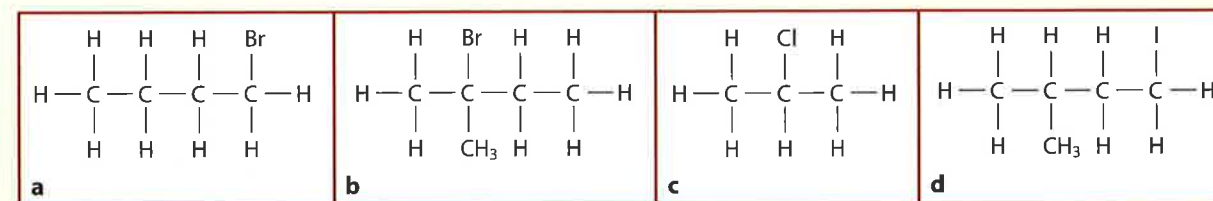
Halogenoalkanes have molecules that contain a halogen atom as the functional group. Halogenoalkanes are named using the format **x-haloalkane**, where *x* indicates the position of the halogen atom on the chain. Examples of some names of simple halogenoalkanes are given in Table 10.7.

$\begin{array}{c} \text{Cl} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{Br} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{Br} \quad \text{Br} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
1-chloropropane	2-bromobutane	2,3-dibromobutane

Table 10.7 The names of some simple halogenoalkanes.

? Test yourself

7 Name the following compounds:



Learning objective

- Use IUPAC rules to name alcohols, ethers, aldehydes, ketones, carboxylic acids and esters



The World Health Organisation estimates that there are about 2.5 million alcohol-related deaths worldwide each year. This is more than the combined total of deaths through AIDS and malaria. The use and abuse of alcohol is a major social and economic problem in many countries and seems set to put an increasing strain on health systems in these countries in years to come.

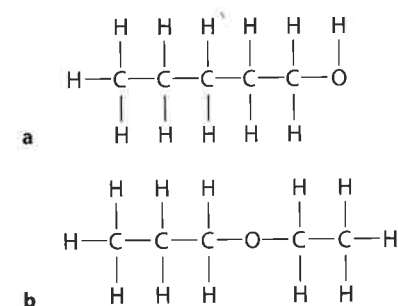
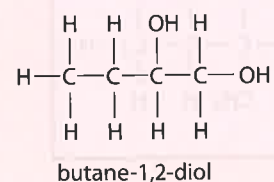


Figure 10.12 The alcohol **a** and ether **b** both have molecular formula $C_5H_{12}O$ and are isomers – functional group isomers.

The name changes slightly when more than one $-OH$ group is present:



10.1.5 Naming organic compounds containing oxygen

Alcohols and ethers

Alcohols and ethers both contain oxygen. All alcohols contain the $-OH$ functional group, whereas for ethers the functional group is $C-O-C$. Alcohols and ethers have the general molecular formula $C_nH_{2n+2}O$, and they can be isomers (see Subtopic 10.1.7) as shown in Figure 10.12.

Naming alcohols

Alcohols are named as **alkan- x -ol** (x -alkanol is also acceptable). Carbon atoms are always numbered to give the lowest possible value for x .

Table 10.9 lists the first six alcohols and Table 10.10 gives some examples where x is not equal to 1.

Name	Molecular formula	Structural formula	
		Condensed	Full
methanol	CH_3OH	CH_3OH	<pre> H H H - C - O H </pre>
ethanol	C_2H_5OH	CH_3CH_2OH	<pre> H H H H - C - C - O H H </pre>
propan-1-ol	C_3H_7OH	$CH_3CH_2CH_2OH$	<pre> H H H H H - C - C - C - O H H H </pre>
butan-1-ol	C_4H_9OH	$CH_3(CH_2)_2CH_2OH$	<pre> H H H H H H - C - C - C - C - O H H H H </pre>
pentan-1-ol	$C_5H_{11}OH$	$CH_3(CH_2)_3CH_2OH$	<pre> H H H H H H H - C - C - C - C - C - O H H H H </pre>
hexan-1-ol	$C_6H_{13}OH$	$CH_3(CH_2)_4CH_2OH$	<pre> H H H H H H H H - C - C - C - C - C - C - O H H H H </pre>

Table 10.9 The first six members of the alcohol homologous series.

<pre> H OH H H - C - C - C - H H H H </pre>	<pre> OH H H H H H H - C - C - C - C - C - H H H H H CH₃ H </pre>	<pre> H H OH H H H - C - C - C - C - H H H H CH₃ H </pre>	<pre> CH₃ OH H H H - C - C - C - C - CH₃ H H H CH₃ </pre>
propan-2-ol	5-methylhexan-1-ol	2-methylpentan-3-ol	5-methylhexan-3-ol

Table 10.10 When x is not equal to 1 the numbering is chosen to give a lower number to the OH group than to an alkyl group.

Naming ethers

Ethers contain the $C-O-C$ functional group and many ethers have two alkyl groups separated by an oxygen atom. The shorter group and the oxygen together is called an **alkoxy** group and is named as a substituent on the main chain.

In the molecule shown in Figure 10.13, the longer carbon chain has three carbons and if the OCH_3 (methoxy) group were replaced by a hydrogen it would be called propane. The methoxy group is on carbon 1 and so the molecule is called 1-methoxypropane – this is often just called methoxypropane.

If the OC_2H_5 group in the molecule in Figure 10.14 were replaced by an H the molecule would be called 2-methylbutane. With the ethoxy group on carbon 2, it is called 2-ethoxy-2-methylbutane.

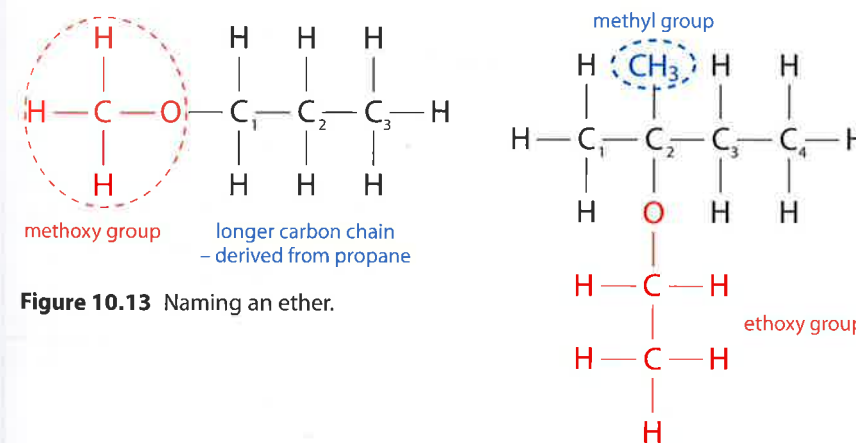


Figure 10.13 Naming an ether.

Figure 10.14 Naming an ether.

? Test yourself

- Draw and name all the isomers of $C_4H_{10}O$.

Functional group		
aldehyde	ketone	carboxylic acid

Table 10.11 The functional groups in aldehydes, ketones and carboxylic acids.

Naming aldehydes, ketones, carboxylic acids and esters

Aldehydes and ketones are known as **carbonyl** compounds and contain the carbonyl (C=O) functional group. Carboxylic acids contain the COOH functional group. Table 10.11 shows the functional group unit of each of these compounds.

- Aldehydes are named based upon alkanal.
- Ketones are named as alkan-*x*-one (*x*-alkanone is also acceptable).
- Carboxylic acids have names based on alkanonic acid.

In aldehydes and carboxylic acids, the carbon of the CHO or COOH group is numbered carbon 1 and everything else is numbered relative to that. For ketones, the numbering scheme is chosen to give the C=O group the lowest possible number. Examples of some names of aldehydes and ketones are given in Table 10.12 and carboxylic acids in Table 10.13.

Condensed structural formulas for aldehydes can be written using the CHO group – so ethanal can be written as CH₃CHO and butanal as CH₃CH₂CH₂CHO. The condensed structural formulas for ketones can be written using the CO group – so propanone can be written as CH₃COCH₃ or (CH₃)₂CO and pentan-2-one as CH₃COCH₂CH₂CH₃.

	methanal		aldehydes
	propanal		
	4-methylpentanal	numbering starts from the aldehyde group	
	propanone		ketones
	pentan-2-one		
	4-methylpentan-2-one	the ketone group is given the lower number	

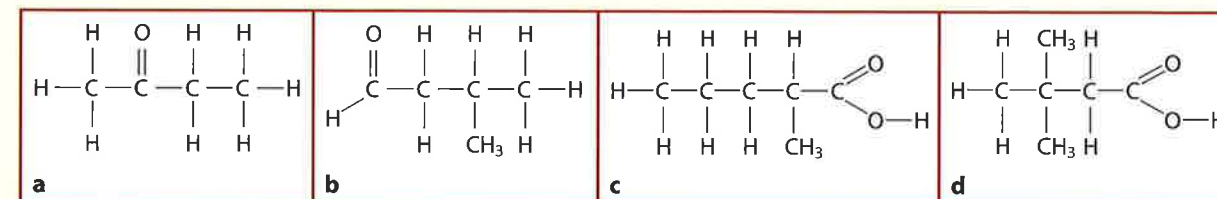
Table 10.12 The names of some aldehydes and ketones.

	methanoic acid		carboxylic acids
	ethanoic acid		
	propanoic acid		
	butanoic acid		
	4-methylpentanoic acid	numbering starts at the carboxylic acid group	
	2,3-dimethylbutanoic acid		
	butanedioic acid		

Table 10.13 The names of some carboxylic acids.

? Test yourself

9 Name the following compounds:



10 Draw the structures of each of the following molecules:

a butanal

b 2-methylpentanal

c pentan-3-one

Naming esters

Esters are formed by a reaction between a carboxylic acid and an alcohol and are named according to the carboxylic acid from which they are derived – two examples are given in Figure 10.15.

When writing condensed structural formulas, the ester group can be represented as 'COOC' – so ethyl ethanoate can be written $\text{CH}_3\text{COOCH}_2\text{CH}_3$.

The names of some more complicated esters are shown in Table 10.13.

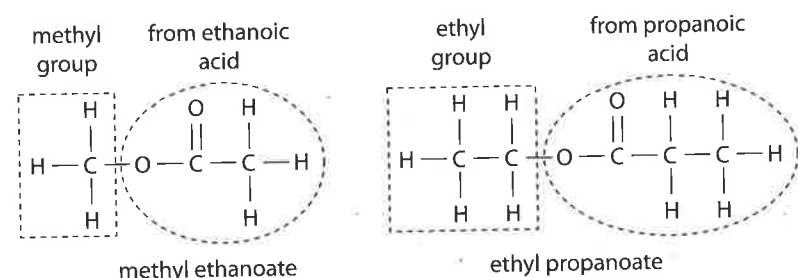


Figure 10.15 Naming esters.



Uses of esters

Many esters have a sweet, fruity smell and are used as artificial flavours and odours. Esters are often used to flavour sweets.

Probably the most controversial use of esters is as plasticisers (Option A), which are added to polymers such as PVC to make them more flexible. The use of phthalate esters such as DEHP is controlled in some countries due to fears that they could cause cancer.

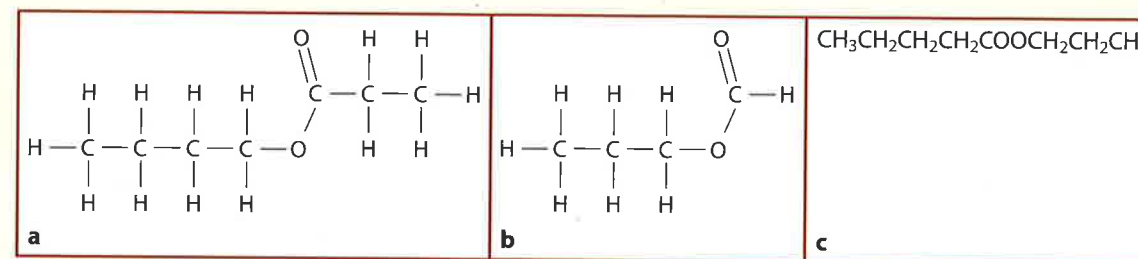


	ethyl 2-methylpropanoate	numbering in the acid derivative starts from the C=O group
	1-methylpropyl ethanoate	The longest carbon chain ending with the C attached to the O is taken. Thus, although there is a continuous carbon chain of 4 C atoms in the alkyl group, it does not have the C attached to the O at the end of the chain.

Table 10.13 Names of some esters.

? Test yourself

11 Name the following esters:



10.1.6 Primary, secondary and tertiary organic compounds

Primary, secondary and tertiary alcohols

Alcohols are described as **primary**, **secondary** or **tertiary** depending on the number of carbon atoms attached to the carbon with the $-\text{OH}$ group.

Ethanol is a primary alcohol because it has one carbon atom attached to the C with the $-\text{OH}$ group (Figure 10.16). Hence, a primary alcohol contains the $-\text{CH}_2\text{OH}$ group.

Propan-2-ol is a secondary alcohol because it has two carbon atoms attached to the C with the $-\text{OH}$ group. Hence, secondary alcohols (Figure 10.17) contain the $-\text{CHOH}$ group.

2-methylpropan-2-ol is a tertiary alcohol (Figure 10.18) because it has three C atoms attached to the C with the $-\text{OH}$ group.

With methanol, even though there are no other carbon atoms attached to the C with the $-\text{OH}$ group, it is worth noting that it is also a primary alcohol because it contains the $-\text{CH}_2\text{OH}$ group.

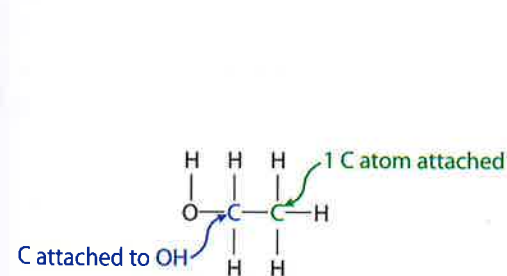


Figure 10.16 A primary alcohol – ethanol.

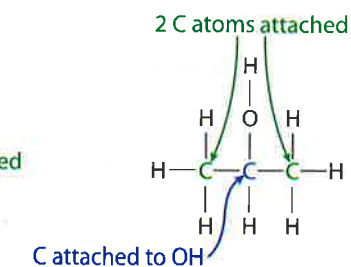


Figure 10.17 A secondary alcohol – propan-2-ol.

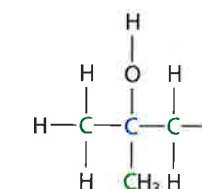
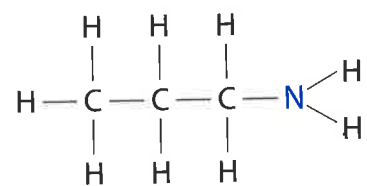


Figure 10.18 A tertiary alcohol – 2-methylpropan-2-ol.

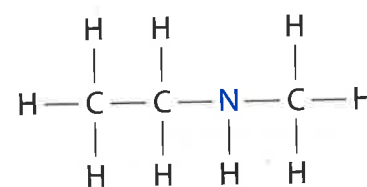
Learning objectives

- Distinguish between primary, secondary and tertiary alcohols
- Distinguish between primary, secondary and tertiary halogenoalkanes
- Distinguish between primary, secondary and tertiary amines

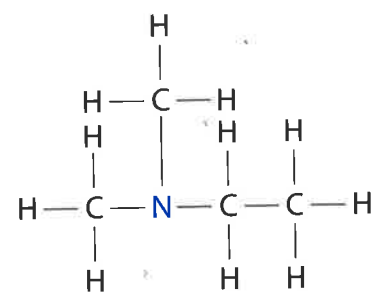
The symbol 1° is sometimes used for 'primary'. 2° can be used for 'secondary' and 3° for 'tertiary'.



a primary amine



b secondary amine

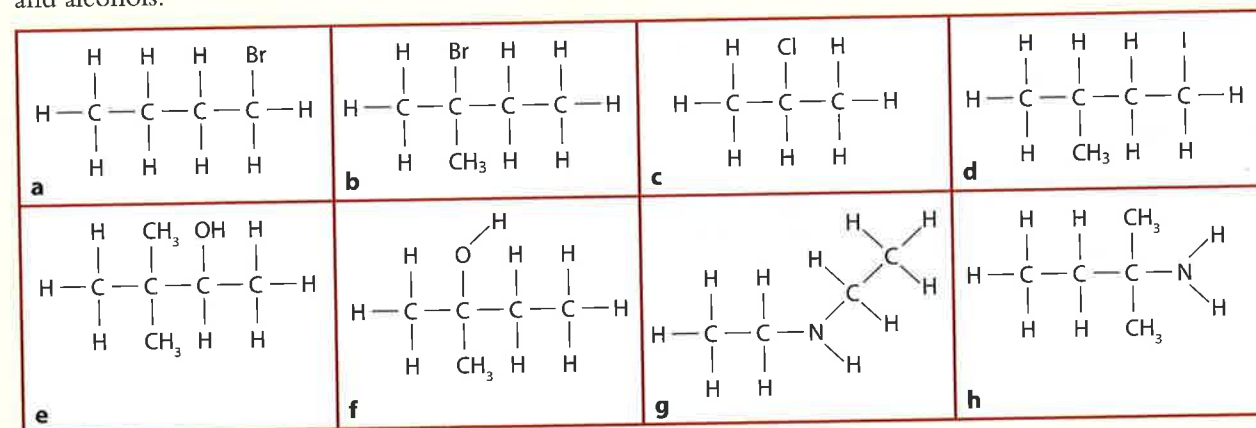


c tertiary amine

Figure 10.19 The structure of:
a propylamine; b ethylmethylamine;
c ethyldimethylamine.

? Test yourself

12 Classify each of the following molecules as primary, secondary or tertiary and name the halogenoalkanes and alcohols:



Primary, secondary and tertiary halogenoalkanes

Like alcohols, halogenoalkanes are also described as **primary**, **secondary** or **tertiary** depending on the number of carbon atoms (or alkyl groups) attached to the carbon atom of the C–X group. Table 10.14 summarises the three types.

	primary	The C attached to the Cl has only one C atom attached – one C attached = 'primary'.
	secondary	The C attached to the Br has two other C atoms attached – two Cs attached = 'secondary'.
	tertiary	The C attached to the Cl has three other C atoms attached – three Cs attached = 'tertiary'.

Table 10.15 Examples of primary, secondary and tertiary halogenoalkanes.

Primary, secondary and tertiary amines

Amines are also classified as primary, secondary or tertiary – but using slightly different reasoning. The focus here is on the nitrogen atom in the amine functional group. If the nitrogen atom is attached to one carbon atom and two hydrogen atoms then it is part of a primary amine; if nitrogen is attached to two carbon atoms and one hydrogen atom it is a secondary amine, and if nitrogen is attached to three carbon atoms and has no hydrogen atoms it is a tertiary amine. This means that:

- primary amines contain the –NH_2 functional group
- secondary amines contain –NHR (where 'R' represents an alkyl group)
- tertiary amines contain –NR_2 (see Figure 10.20).

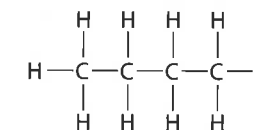
10.1.7 Isomers

There are various forms of isomerism – the simplest is **structural isomerism**.

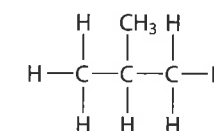
Structural isomers are two or more compounds that have the same molecular formula but different structural formulas – the atoms are joined together in different ways.

The two structural isomers with the molecular formula C_4H_{10} are:

- butane

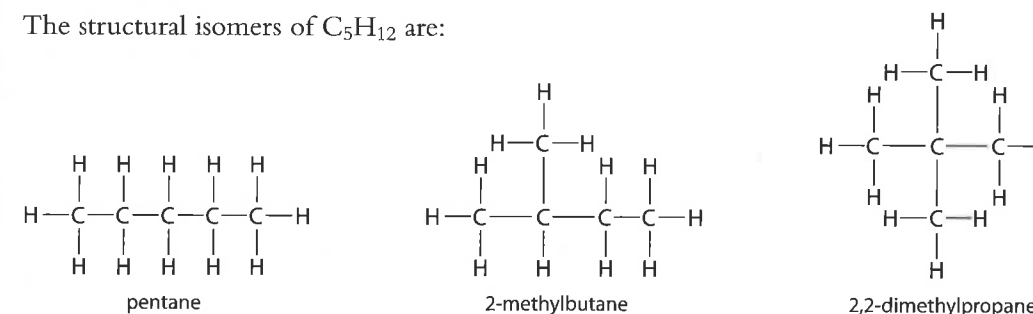


- 2-methylpropane



The second molecule has a branched chain and a longest carbon chain of three.

The structural isomers of C_5H_{12} are:



It is important to note that the structures shown in Figure 10.20 are *not* separate isomers of C_5H_{12} but are identical to each other. In a molecule in which only C–C single bonds are present, there is fairly free rotation about the single bond. Therefore, although we can show molecules bent into various conformations, if the atoms are joined together in the same way the molecules are *not* isomers.

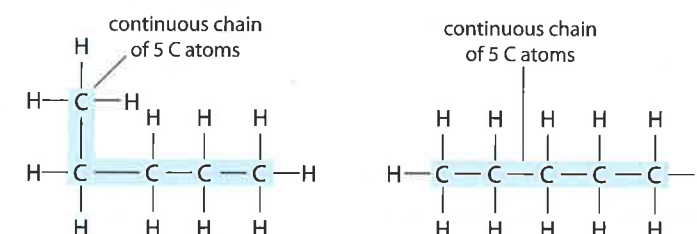


Figure 10.20 These two structures are drawn slightly differently. Careful examination reveals that all the atoms are joined together in exactly the same way and that there is a continuous chain of five carbon atoms in both structures. They are 'both' called Pentane.

Learning objectives

- Understand what is meant by structural isomerism
- Draw structural isomers for molecules with up to six carbon atoms

The '2' in this name is usually included, although the name would be unambiguous without it – there is only one possible structure for methylpropane. 1-methylpropane is butane!

Longest carbon chain in the molecule	Isomers		
chain of six C atoms	$ \begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{hexane} \end{array} $		
chain of five C atoms	<table border="0"> <tr> <td> $\begin{array}{cccccc} \text{H} & \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \\ \text{3-methylpentane} \end{array}$ </td> <td> $\begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ \text{2-methylpentane} \end{array}$ </td> </tr> </table>	$ \begin{array}{cccccc} \text{H} & \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \\ \text{3-methylpentane} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ \text{2-methylpentane} \end{array} $
$ \begin{array}{cccccc} \text{H} & \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \\ \text{3-methylpentane} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ \text{2-methylpentane} \end{array} $		
chain of four C atoms	<table border="0"> <tr> <td> $\begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ (\text{CH}_3)_3\text{CCH}_2\text{CH}_3 \\ \text{2,2-dimethylbutane} \end{array}$ </td> <td> $\begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} & & \\ (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 \\ \text{2,3-dimethylbutane} \end{array}$ </td> </tr> </table>	$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ (\text{CH}_3)_3\text{CCH}_2\text{CH}_3 \\ \text{2,2-dimethylbutane} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} & & \\ (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 \\ \text{2,3-dimethylbutane} \end{array} $
$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ (\text{CH}_3)_3\text{CCH}_2\text{CH}_3 \\ \text{2,2-dimethylbutane} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} & & \\ (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 \\ \text{2,3-dimethylbutane} \end{array} $		

Table 10.16 Isomers of C_6H_{14} .

The isomers of C_6H_{14} are shown in Table 10.16.

In general, branched-chain isomers have lower boiling points than straight-chain isomers. This is because the branches prevent the main chains from getting as close together, and so the London forces between the branched molecules are weaker.

Some isomers of C_6H_{12} are shown in Table 10.17. Different isomers can be obtained simply by moving the double bond to a different position.

$ \begin{array}{cccccc} \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} \\ \text{hex-2-ene} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} \\ \text{hex-3-ene} \end{array} $	$ \begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{CH}_3 & & \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}=\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & & \\ \text{2-methylpent-1-ene} \end{array} $
$ \begin{array}{cccccc} & & \text{H} & \text{CH}_3 & \text{H} & \\ & & & & & \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ \text{4-methylpent-1-ene} \end{array} $	$ \begin{array}{cccccc} & & \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ \text{2-methylpent-2-ene} \end{array} $	$ \begin{array}{cccccc} & & \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ & & & & & \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{H} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ \text{3-methylpent-2-ene} \end{array} $

Table 10.17 Some isomers of C_6H_{12} .

Isomers may have different functional groups – Figure 10.21 shows another isomer of C_6H_{12} that is not an alkene but contains a ring of (four) carbon atoms.

Isomers with different functional groups are sometimes called **functional group isomers**. Some functional group isomers are shown in Table 10.18.

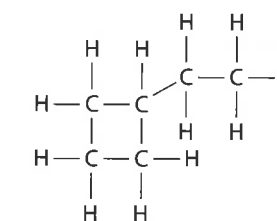


Figure 10.21 Ethylcyclobutane.

$ \begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{O} \\ & & \\ \text{H} & \text{H} & \\ \text{alcohol} \end{array} $	$ \begin{array}{ccc} \text{H} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\ & & \\ \text{H} & & \text{H} \\ \text{ether} \end{array} $
$ \begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C} \\ & & \backslash \\ \text{H} & \text{H} & \text{O}-\text{H} \\ \text{carboxylic acid} \end{array} $	$ \begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \\ \text{ester} \end{array} $
$ \begin{array}{ccc} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \\ \text{aldehyde} \end{array} $	$ \begin{array}{ccc} \text{H} & \text{O} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & \\ \text{H} & & \text{H} \\ \text{ketone} \end{array} $

Table 10.18 Some pairs of functional group isomers.

? Test yourself

- Draw and name all the isomers of C_4H_8 that are alkenes.
- Draw and name all the isomers of C_5H_8 that are alkynes.
- Draw all the esters that are isomeric with these carboxylic acids:
 - butanoic acid
 - pentanoic acid.



Chemists have agreed on a system for naming and classifying different molecules. Using various types of formula and this agreed system of names, chemists have their own language so that they can communicate with each other even when – in their everyday lives – they speak different languages.

How precise must the set of rules for this language be for chemists to make themselves understood? For instance, if you named pentane '1-methylbutane' or named 2-methylpentane '4-methylpentane' would everyone still understand what you meant? What if you named 2,2-dimethylbutane '2-dimethylbutane'?

Beyond school level, chemists often do not use systematic names when communicating with each other – why not?

Learning objective

- Explain the evidence for a delocalised structure for benzene



Figure 10.22 Kekulé benzene.

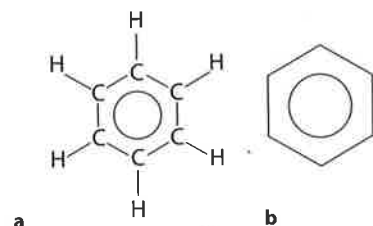


Figure 10.23 Benzene ring showing: **a** all the atoms; **b** the usual representation.

Delocalisation: electrons shared between three or more atoms.

Exam tip

The idea of delocalisation is not required at Standard Level but it helps to understand the structure of benzene.

The 'resonance hybrid' approach to the structure of benzene is discussed in Topic 4.

10.1.8 Benzene and aromatic compounds

Evidence for the structure of benzene

Benzene was first isolated in 1825 by Michael Faraday and its formula was known early on, but it was 40 years before a plausible structure was suggested. Kekulé proposed the original structure for benzene (Figure 10.22) and so it is usually called 'Kekulé benzene'. The structure consists of a planar, hexagonal ring of carbon atoms, with a hydrogen atom joined to each carbon atom.

This structure has alternating single and double bonds between the carbon atoms. A systematic name for this molecule would be cyclohexa-1,3,5-triene or 1,3,5-cyclohexatriene.

The structure was accepted for many years but eventually the weight of evidence against it became too great and a modified structure was proposed.

The structure of benzene is nowadays better represented as in Figure 10.23. Each carbon atom seems to form just three bonds – two to C atoms and one to an H atom.

The remaining electrons form a delocalised system of six electrons – this is represented by the circle in the centre of the structure. These six electrons are not localised between individual carbon atoms in double bonds but instead are spread over the whole ring.

The ring of electrons is formed when p orbitals overlap side-on to form a π delocalised system (Figure 10.24).

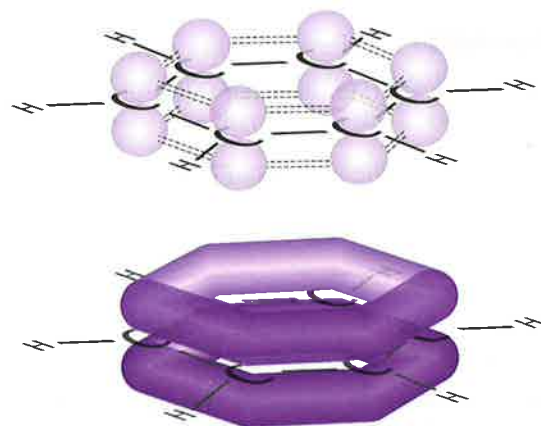


Figure 10.24 Formation of the benzene delocalised system.



Benzene is recognised as a human carcinogen which can cause leukemia. The main source of exposure to benzene in Europe is from car exhaust fumes, but benzene is used in some industrial applications and some people are exposed to it at work. Limits are usually set for occupational exposure to benzene but different countries set different limits on human exposure.

Evidence from carbon-carbon bond lengths

All C–C bond lengths are equal in benzene and also intermediate in length between a C–C single bond and a C=C double bond (Table 10.19). If the structure of benzene were cyclohexa-1,3,5-triene (Kekulé benzene) then it would be expected that there would be three short C=C bonds (approximately 0.133 nm) and three longer C–C bonds (approximately 0.154 nm).

The delocalised structure of benzene suggests a C–C bond length between that of a C–C bond and a C=C double bond because there are, on average, three electrons (two from the single bond and one from the delocalised electrons) between each pair of carbon atoms compared with four electrons in a C=C bond and two in a C–C bond.

Thermochemical evidence

When cyclohexene (C_6H_{10}) is heated with hydrogen in the presence of a nickel catalyst, cyclohexane (C_6H_{12}) is formed. This is an addition reaction in which hydrogen adds across the C=C bonds of the cyclohexene (Figure 10.25) – the enthalpy change is approximately -120 kJ mol^{-1} .

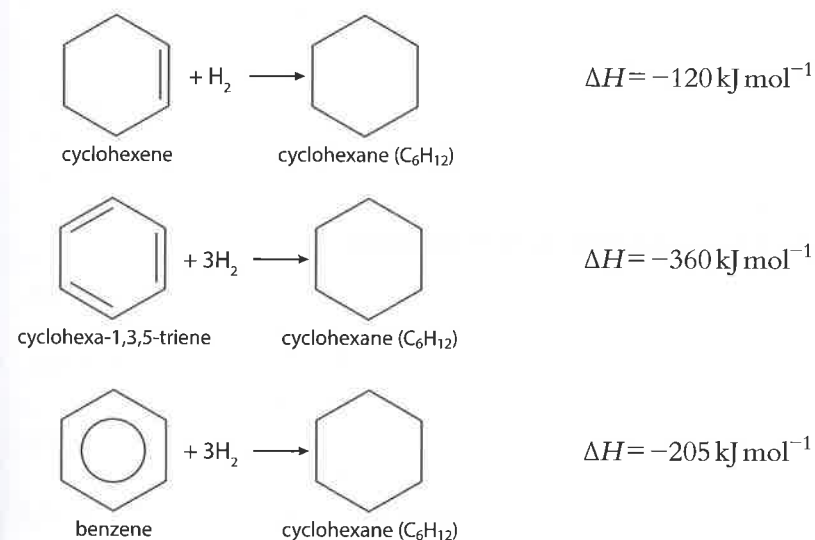


Figure 10.25 Comparing enthalpies of hydrogenation.

Cyclohexene molecules contain one C=C bond whereas cyclohexa-1,3,5-triene (Kekulé benzene) contains three. It would, therefore, be expected that the enthalpy change for the complete hydrogenation of cyclohexa-1,3,5-triene to cyclohexane would be 3×-120 , i.e. -360 kJ mol^{-1} . However, the enthalpy change when benzene undergoes complete hydrogenation to cyclohexane is only -205 kJ mol^{-1} .

If an enthalpy level diagram (Figure 10.26) is drawn for the hydrogenation reactions of benzene and cyclohexa-1,3,5-triene (Kekulé benzene), it is seen that benzene is 155 kJ mol^{-1} more stable than 'expected' – i.e. 155 kJ mol^{-1} more stable than would be predicted if it had the structure with alternating single and double carbon-carbon bonds.

The extra stability of benzene compared to the structure with alternating double and single bonds is due to the delocalisation of electrons.

Bond	Compound	Bond length / nm
C=C	ethene	0.133
C–C	ethane	0.154
C=C	benzene	0.140

Table 10.19 Bond lengths in ethene, ethane and benzene.

C–C bond lengths, and others, can be determined by X-ray crystallography.

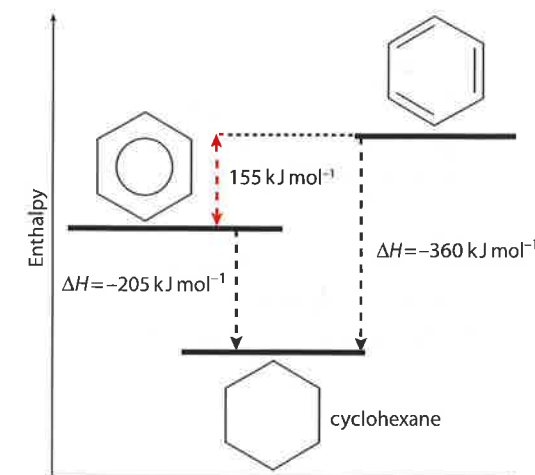


Figure 10.26 Comparative enthalpy changes for the hydrogenation reactions of benzene and Kekulé benzene.

Evidence from the number of isomers of C₆H₄Cl₂

Further evidence for a delocalised structure for benzene comes from examining the number of isomers that are possible for C₆H₄X₂ assuming a Kekulé structure and a delocalised structure (Figure 10.27).

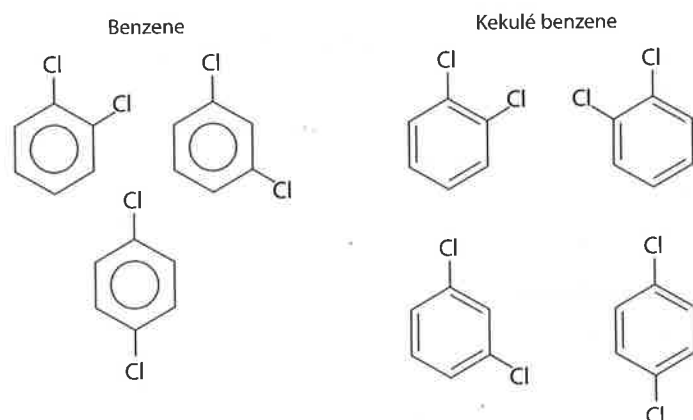


Figure 10.27 Possible isomers for C₆H₄Cl₂.

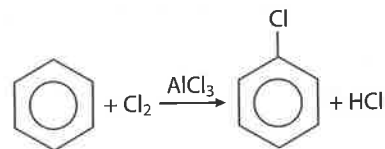
Only three isomers have ever been found for C₆H₄Cl₂ but the structure with alternating double and single bonds suggests that there should be four. The difference arises because two chlorine atoms that are on adjacent carbon atoms in the ring can either be separated by a C–C single bond or a C=C double bond, if benzene is assumed to have the the Kekulé structure.

Evidence from the reactions of benzene

Cyclohexa-1,3,5-triene (Kekulé benzene) would be expected to undergo addition reactions (like all other alkenes) and to decolorise bromine water. However, benzene does not react like alkenes – it does *not* undergo addition reactions under normal conditions and will *not* decolorise bromine water. An addition reaction would involve the destruction of the delocalised system and the loss of the extra stability associated with it.

Therefore benzene undergoes **substitution** reactions which involve replacement of one or more atoms on the ring with another atom or group.

For example, benzene reacts with chlorine in the presence of a catalyst such as aluminium chloride to form chlorobenzene, C₆H₅Cl:



Nature of science

The structure of benzene will never be directly observed but can be inferred from experimental data. All the evidence taken together can be explained in terms of the delocalised structure of benzene. Science often works like this – scientists use reasoning to explain things we can see in terms of things we cannot.

Although the delocalised ring may be temporarily disrupted in reactions, it is restored so that the extra stability is not lost.

Exam tip

The evidence for the structure of benzene can be classified as either **chemical** (enthalpy changes of hydrogenation and products of substitution reactions) or **physical** (C–C bond lengths, number of isomers).

10.2 Functional group chemistry

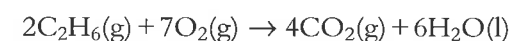
10.2.1 Alkanes

The alkanes are non-polar molecules with only London forces between molecules. This means that they are volatile (evaporate easily) – the first four members are gases at room temperature. Because of their non-polar nature, they are insoluble in water.

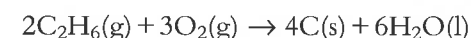
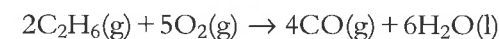
Reactions of alkanes

From a global perspective, the most important reaction of alkanes is **combustion** – these compounds form the basis of fuels such as petrol and natural gas (Figure 10.28).

Complete combustion of hydrocarbons requires the presence of excess air/oxygen and produces carbon dioxide and water:



When there is a limited supply of air/oxygen, **incomplete combustion** occurs – this produces carbon monoxide and soot (C) as well as water:



The actual equation for the combustion of ethane is a combination of these three equations, and CO₂, CO and carbon are all produced if there is not sufficient oxygen present for complete combustion.

Incomplete combustion is dirtier than complete combustion, producing a smoky flame and the toxic gas carbon monoxide (which binds to hemoglobin more strongly than oxygen does, so oxygen is prevented from being transported by the blood).

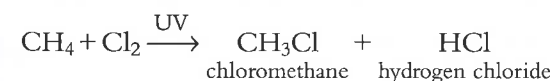
Unreactivity of alkanes

Apart from combustion, alkanes are generally fairly unreactive. The reasons for this are:

- the high strengths of C–C and C–H bonds means that it is generally energetically unfavourable to break them in a reaction
- C–C and C–H bonds are essentially non-polar and so are unlikely to attract polar molecules or ions.

Reaction of alkanes with halogens

Alkanes react with halogens in the presence of sunlight or ultraviolet (UV) light. There is no reaction in the dark at room temperature. The equation for the reaction between methane and chlorine in the presence of UV light is:



Learning objectives

- Write equations for the complete and incomplete combustion of alkanes
- Explain why alkanes are not very reactive
- Write equations for the reactions of alkanes with halogens
- Explain the free radical substitution mechanism



Figure 10.28 The carbon compounds in crude oil can be used to make medicines, plastics (polymers) and lots of other extremely useful chemicals and products. Is crude oil too valuable to burn?



Many deaths occur each year through accidental carbon monoxide

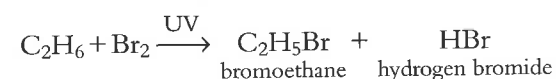
poisoning, which occurs as a result of poorly serviced or poorly ventilated heating systems. Worldwide, carbon monoxide poisoning is probably the leading cause of death/injury through poisoning. The famous French author Émile Zola died of carbon monoxide poisoning.



Chloromethane is an important contributor to the destruction

of the ozone layer (page 174). A significant source of chloromethane is from natural sources such as wood-rotting fungi.

That between ethane and bromine is:



If we look at this reaction in terms of full structural formulas (Figure 10.29), we can see what is happening more clearly.

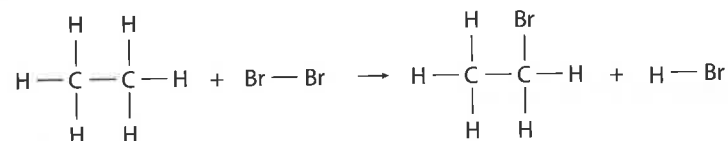


Figure 10.29 The reaction between ethane and bromine.

A **substitution** reaction is one in which an atom or a group is replaced by a different atom or group. In Figure 10.29, a hydrogen atom in ethane is replaced by a bromine atom.

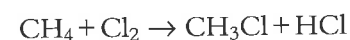
The reactions shown here all involve mono-substitution – the replacement of *one* hydrogen atom in the molecule by *one* halogen atom. However, the reaction is difficult to control and a mixture of products, some of which involve multiple substitutions, is formed:



The mechanism for these reactions is called **free radical substitution**. It proceeds in a series of steps.

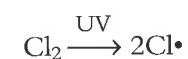
Free radical substitution

Consider the reaction between methane and chlorine:



Initiation

The first stage involves breaking apart chlorine molecules into separate chlorine atoms:



The energy needed to do this is provided by the UV light. The Cl–Cl bond (242 kJ mol^{-1}) is weaker than the C–H bond (412 kJ mol^{-1}) and, therefore, it is the Cl–Cl bond that is broken.

The chlorine atoms produced have only seven electrons in their outer shell and so each has an unpaired electron – this is represented by the dot in the symbol. The chlorine atoms are described as **free radicals**.

Free radicals are species (atoms or groups of atoms) with an unpaired electron. Free radicals are very reactive because of this unpaired electron.

This first step in the reaction mechanism involves an increase in the number of free radicals – it is called the **initiation step**.

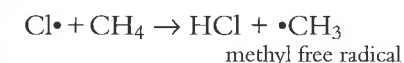
This process is called **homolytic fission**. When the covalent bond (made up of two electrons) breaks, one electron goes back to each atom that made up the original molecule – in this case to form two species that are the same ('homo' means 'same').

This movement of one electron going back to each atom can be shown with single-headed curly arrows (fish-hooks):

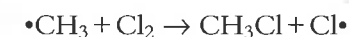


Propagation

A chlorine free radical is a very reactive species – when it collides with a methane molecule in the reaction mixture, it will combine with a hydrogen atom to pair up its unpaired electron:



A highly reactive methyl free radical is generated in this step, and this will react with a Cl_2 molecule to form a C–Cl bond:

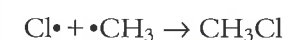


The $\text{Cl}\cdot$ generated in this step can go on to react with another methane molecule, so that the **propagation** cycle starts again (Figure 10.30).

This is an example of a **chain reaction** because one initial event causes a large number of subsequent reactions – with the reactive species being regenerated in each cycle of reactions.

Termination

In the reaction mixture, the free radicals are always present in very low concentrations so the chance of two colliding is very low. However, they do collide sometimes and this brings the chain reaction to an end. There are several possible **termination** reactions:



Each termination reaction involves a decrease in the number of free radicals.

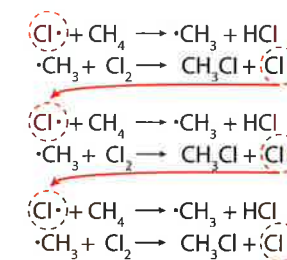
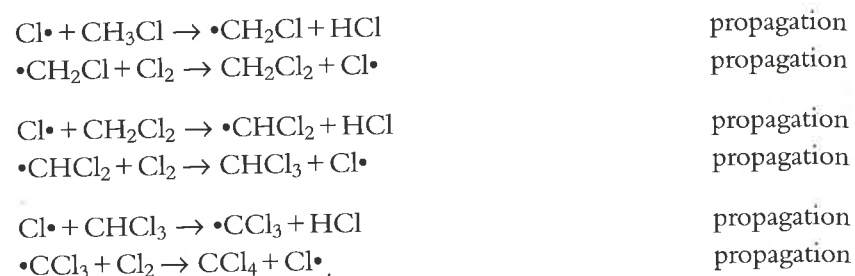


Figure 10.30 The propagation step is repeated over and over again.

- Initiation: increase in the number of free radicals.
- Propagation: no change in the number of free radicals.
- Termination: decrease in the number of free radicals.

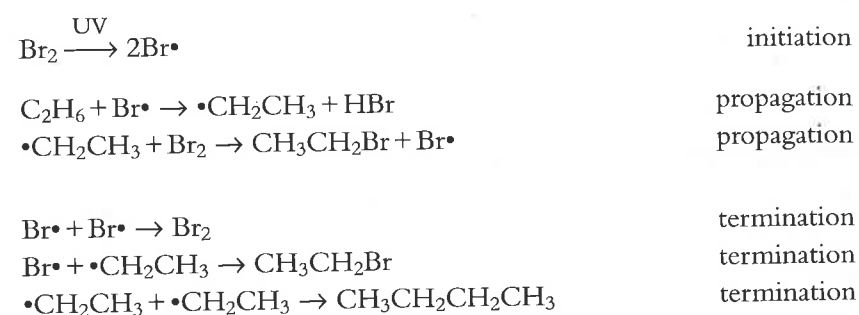
Formation of other products

Formation of multi-substituted products occurs when a chlorine free radical collides with a different molecule in the first propagation step:



Ethane and bromine

The mechanism for the reaction of ethane with bromine can be shown as follows:



Other alkanes

These reactions do not just occur with methane and ethane – all alkanes react in a similar way. Figure 10.31 shows what happens when butane reacts with chlorine in the presence of UV light; there are two possible mono-chlorinated products.

There are, of course, many multi-substituted products as well.

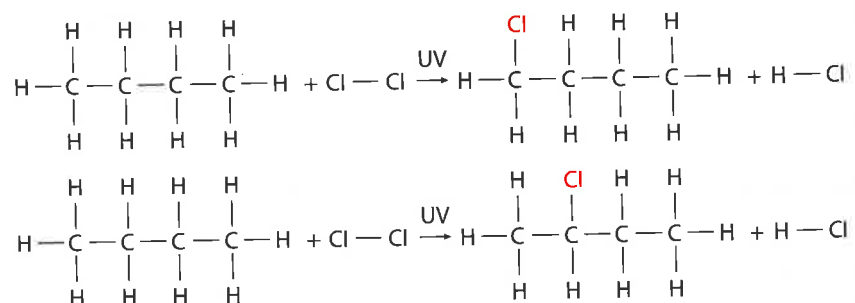


Figure 10.31 The formation of more than one mono-substituted product when butane reacts with chlorine.

? Test yourself

- Write an equation for the complete combustion of pentane.
- Write an equation for the incomplete combustion of propane producing carbon monoxide.
- Write an equation for the reaction of ethane with chlorine in the presence of UV light.
- How many mono-chlorinated organic products are possible when chlorine reacts with each of the following molecules in the presence of UV light?
 - hexane
 - 2-methylpropane
 - 2,2-dimethylpropane
- Write the mechanism for the reaction between chlorine and ethane in the presence of UV light.

10.2.2 Reactions of alkenes and alkynes

Alkenes have C=C double bonds – another way of saying this is that the functional group in alkenes is C=C.

The alkenes, like the alkanes, have non-polar molecules with only London forces between them. This means that they are volatile – the first four members are gases at room temperature. They are also insoluble in water because of their non-polar nature.

Saturated and unsaturated compounds

As mentioned above, alkenes and alkynes are called **unsaturated** compounds because they contain C=C bonds or C≡C bonds. Alkanes, and other compounds not containing multiple bonds, are described as **saturated**.

Reactions of alkenes

Alkenes are more reactive than alkanes. There are two reasons for this:

- the double bond (612 kJ mol^{-1}) is not twice as strong as a single bond.

The reactions of alkenes usually involve the C=C bond breaking to form a C–C bond (348 kJ mol^{-1}). The second component (π bond) of the C=C bond is weaker than a normal C–C single bond (σ bond) and is, therefore, more easily broken.

- the double bond (four electrons) represents a region of high electron density, and therefore it attracts electrophiles.

Addition reactions

Alkenes undergo **addition reactions**. The general reaction is shown in Figure 10.32 – ‘R’ represents either an alkyl group or hydrogen:

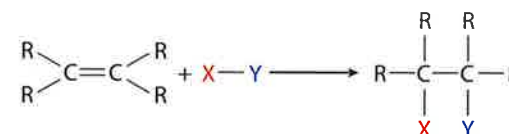


Figure 10.32 Addition reaction of alkenes.

Learning objectives

- Understand why alkenes are more reactive than alkanes
- Describe the addition reactions of alkenes
- Explain how to distinguish between alkanes and alkenes using bromine water
- Understand that benzene reacts differently to alkenes
- Understand the polymerisation reactions of alkenes

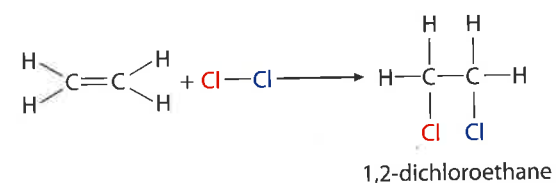
An **electrophile** is a reagent (a positively charged ion or the positive end of a dipole) that is attracted to regions of high electron density and accepts a pair of electrons (Lewis acid) to form a covalent bond.

The reaction of an alkene with iodine is very slow at room temperature.

The molecule X–Y is added across the double bond, which leaves a single bond between the carbon atoms.

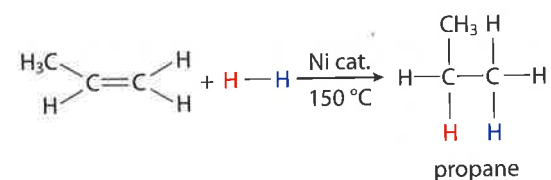
Alkenes and halogens

Alkenes react with halogens at room temperature:



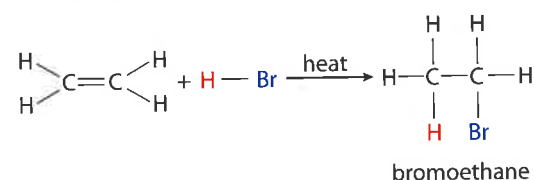
Alkenes and hydrogen

Alkenes react with hydrogen when heated in the presence of a catalyst, such as finely divided nickel, to form alkanes. This reaction is called **hydrogenation**.

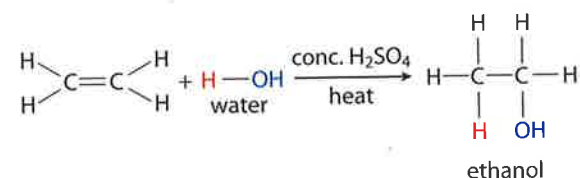


Alkenes and hydrogen halides

Alkenes react with hydrogen halides, such as hydrogen bromide, by bubbling the alkene through a concentrated solution of the hydrogen halide at 100 °C.



Alkenes and water



In the laboratory, this reaction can be carried out by passing ethene through concentrated sulfuric acid at room temperature and then warming the product with water.



The reaction between an alkene and water is called **catalytic hydration** and is used in the industrial production of ethanol, an important solvent. The process is carried out by reacting ethene (from crude oil) with steam at 300 °C and 6000 kPa pressure with an H₃PO₄ catalyst. Ethanol can also be produced by fermentation, which uses a renewable raw material (sugar) and a much lower temperature (although a major energy input can come when ethanol is distilled). The proportion of ethanol (Figure 10.33) produced by these processes varies from country to country and has also varied over time as the use of ethanol as a fuel additive has increased. The leading producers of ethanol for fuel use by fermentation are the US and Brazil. Brazil has pioneered the use of gasoline–ethanol blends as fuels for light vehicles and indeed pure gasoline is no longer available in Brazil as a fuel for cars.



Figure 10.33 Blends of ethanol and gasoline are becoming ever more important fuels for cars in some parts of the world.



Unsaturated fats (C=C bonds present) from vegetable sources tend to be liquids at room temperature and are called oils. Saturated fats (no C=C bonds) from animal sources are solids at room temperature.

Hydrogenation of alkenes is used in the manufacture of margarine. A polyunsaturated oil contains many C=C bonds (Figure 10.34). The double bonds are all shown as *cis* (groups either side of the C=C bond are on the same side – see page 390). It is the presence of *cis* double bonds that gives an oil its low boiling point.

Margarine is made from vegetable oils (liquids) and partial hydrogenation can be carried out to convert some of the C=C bonds into C–C single bonds. This increases the melting point of the margarine so that it is a solid at room temperature (Figure 10.35). However, the process produces *trans*-fatty acids (groups either side of the C=C bond are on opposite sides) and these are believed to be bad for health. Partially hydrogenated

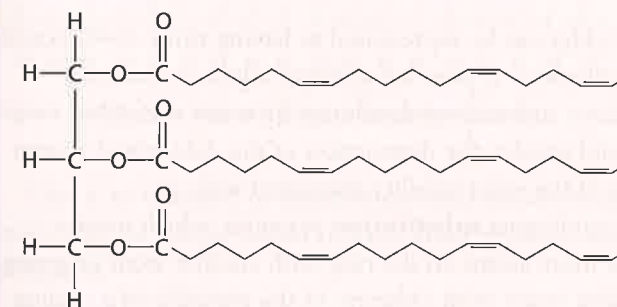


Figure 10.34 The basic structure of a polyunsaturated oil.

vegetable oils have been banned in some countries.

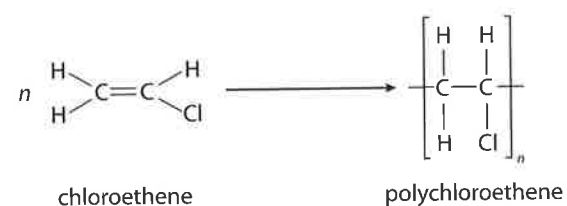
Some countries have a very high consumption of saturated fat and this has been linked to increased rates of cardiovascular disease (but the data are not conclusive and the link not universally accepted). The so-called ‘Mediterranean diet’ is regarded by many people as a particularly healthy one and has been linked with low incidences of heart disease. This diet is low in saturated fats, with fat consumption mainly in the form of olive oil, which is rich in monounsaturated fats.



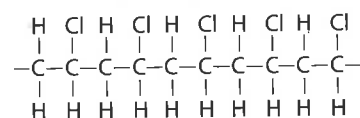
Figure 10.35 Different cooking oils and spreads contain different amounts of saturated/unsaturated fats.

PVC – polyvinylchloride

This is more properly known as polychloroethene. It is made by the polymerisation of chloroethene monomers at a moderate temperature and pressure in the presence of an organic peroxide:



The structure shown in square brackets as the product of this reaction is called the **repeating unit** of polychloroethene – many of these are joined to make a polymer chain:



Polypropene

Remember that it is important to understand that it is only the C=C group that reacts when polymerisation occurs – all the other groups attached to the C=C unit are unaffected. This can be seen if we look at the polymerisation of propene (Figure 10.39). The methyl group attached to the C=C unit does not become part of the main polymer chain – just a side group on the chain.

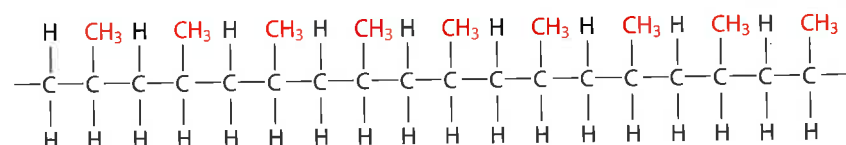
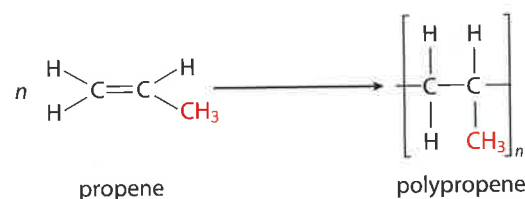


Figure 10.39 Polymerisation of propene.

The repeating unit of a polymer is the base from which the whole polymer chain can be made up. In each of the equations used so far, this has been shown in square brackets. The repeating unit for polypropene is shown in Figure 10.40.

The repeating unit for any polymer (Figure 10.41) can be identified simply by taking any two adjacent carbon atoms in the main polymer chain.

The monomer of a polymer can be derived (Figure 10.42) by simply placing a double bond between the two carbon atoms of the repeating unit.

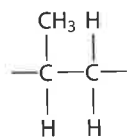


Figure 10.40 Repeating unit of polypropene.

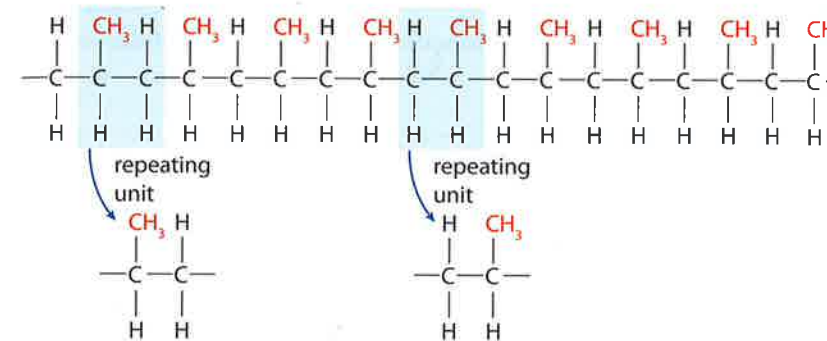


Figure 10.41 Identifying a repeating unit.

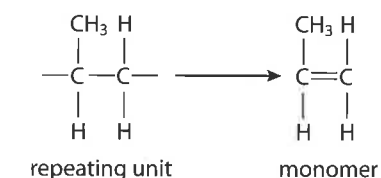


Figure 10.42 Identifying a monomer.



Economic importance of polymers

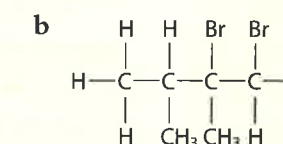
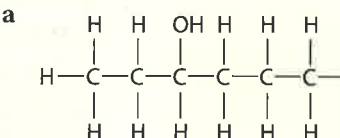
The polymers described here are more commonly known as ‘plastics’ and find extensive uses in everyday life. Among other things, polyethene is used for making plastic bags, washing-up bowls and bottles; polychloroethene is used for making insulation for electrical cables and window frames; and polypropene is used for making car bumpers and carpet fibres.

These substances are produced in vast quantities by the petrochemicals industry and present a huge environmental problem, both from the point of view of using crude oil (petroleum) – a limited natural resource – and in their disposal after use because they are non-biodegradable. Different countries tackle the problem of disposal of plastics in different ways – countries such as Denmark and Switzerland mostly incinerate plastics, whereas Finland and Ireland mainly use landfill sites. Recycling is growing in importance in some countries but attitudes towards environmental problems are far from uniform across the world.

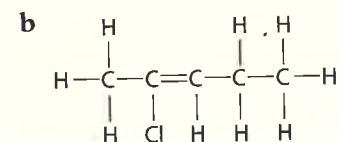
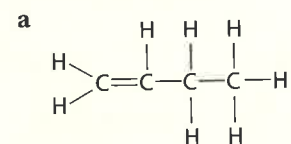
? Test yourself

- 21 Draw the structures of the products of the following reactions (which occur under the appropriate conditions):
- but-1-ene + hydrogen
 - hex-3-ene + hydrogen bromide
 - pent-2-ene + chlorine
 - but-2-ene + water

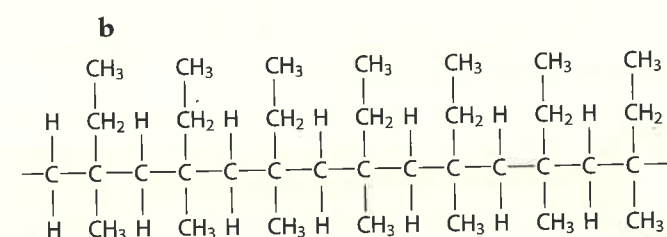
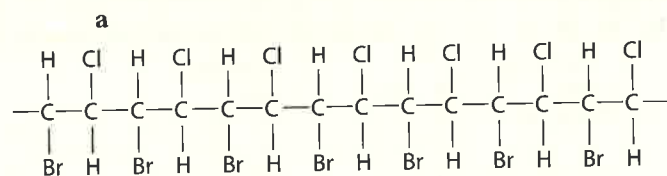
- 22 Write equations, using structural formulas, for the formation of the following compounds from appropriately chosen alkenes:



23 Draw the repeating units for the polymers formed from these alkenes:



24 Draw the monomers used to make the following polymers:



Learning objectives

- Write equations for the complete combustion of alcohols
- Describe the oxidation reactions of alcohols
- Understand that carboxylic acids can react with alcohols to form esters

Exam tip

Don't forget the word 'acidified' when describing the oxidising agent.

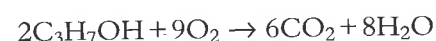
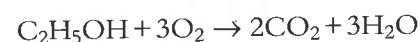
The potassium ions are not important in these reactions – the $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- ions are the important parts – the sodium salts would work equally well.

10.2.3 Reactions of compounds containing oxygen

Reactions of alcohols

Combustion of alcohols

In a plentiful supply of oxygen, alcohols burn to produce carbon dioxide and water:



Exam tip

When balancing these equations, don't forget the oxygen in the alcohol!

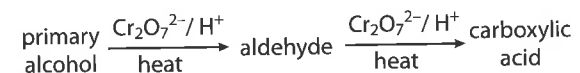
Oxidation

Alcohols can be classified as primary, secondary or tertiary (page 439) according to the number of carbon atoms joined to the carbon attached to the OH group.

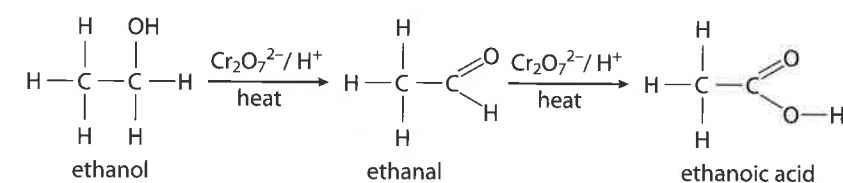
Primary and secondary alcohols can be oxidised using an oxidising agent such as acidified potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$) or acidified potassium manganate(VII) (KMnO_4/H^+).

Primary alcohols

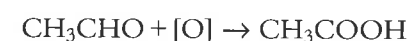
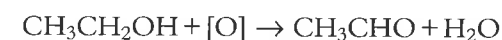
Primary alcohols are oxidised, first to an aldehyde (partial oxidation). Then the aldehyde is oxidised further to a carboxylic acid (complete oxidation).



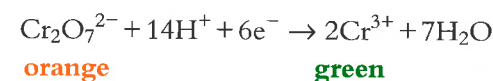
For example:



Each reaction can be shown as a balanced equation using [O] to represent oxygen from the oxidising agent:



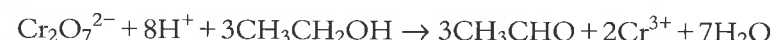
However, if a fully balanced equation for the oxidation of an alcohol using acidified dichromate(VI), is required we must consider the half-equations involved. $\text{Cr}_2\text{O}_7^{2-}$ (orange) is the oxidising agent and is reduced during the reaction (to the green $\text{Cr}^{3+}(\text{aq})$ ion). The half-equation for the reduction is:



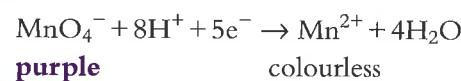
In the first reaction, the oxidation half-equation is:



The two half-equations can be combined by multiplying the oxidation half-equation by three to generate 6e^- and then adding them together. When H^+ ions are cancelled from both sides the overall equation obtained is:



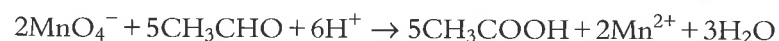
The half-equation for the reduction of manganate(VII) ions (purple) to colourless $\text{Mn}^{2+}(\text{aq})$ ions is:



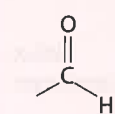
The half-equation for the oxidation of ethanal to ethanoic acid is:



To get the overall redox equation for the oxidation of ethanal by acidified manganate(VII) we need to balance the electrons – so the oxidation half-equation is multiplied by five and the reduction half-equation by two:

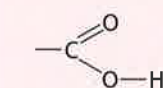


Aldehydes contain the



functional group.

Carboxylic acids have the



functional group.

Colour change: orange → green

Colour change: purple → colourless

Exam tip

The half-equations for the reduction of $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ and $\text{MnO}_4^-/\text{H}^+$ are given in the IB Chemistry data booklet.

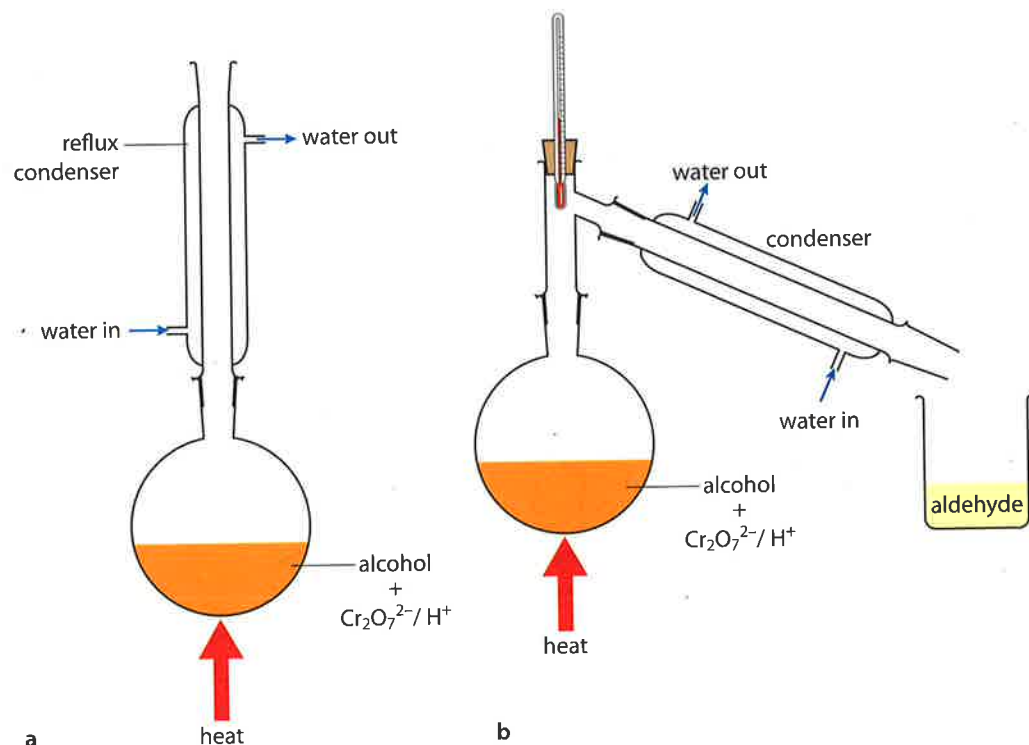
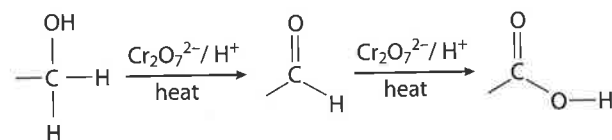


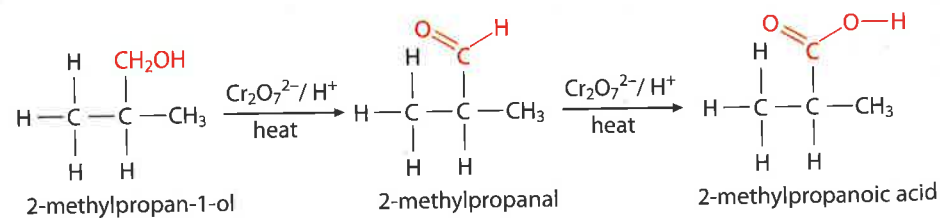
Figure 10.43 **a** Apparatus for reflux – this produces a carboxylic acid (complete oxidation); **b** apparatus for distillation – this produces an aldehyde (partial oxidation).

If a reaction mixture containing ethanol and acidified potassium dichromate(VI) is heated under **reflux**, ethanoic acid is obtained as the main product and the aldehyde is not usually isolated. However, it is possible to set up the apparatus so that the aldehyde is **distilled** off as soon as it is formed and before it can be oxidised further (Figure 10.43). This technique works because aldehydes have lower boiling points than the equivalent alcohols (and all other components of the reaction mixture) because they do not have a hydrogen atom attached directly to an oxygen atom, and therefore there is no hydrogen bonding between molecules.

If we look at the oxidation of primary alcohols in terms of changes to the functional groups, it is easier to generalise the reaction to other compounds:



Consider the oxidation of 2-methylpropan-1-ol:



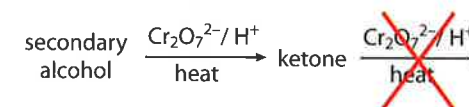
The only changes involve the groups highlighted in red – the rest of the molecule is unchanged.



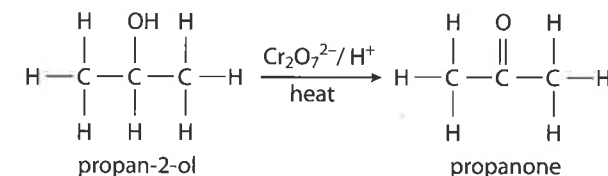
Here we are using inductive reasoning. We are making the assumption that because all primary alcohols we have so far encountered can be oxidised by acidified potassium dichromate(VI) to an aldehyde and then a carboxylic acid, then *all* primary alcohols will be oxidised in this way. Can we ever know this?

Secondary alcohols

Secondary alcohols are also oxidised by heating with acidified potassium dichromate(VI) (or acidified potassium manganate(VII)). They are oxidised to **ketones**, which cannot be oxidised any further.



For example:



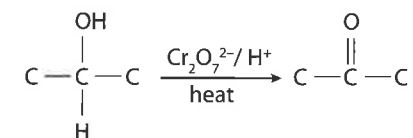
The balanced equation for the reaction is:



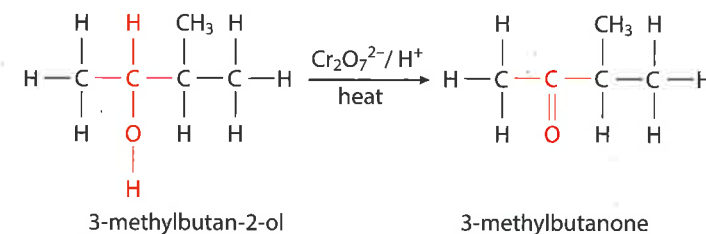
or



In terms of changes to the functional group, the reaction can be represented as:

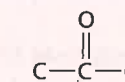


Looking at the reaction of another secondary alcohol:



The only change is to the group highlighted in red – the rest of the molecule is unchanged.

Ketones contain the

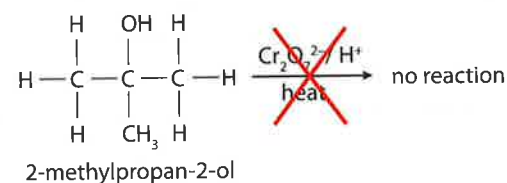


functional group.

[O] represents oxygen from the oxidising agent.

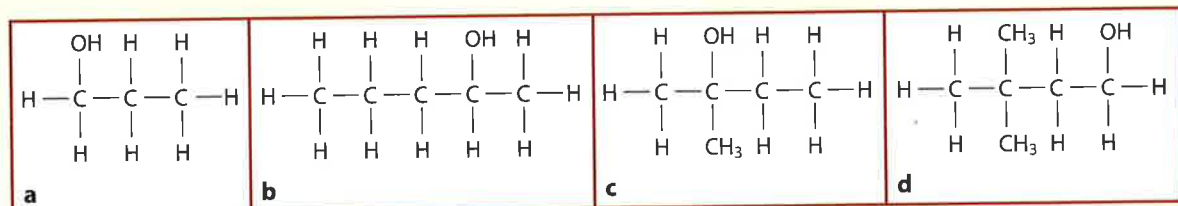
Tertiary alcohols

Tertiary alcohols are resistant to oxidation.



? Test yourself

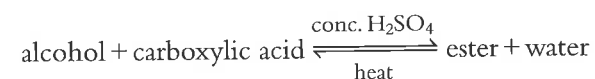
- 25 Write a balanced equation for the complete combustion of butan-1-ol.
26 Name the following alcohols and classify each as primary, secondary or tertiary:



- 27 For each of the alcohols in question 26, give the structural formula of the product (if any) of complete oxidation when they are heated with acidified potassium dichromate(VI).
28 Give the structure of the organic product formed when each of the following alcohols is heated with acidified potassium dichromate(VI) with the apparatus set up for distillation:
a 3-methylbutan-1-ol
b 2-methylpentan-3-ol
c 2,3-dimethylpentan-1-ol

Esters

When an alcohol is heated with a carboxylic acid in the presence of a small amount of concentrated sulfuric acid as a catalyst, an ester is formed. The reaction is called **esterification**:



For example:

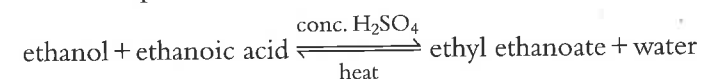


Figure 10.44 shows the reaction more clearly using structural formulas.

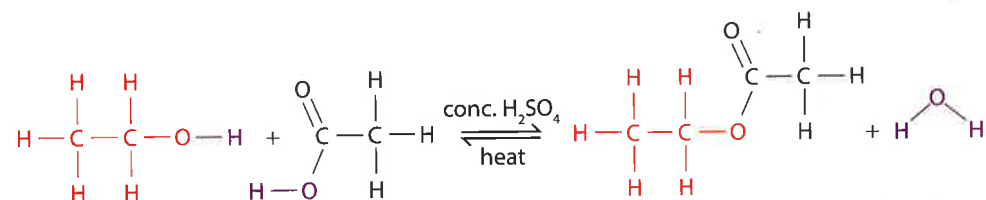


Figure 10.44 An esterification reaction.

The alcohol and the carboxylic acid have been joined together and water has been eliminated – one H atom from the alcohol joins with the –OH group from the carboxylic acid.

The product formed when any alcohol and any carboxylic acid come together can be worked out simply by putting the alcohol and carboxylic acid together (Figure 10.45) so that the two O–H groups are next to each other – the H from the OH of the alcohol along with the OH of the carboxylic acid are removed and the O of the alcohol is joined to the C=O group of the carboxylic acid.

Other examples of esterification reactions are shown in Figure 10.46. The reaction between an alcohol and a carboxylic acid can be described as a **nucleophilic substitution** reaction. The alcohol acts as a **nucleophile** and substitutes (replaces) the OH group of the carboxylic acid.

The esterification reaction can also be classified as a **condensation reaction** – a reaction in which two molecules join together with the elimination of the elements of water.

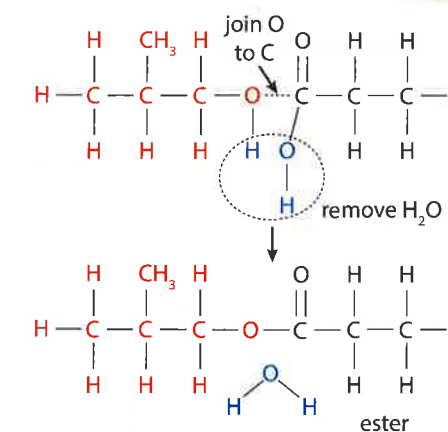


Figure 10.45 The esterification reaction dissected.

Nucleophilic substitution reactions are covered in more detail in the following pages.

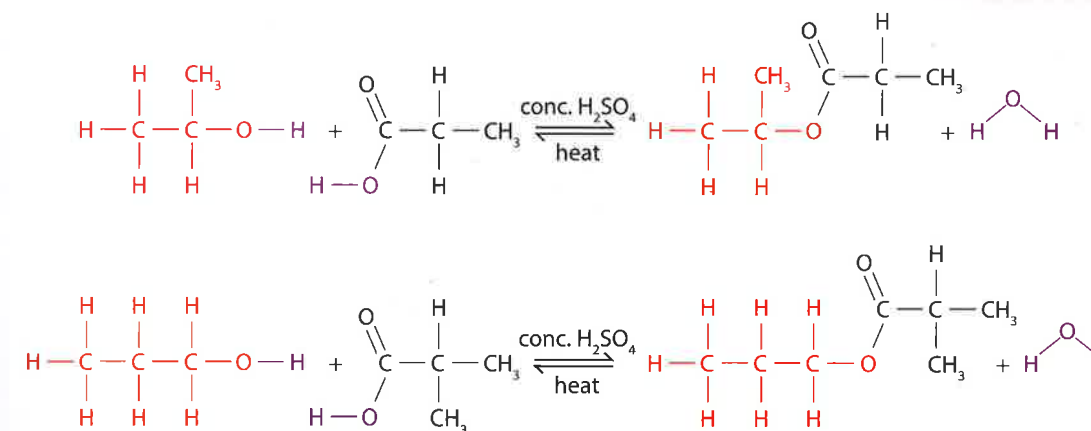


Figure 10.46 Typical esterification reactions.

? Test yourself

29 Copy and complete the following table:

	Alcohol	Carboxylic acid	Ester
a	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O} \\ & & & \\ \text{H} & \text{H} & \text{H} & \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C} \\ \\ \text{O}-\text{H} \end{array}$	
b	$\begin{array}{cccc} & \text{CH}_2\text{OH} & & \\ & & & \\ \text{H} & \text{C} & \text{H} & \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & \text{CH}_3 & \text{H} & \end{array}$	$\begin{array}{cccc} \text{H} & \text{CH}_3 & \text{H} & \text{O} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C} & & & \\ & & & \\ \text{H} & \text{CH}_3 & \text{H} & \text{O}-\text{H} \end{array}$	
c			$\begin{array}{c} \text{O} & \text{H} \\ & \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{CH}_3 \\ & \\ \text{CH}_3 & \text{H} \end{array}$
d			$\begin{array}{cccc} & \text{O} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{H} & \text{C} & \text{C} & \text{C} & \text{C}-\text{H} \\ & & & & \\ \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} \end{array}$

30 Name the ester formed in question 29a.

31 Write a balanced chemical equation for the reaction occurring in question 29a.

Learning objectives

- Describe the reaction of halogenoalkanes with aqueous sodium hydroxide
- Understand that halogenoalkanes undergo nucleophilic substitution reactions

Substitution reaction: one atom or group is replaced by another atom or group.

10.2.4 Halogenoalkanes

Nucleophilic substitution reactions

Halogenoalkanes usually undergo **substitution reactions**. Figure 10.47 shows what happens when, for example, 1-bromopropane is heated with aqueous sodium hydroxide – the Br atom is replaced by an OH group to form propan-1-ol:

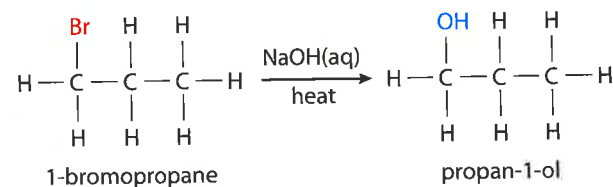
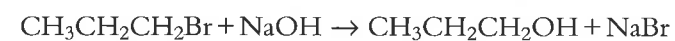
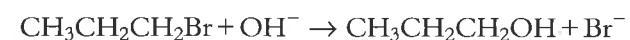


Figure 10.47 A nucleophilic substitution reaction.

The balanced equation for this reaction is:



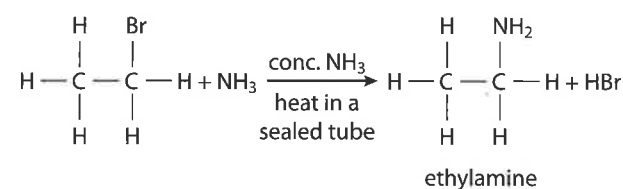
or, as an ionic equation:



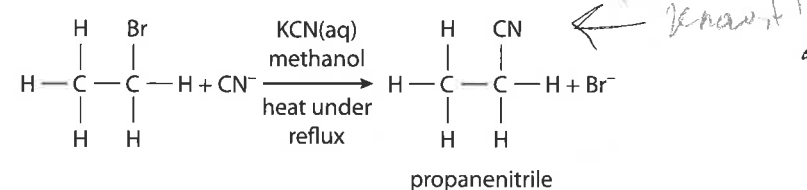
This reaction is also known as **hydrolysis** because it is essentially equivalent to breaking molecules apart using water.

The type of mechanism by which this reaction occurs is **nucleophilic substitution** – the halogenoalkane is attacked by a **nucleophile** and the nucleophile replaces the halogen atom. It is covered in more detail in the Higher Level section on the next page.

Halogenoalkanes can also react with ammonia to form amines:



... and with potassium cyanide to form nitriles:



Note that the nitrile contains the $-\text{CN}$ functional group with a triple bond between the carbon atom and the nitrogen atom. The longest continuous carbon chain in the molecule is now three C atoms, and so the name is **propanenitrile**. This makes this type of reaction useful because it provides a way of increasing the length of the carbon chain.

We have seen in this section that halogenoalkanes are more reactive than alkanes – this is due to the presence of the halogen atom. For instance, if a chlorine atom (very electronegative) is present in a molecule, the $\text{C}-\text{Cl}$ bond will be polar and a nucleophile will be attracted to the δ^+ carbon atom. Another factor is that Cl^- is classified as a ‘good leaving group’ – the $\text{C}-\text{Cl}$ bond is weaker than a $\text{C}-\text{C}$ bond or a $\text{C}-\text{H}$ bond and Cl^- is stable in many solvents.

Nature of science

Data is extremely important in science. The collection of large amounts of data about functional group interconversions has been fundamental in developing synthetic routes to making vast numbers of key organic compounds.

A **nucleophile** is a molecule or negatively charged ion that has a lone pair of electrons – it is attracted to a relatively highly positively charged region in a molecule (a region with lower electron density) and donates a lone pair of electrons to form a covalent bond.

There are various ways of naming amines and the amine shown here could also be called ethanamine or aminoethane.

Learning objectives

- Explain S_N1 and S_N2 mechanisms
- Explain the factors that affect the rate of nucleophilic substitution of halogenoalkanes

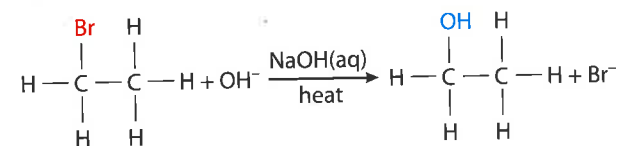
10.3 Types of organic reactions (HL)

10.3.1 Nucleophilic substitution mechanisms

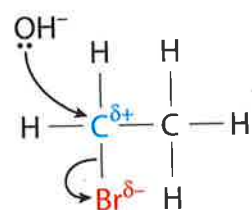
The exact nature of a nucleophilic substitution reaction depends on which type of halogenoalkane is involved in the reaction – primary, secondary or tertiary.

Primary halogenoalkanes – the S_N2 mechanism

Consider the reaction of bromoethane with sodium hydroxide:



Br is more electronegative than C, so the carbon atom is slightly positive (δ^+) and the OH^- ion is attracted to it. The hydroxide ion is a **nucleophile** and donates a lone pair of electrons to the carbon atom to form a (coordinate) covalent bond (it acts as a Lewis base) – see Figure 10.48. The curly arrow shows the lone pair on OH^- becoming a bonding pair of electrons between the oxygen and carbon. A carbon atom can have a maximum of eight electrons in its outer shell, and therefore as the C–O bond forms, the C–Br bond must break.



The arrows are called **curly arrows** and represent the movement of a pair of electrons.

Figure 10.48 The nucleophile (OH^-) attacks.

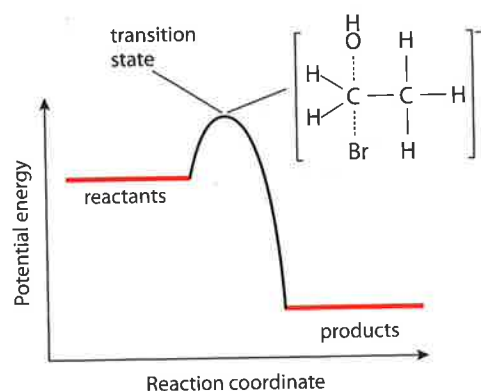


Figure 10.49 Potential energy profile of nucleophilic substitution.

The C–Br bond breaks such that both electrons from the C–Br bond go back to the bromine atom to form a bromide ion – as shown by the curly arrow from the C–Br bond to the Br. This is called **heterolytic fission** – the bond breaks so that both electrons go to the same atom. (This should be contrasted with the homolytic fission of the Cl–Cl bond during the free radical substitution mechanism described on page 448–449.)

Part way through this nucleophilic substitution process, both the OH and the bromine are partially joined to the carbon (Figure 10.49), and this is often shown in the mechanism. This is not an intermediate in the reaction but is the highest point on the potential energy profile – often called the **transition state** or **activated complex**.

Figure 10.50 shows the full mechanism for the reaction of bromoethane with aqueous sodium hydroxide.

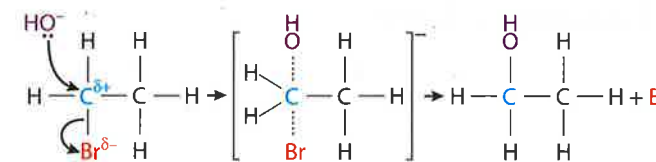


Figure 10.50 A typical S_N2 reaction mechanism.

This is a single-step mechanism and the formation of the transition state is just part of the way along this step. The mechanism could be shown just as well without this, as in Figure 10.51.

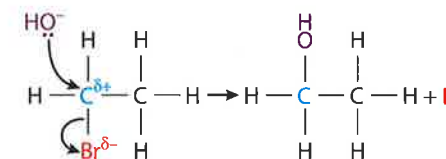


Figure 10.51 A simplified version of the S_N2 mechanism.

S_N2 is the main mechanism for substitution in reactions of primary halogenoalkanes. The 'shorthand' is explained in Figure 10.52.

The '2' indicates the molecularity of the reaction – this was introduced in Topic 6. It refers to the number of molecules (or ions) that take part in a particular step (usually the rate-determining step) in a mechanism.

The rate-determining step is the slowest step and, therefore, the step that governs the overall rate of reaction. The S_N2 mechanism occurs in a single step, so this must be the rate-determining step. The rate equation for the above reaction is:

$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$$

This means that if the concentration of either bromoethane or sodium hydroxide is doubled, the rate of reaction is doubled.

In the S_N2 mechanism the OH^- ion approaches the $\text{C}^{\delta+}$ atom from the opposite side to the Br, and this results in inversion of the tetrahedral configuration of the central carbon atom – like an umbrella turning inside out (Figure 10.53).

This reaction is described as *stereospecific* because the stereochemistry (arrangement of groups around a chiral centre) of the reactant determines the stereochemistry of the product. If a nucleophile attacks a chiral centre, the reaction will occur with inversion of configuration. This will be discussed further in the section on optical isomers on page 495.

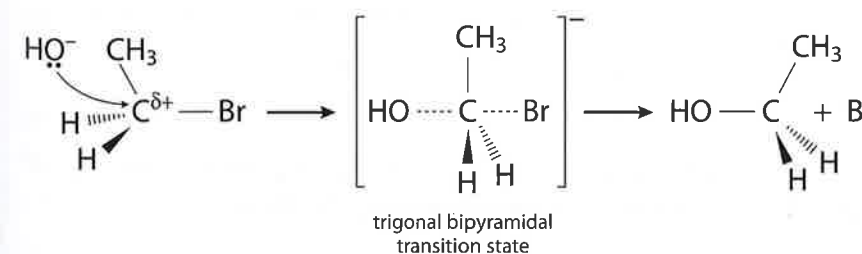


Figure 10.53 A change in spatial configuration.

Exam tip

In the transition state, you must show that the oxygen of the OH is joined to the carbon (OH---C is not correct).

Exam tip

Note that the transition state must be shown in an answer to an exam question.

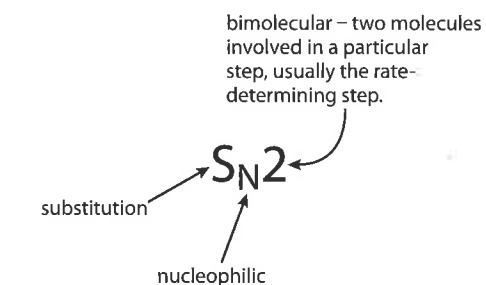
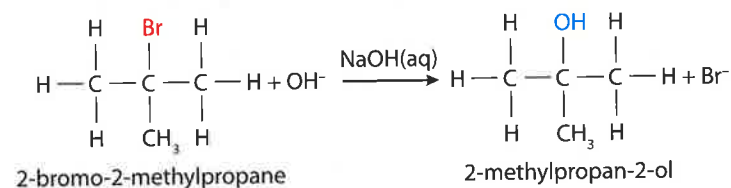


Figure 10.52 What S_N2 means.

Molecularity and order are not the same thing. 'Order' is an experimentally determined quantity that relates the concentrations of reactants to the rate. 'Molecularity' refers to the number of molecules (or ions) that take part in a particular step (usually the rate-determining step) in a mechanism.

Tertiary halogenoalkanes

Consider the reaction of 2-bromo-2-methylpropane with aqueous sodium hydroxide. This occurs fairly rapidly at room temperature:



Studies of the rate of this reaction have determined that the rate does not depend on the concentration of the sodium hydroxide, unlike in the S_N2 mechanism discussed earlier. This reaction must, therefore, have a different mechanism.

In the first step, the C–Br bond breaks to form a positively charged carbocation (Figure 10.54). This is the rate-determining step in the mechanism.

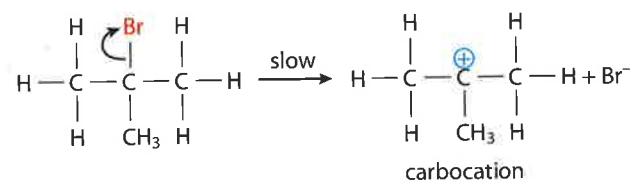


Figure 10.54 An intermediate species is formed.

Once formed, the carbocation is open to attack by nucleophiles, such as the OH⁻ ion (Figure 10.55).

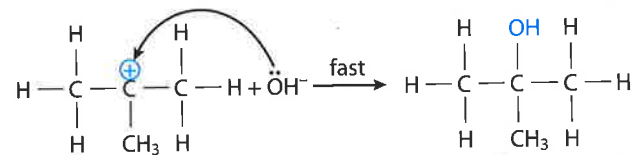


Figure 10.55 The intermediate is attacked by a nucleophile rapidly.

This mechanism is described as S_N1 – ‘substitution nucleophilic unimolecular’ because there is only one molecule (the halogenoalkane) involved in the rate-determining step.

The nucleophile is only involved in the mechanism in a fast step that happens after the rate-determining step and so does not appear in the rate equation. The rate equation for the above reaction is:

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

The effects of changing the concentration of a nucleophile on the rate of S_N1 and S_N2 mechanisms are summarised in Table 10.20.

Mechanism	Rate equation	Effect of doubling the concentration of the nucleophile
S _N 1	rate = k [halogenoalkane]	No effect – nucleophile is only involved in a fast step after the rate-determining step.
S _N 2	rate = k [halogenoalkane][nucleophile]	Rate doubles – nucleophile is involved in the rate-determining step.

Table 10.20 The effect of changing the concentration of the nucleophile on the rate of S_N1 and S_N2 mechanism reactions.

In the first step of the S_N1 mechanism, the carbocation formed is planar (Figure 10.56) and so the nucleophile is equally likely to attack the central carbon from either side in the second step.

This reaction is not stereospecific – the stereochemistry of the final product is random. A racemic mixture would be formed if the original halogenoalkane were optically active (see page 499).

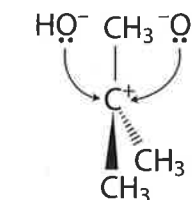


Figure 10.56 The nucleophile is equally likely to attack from either side.

The effect of the halogen on the rate of nucleophilic substitution

The rate of nucleophilic substitution of halogenoalkanes by hydroxide ions is fastest with iodo-compounds – the order of decreasing rate is R–I > R–Br > R–Cl > R–F.

Both S_N2 and S_N1 mechanisms involve the C–X bond breaking in the rate-determining step. The C–I bond is easiest to break (Table 10.21), so the reaction will be fastest using iodoalkanes.

This factor is much more important than any effects due to electronegativity differences – the C–X bond is least polar in iodoalkanes, so it might be expected that the carbon atom should attract a nucleophile least strongly.

The effect of the nucleophile on the rate of nucleophilic substitution

S_N2 reactions are generally faster when ions are involved rather than neutral molecules. OH⁻ ions will react faster than H₂O molecules because the higher negative charge on the O in OH⁻ means it will be more strongly attracted to the C^{δ+} atom in the halogenoalkane.

The rate of an S_N1 reaction is not affected by changing the nucleophile because the nucleophile attacks only *after* the rate-determining step.

Why two different mechanisms?

For primary halogenoalkanes, the dominant mechanism is S_N2, whereas for tertiary halogenoalkanes it is S_N1. Secondary halogenoalkanes undergo nucleophilic substitution via a mixture of the two mechanisms – the more dominant mechanism will depend on the specific conditions of the reaction.

Why is S_N2 more favourable for primary halogenoalkanes than for tertiary halogenoalkanes?

This is mainly because of **steric effects**. The alkyl groups surrounding the central carbon in a tertiary halogenoalkane make it much more difficult

Bond	Bond energy / kJ mol ⁻¹
C–F	484
C–Cl	338
C–Br	276
C–I	238

Table 10.21 C–halogen bond enthalpies.

Extension

I⁻ is described as a better leaving group than Cl⁻. The polarisability of the iodine atom and the stability of the I⁻ ion in solution also play a role in making I⁻ a better leaving group than Cl⁻.

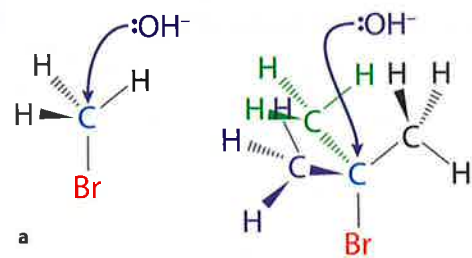


Figure 10.57 **a** Attack of OH^- on a primary and a tertiary halogenoalkane – steric effects are to do with the size/bulkiness of groups; **b** A space-filling model of 2-bromo-2-methylpropane – the nucleophile must attack the area highlighted pink.

- The more highly substituted the C, the slower the rate of $\text{S}_{\text{N}}2$.
- The more highly substituted the C, the faster the rate of $\text{S}_{\text{N}}1$.

Extension

The electron-releasing effect of alkyl groups can be understood in terms of donation of electron density from a σ bond of the carbon atom attached to the C^+ into the vacant p orbital on the C^+ . This is called σ conjugation, or hyperconjugation.

for the nucleophile to get in to attack the central carbon atom as shown in Figure 10.57a. This can also be seen if we look at the space-filling model of 2-bromo-2-methylpropane in Figure 10.57b.

Another way of explaining this is that if the OH^- did get in to attack the carbon, there would be five large groups surrounding the central carbon atom in the transition state – this would lead to instability and the activation energy would be very high.

So the overall rate of reaction for $\text{S}_{\text{N}}2$ reactions of halogenoalkanes is: primary > secondary > tertiary.

Why is $\text{S}_{\text{N}}1$ more favourable for tertiary halogenoalkanes?

This is because of the stability of the intermediate carbocation. Methyl groups (and alkyl groups in general) have an **electron-releasing** effect (also called a positive inductive effect) so that they are able to stabilise a positively charged carbon atom to which they are bonded. The order of stability of carbocations is shown in Figure 10.58.

This electron-releasing effect of alkyl groups means that the charge is spread out most in the tertiary carbocation – it has most alkyl groups around the positively charged carbon atom. This stabilises the ion, making it more likely to be formed. So the overall rate of reaction for $\text{S}_{\text{N}}1$ reactions of halogenoalkanes is: tertiary > secondary > primary.

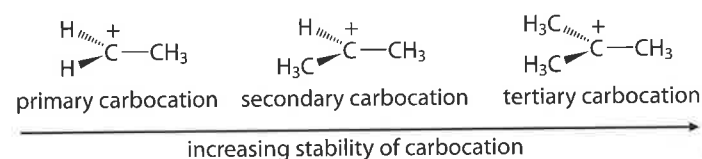


Figure 10.58 The order of stability of carbocations.

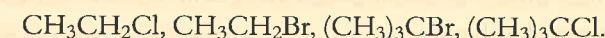
In the reactions of aqueous sodium hydroxide with halogenoalkanes, the $\text{S}_{\text{N}}1$ reactions of tertiary halogenoalkanes are faster than $\text{S}_{\text{N}}2$ reactions of primary halogenoalkanes.

Extension

It is very difficult to draw an overall conclusion about the effect of the structure of a halogenoalkane (primary, secondary, tertiary) on the rate of nucleophilic substitution because it depends on so many factors. Measurement of the rate of reaction of a series of related compounds with dilute aqueous ethanolic sodium hydroxide by the pioneer in this field, Christopher Ingold, produced the order $(\text{CH}_3)_3\text{CBr} > \text{CH}_3\text{Br} > \text{CH}_3\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHBr}$. However, it is also possible to carry out simple laboratory experiments, by adding silver nitrate solution to a series of isomeric primary, secondary and tertiary halogenoalkanes dissolved in ethanol, that produces the order tertiary > secondary > primary.

Worked example

10.1 Arrange the following in order of rate of nucleophilic substitution by aqueous sodium hydroxide:



The first two are primary halogenoalkanes and will react via an $\text{S}_{\text{N}}2$ mechanism; the final two are tertiary halogenoalkanes and will react via an $\text{S}_{\text{N}}1$ mechanism.

Tertiary halogenoalkanes react more quickly than primary halogenoalkanes.

A C–Br bond is weaker than a C–Cl bond and is therefore broken more easily meaning that, within each type of halogenoalkane, bromo-compounds react faster.

The overall order is $(\text{CH}_3)_3\text{CBr} > (\text{CH}_3)_3\text{CCl} > \text{CH}_3\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{Cl}$.

The effect of the solvent on the rate of nucleophilic substitution

The nature of the solvent can have a big effect on the rate of nucleophilic substitution reactions. Solvents can be divided into two broad classes – non-polar and polar. Non-polar solvents include hydrocarbons such as hexane (C_6H_{14}) and tetrachloromethane (CCl_4). Polar solvents can be further subdivided into protic and aprotic solvents:

- **Protic** solvents have a hydrogen atom joined to N or O and can participate in hydrogen bonding – examples are water, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and ammonia.
- **Aprotic** polar solvents do not have a hydrogen atom joined to N or O and cannot participate in hydrogen bonding – examples are propanone, $[(\text{CH}_3)_2\text{CO}]$ and dimethyl sulfoxide (DMSO), $(\text{CH}_3)_2\text{SO}$. These solvents do not act as proton donors.

Protic polar solvents are able to solvate both negative ions and positive ions in solution. Negative ions are solvated by interaction (Figure 10.59) with the H atoms that are attached to O or N using hydrogen bonding.

Aprotic polar solvents are good at solvating positive ions but the absence of very positive hydrogen atoms means that they are not very good at solvating negative ions.

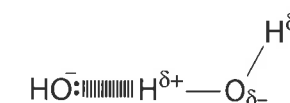


Figure 10.59 Negative ions (OH^-) are solvated by hydrogen bonding interactions with protic solvents.

- $\text{S}_{\text{N}}1$ reactions are favoured by protic, polar solvents.
- $\text{S}_{\text{N}}2$ reactions are favoured by aprotic, polar solvents.

Two ions are formed in the rate-determining step of an $\text{S}_{\text{N}}1$ reaction and these are stabilised by the presence of a protic solvent, which is able to solvate both ions effectively. The rate of an $\text{S}_{\text{N}}1$ reaction would be decreased by switching from a protic solvent to an aprotic polar solvent – the aprotic solvent is not as good at solvating the negative ion formed in the rate-determining step.

The rate-determining step of an S_N2 mechanism involves the attack of a negative ion on the halogenoalkane. In the presence of a protic solvent, this negative ion will be surrounded by solvent molecules and will not be a very effective nucleophile – it is being kept away from the δ^+ carbon atom by the solvent molecules that are surrounding it. In an aprotic polar solvent, the nucleophile is not surrounded by solvent molecules and is free to attack the δ^+ carbon atom. The rate of an S_N2 reaction would be decreased by switching from an aprotic polar solvent to a protic polar solvent – solvation by the protic solvent makes the nucleophile less effective.

When the nucleophile is a negative ion, the S_N2 mechanism is favoured by switching to a non-polar solvent. This does not solvate the nucleophile and also, because the negative charge is more spread out in the transition state than in the original nucleophile, the starting materials are destabilised more than the transition state by the presence of a non-polar solvent and the activation energy is lowered, speeding up the reaction. However, when choosing a solvent for a reaction, other factors must also be taken into account and the solvent must be able to dissolve the halogenoalkane and the nucleophile.

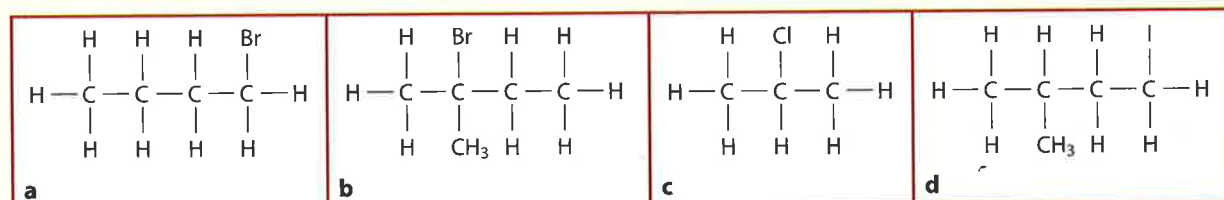
Nature of science

Experimental data have to be collected to allow the development of theories about reaction mechanisms. Determination of the rate equation and looking at the stereochemistry of reactants and products are both important in providing information to propose a mechanism for nucleophilic substitution.

The ideal situation for carrying out scientific experiments is to change just one variable while controlling all others. In order to determine the effect of the nucleophile, the solvent etc. on the rate of nucleophilic substitution, ideally only one factor should be changed each time. The limitations of the data must be considered when trying to draw general conclusions because all the measurements may not have been made under the same conditions. For instance, it is not easy to answer the question ‘Is the S_N1 or S_N2 mechanism faster?’ because several factors influence the reaction rate.

? Test yourself

- 32 State whether each of the halogenoalkanes below reacts with NaOH(aq) via an S_N1 mechanism or an S_N2 mechanism.



- 33 Give the structural formula of the products formed when each of the substances in question 32 reacts with NaOH(aq) .

10.3.2 Electrophilic addition reactions of alkenes

The addition reactions of alkenes were covered earlier (page 451–452). The mechanism for these reactions is **electrophilic addition**.

An electrophile is an electron-deficient species (a positively charged ion or the positive end of a dipole) that is attracted to regions of relatively high electron density and accepts a pair of electrons to form a covalent bond – electrophiles are Lewis acids (page 310).

The $\text{C}=\text{C}$ bond has four electrons and is a region of relatively high electron density in a molecule. Electrophiles will be attracted to this.

The reaction of ethene with hydrogen bromide

The overall equation is shown in Figure 10.60.

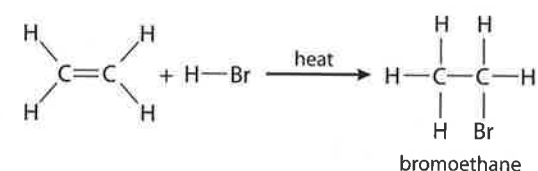


Figure 10.60 Addition to an alkene.

The mechanism is shown in Figure 10.61.

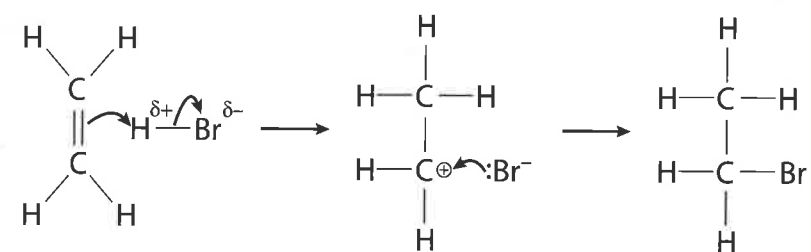


Figure 10.61 The mechanism of the reaction of ethene with hydrogen bromide.

$\text{H}-\text{Br}$ is polar – as shown by $\text{H}^{\delta+}$ and $\text{Br}^{\delta-}$. The hydrogen atom is attracted to the high electron density region in the $\text{C}=\text{C}$ bond.

The curly arrow from the π component of the $\text{C}=\text{C}$ bond to $\text{H}^{\delta+}$ represents the movement of a pair of electrons.

In the first stage, a pair of electrons is donated from the π bond in $\text{C}=\text{C}$ to form a bond between C1 (Figure 10.62) and the hydrogen atom of the $\text{H}-\text{Br}$ molecule. At the same time, the $\text{H}-\text{Br}$ bond breaks and the pair of electrons from this bond goes to a bromine atom.

Learning objectives

- Explain what is meant by an electrophile
- Explain the electrophilic addition reactions of alkenes
- Predict and explain the formation of the major product when a hydrogen halide reacts with an unsymmetrical alkene

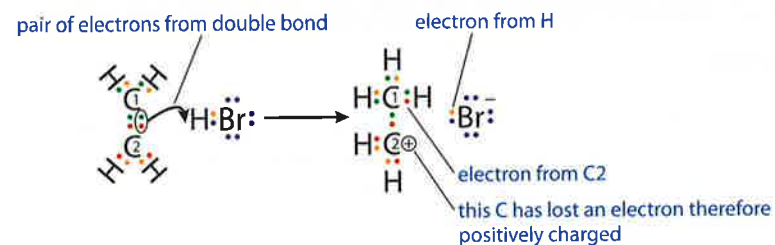


Figure 10.62 Movement of electrons in reaction of ethene with hydrogen bromide.

The alkene can be classified as a Lewis base (electron pair donor) and the hydrogen bromide as a Lewis acid (electron pair acceptor).

C2 has lost an electron (this electron is now in the C–H bond) and so C2 has a positive charge. The intermediate formed is called a **carbocation** (a positively charged organic ion with a positive charge on a carbon atom). The bromine atom gains an electron from the H–Br bond and therefore becomes a negatively charged bromide ion. In the second stage, the Br[−] ion is attracted to the C[⊕] atom and donates a pair of electrons to form a bond (Lewis acid–base reaction). The electron distribution in the final product is shown in Figure 10.63.

The initial type of bond breaking, when the H–Br bond breaks, is called **heterolytic fission** because the bond breaks so that both electrons go to the same atom (Figure 10.64).

This should be compared with homolytic fission of the Cl–Cl bond in the free radical substitution mechanism described on page 448.

Reaction of propene with HBr

When HBr adds to propene, two products are possible – shown in Figure 10.65.

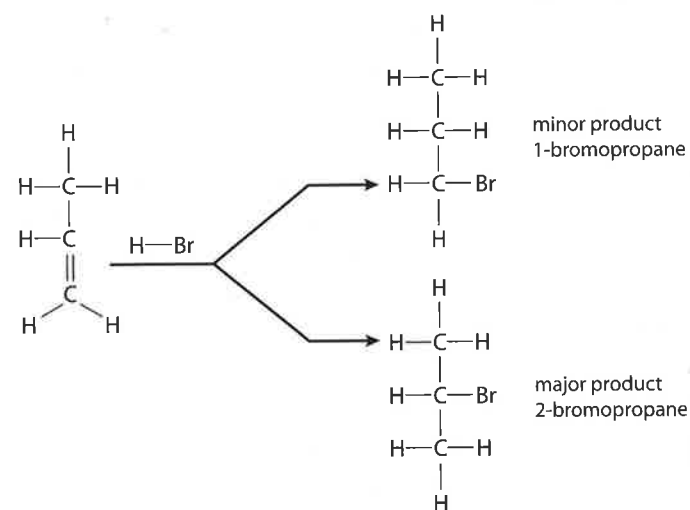


Figure 10.65 Addition of hydrogen bromide to propene.

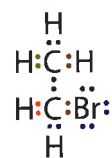


Figure 10.63 The location of the original electrons in the final product, bromoethane.

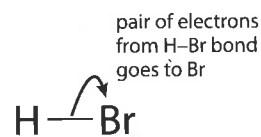


Figure 10.64 Heterolytic fission.

The major product (the minor product is usually made in only very small amounts) can be predicted using **Markovnikov's rule**.

Markovnikov's rule: when H–X adds across the double bond of an alkene, the H atom becomes attached to the C atom that has the larger number of H atoms already attached.

Markovnikov's rule can be used to predict the major product formed when H–X adds to any unsymmetrical alkene. When H–Cl adds to 2-methylpropene, the H atom of the HCl becomes attached to C1 (Figure 10.66) because this has two hydrogen atoms already attached, rather than C2, which has no hydrogen atoms attached.

The explanation for Markovnikov's rule involves the stability of the intermediate carbocation.

The two possible carbocations that can be formed when propene reacts with HBr are shown in Figure 10.67.

A secondary carbocation is more stable than a primary carbocation. This is because of the **electron-releasing effect** of alkyl groups (also called a **positive inductive effect**). There are two alkyl groups next to the positively charged carbon in the secondary carbocation in Figure 10.67 but only one in the primary carbocation. Two alkyl groups reduce the positive charge on the carbon more than one alkyl group and stabilise the ion more. Because the secondary carbocation is more stable, it is more likely to be formed.

The electron-releasing effect depends very little on the size of an alkyl group – a methyl group donates approximately the same amount of electron density as an ethyl group.

In general, the more alkyl groups there are attached to C[⊕], the more stable the carbocation (Figure 10.68).

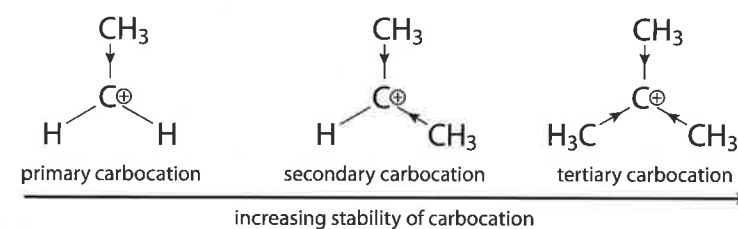


Figure 10.68 Relative stability of carbocations.

Exam tip

When asked to predict and explain the major product when a hydrogen halide adds to an alkene, always explain it in terms of the stability of the intermediate carbocation – it is never enough to just say 'Markovnikov's rule'. You must also make sure that you include a comparison – there are *more* electron-releasing alkyl groups around the positively charged carbon in a secondary carbocation than in a primary carbocation.

Markovnikov's rule could be paraphrased as 'Those who have shall get more'.

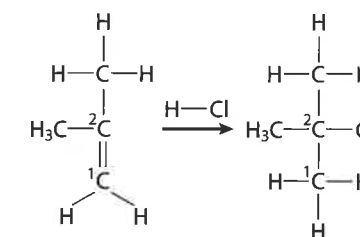


Figure 10.66 Predicting the major product of electrophilic addition.

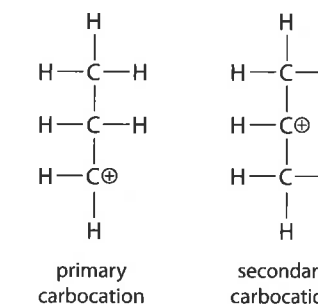


Figure 10.67 Stability of carbocation intermediates.

- A primary carbocation has one carbon atom attached to the C with the positive charge.
- A secondary carbocation has two carbon atoms attached to the C with the positive charge.

Markovnikov's rule can also be used to explain the products obtained when interhalogen compounds react with propene or other unsymmetrical alkenes. The less electronegative halogen atom behaves like hydrogen and, in the major product, becomes attached to the carbon atom that has more hydrogen atoms attached.

Figure 10.69 shows the products of the reaction of Br-Cl with propene.

Bromine is less electronegative than chlorine and becomes attached to C1, which has two hydrogen atoms attached, rather than C2, which only has one hydrogen atom attached.

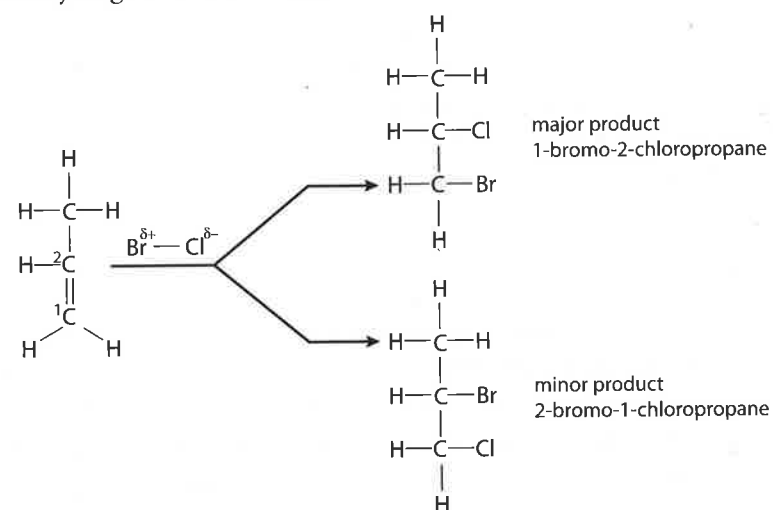


Figure 10.69 Addition of an interhalogen compound to propene.

Reaction of ethene with bromine

The reaction is summarised in Figure 10.70.

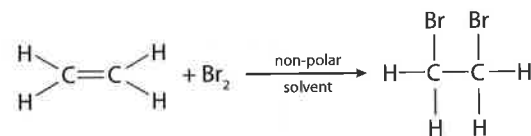


Figure 10.70 The addition reaction of ethene and bromine.

Although bromine molecules are not polar, as one approaches the high electron density in the C=C double bond it becomes polarised (there is an induced dipole). Electrons are repelled in the Br₂ molecule so that the bromine atom closest to the C=C bond has a slight positive charge and the bromine atom further away has a slight negative charge.

The mechanism can be shown in two different ways (Figures 10.71 and 10.72). The first is exactly analogous to the reaction of HBr with ethene – via a carbocation intermediate.

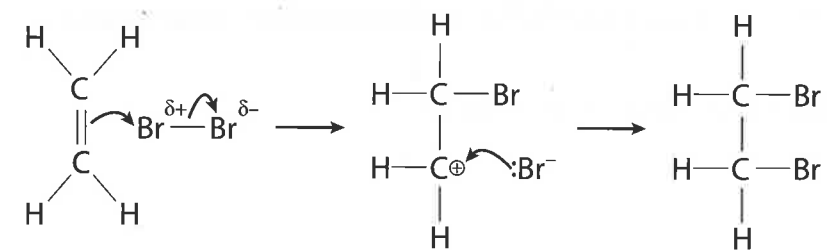


Figure 10.71 A mechanism for the reaction of ethene with bromine.

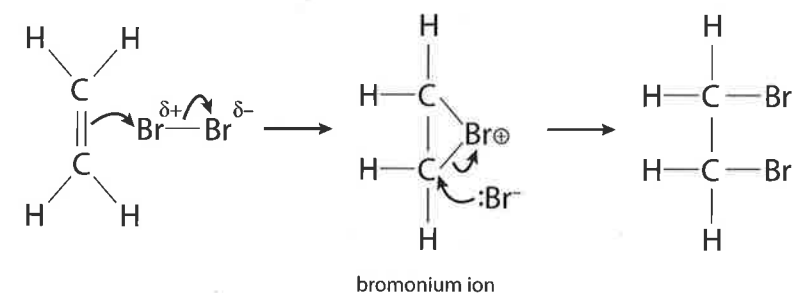


Figure 10.72 Another mechanism for the reaction of ethene with bromine showing the formation of a bromonium ion.

However, the mechanism is probably better represented as shown in Figure 10.72, where a **bromonium ion** rather than a carbocation is formed. In the bromonium ion, the bridging bromine has donated a lone pair to the C[⊕], which stabilises the ion.

Nature of science

Nobel-prize-winning physicist Richard Feynman once said, 'I learned very early the difference between knowing the name of something and knowing something'. Science is about more than knowing the name of something – it is about understanding. There is a lot more to Markovnikov's rule than just knowing the name.

? Test yourself

- State the names of the major products formed when the following alkenes react with HCl:
 - but-1-ene
 - 3-methylbut-1-ene
 - 2,4-dimethylpent-2-ene
- State the name of the major product formed when but-1-ene reacts with ClBr.

Exam tip

You need to learn only one of these mechanisms.

Learning objectives

- Understand that benzene has a delocalised π system
- Understand that the carbon-carbon bond order in benzene is 1.5
- Understand the electrophilic substitution mechanism for the nitration of benzene

10.3.3 Electrophilic substitution reactions

The structure of benzene

The structure of benzene can be described as a resonance hybrid with equal contributions from the two structures (Figure 10.73).

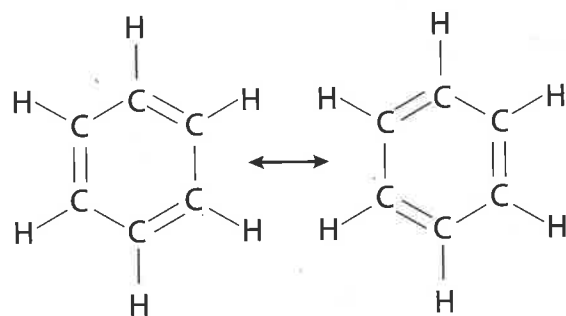
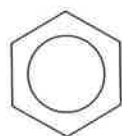


Figure 10.73 Benzene is a resonance hybrid of these two structures.

Because the π component of each double bond is shared between two C-C bonds atoms, the carbon-carbon bond order in benzene is 1.5.

The structure is much better explained by the idea of delocalisation (Figure 10.74). Instead of the p orbitals just overlapping side-on between adjacent C atoms to give three π bonds, delocalisation can occur over the whole structure.

Benzene therefore has a π delocalised ring of electrons which extends all around the ring of carbon atoms. The structure of benzene is usually drawn as a hexagon, with a ring in the middle indicating the π delocalised system:



The π delocalised system, containing six electrons, represents a region of high electron density and, therefore, benzene is susceptible to attack by electrophiles.

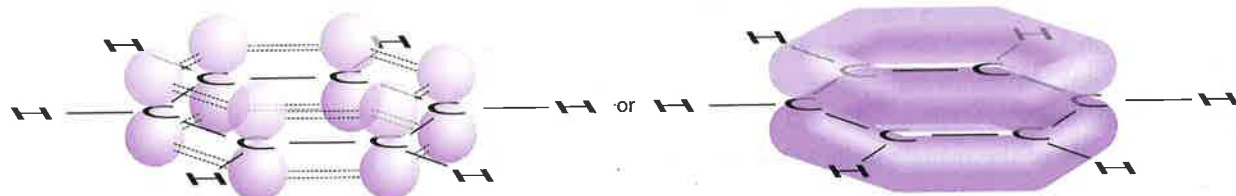


Figure 10.74 Delocalisation in benzene.

The nitration of benzene

When benzene is heated with a mixture of concentrated nitric and sulfuric acids, nitrobenzene is formed:

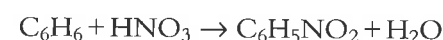


Figure 10.75 shows the reaction in more detail.

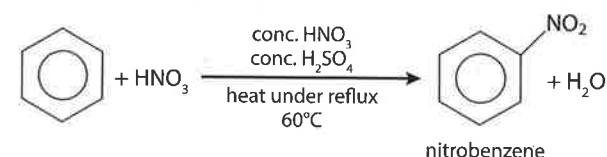


Figure 10.75 Nitration of benzene.

This reaction occurs via **electrophilic substitution**.

The first stage in the reaction is the formation of the **electrophile** – this is the nitronium ion, NO_2^+ , which is formed when concentrated sulfuric acid reacts with concentrated nitric acid:



A simpler version of this equation is:



The second stage starts with a collision between a benzene molecule and the electrophile (Figure 10.76).

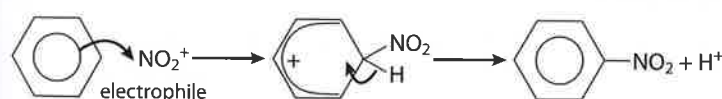


Figure 10.76 Electrophilic substitution.

In the first step in Figure 10.76, a pair of electrons from the benzene π delocalised system is used to form a bond to the NO_2^+ electrophile. To form this bond, a carbon atom must use one of the orbitals that previously formed part of the π delocalised system. The delocalised system can then only extend over the other five carbon atoms (Figures 10.76 and 10.77) – this is shown by the partial ring.

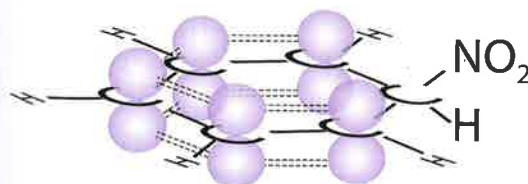


Figure 10.77 Partial delocalisation in the intermediate in electrophilic substitution.

The sulfuric acid (the stronger acid) protonates the $-\text{OH}$ group in nitric acid and the $\text{N}-\text{O}$ bond breaks to form a water molecule.

Exam tip

The curly arrow in the first step in Figure 10.76 must come from the delocalised ring; and the partial ring in the second step must extend over five carbon atoms.

Exam tip

The initial attack of the NO_2^+ on a benzene molecule can be classified as a Lewis acid-base reaction (page 310). The NO_2^+ ion is an electron pair acceptor (Lewis acid) and the benzene molecule is an electron pair donor (Lewis base).

Another way of thinking about this is that the initial reaction involved a neutral species reacting with a positively charged species – therefore the intermediate must also have a positive charge.

There were originally six electrons in the π delocalised system (one from each carbon atom) but two are now used to form the new C–N bond, which leaves only four electrons shared over five C atoms; so the ring has a positive charge.

In the second step in Figure 10.76 (and also in Figure 10.78), the C–H bond breaks. This releases an orbital and a pair of electrons to restore the π delocalised system.

The second stage can also be shown slightly differently with the HSO_4^- ion (formed when the electrophile was formed) removing the H^+ ion (Figure 10.78). The H_2SO_4 is re-formed and can be regarded as a catalyst in this reaction.

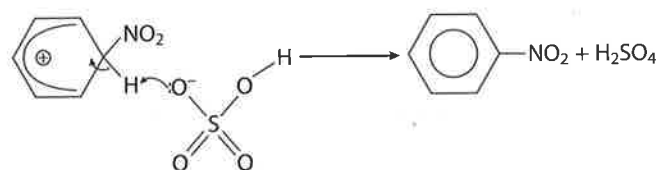


Figure 10.78 HSO_4^- removes H^+ from the intermediate to form nitrobenzene.

Nature of science

Science often involves the collection of large amounts of data and it can often prove useful to classify the data into different categories to make the data more manageable – for instance, classification of organic reactions according to type or mechanism or organic substances in terms of functional groups.

? Test yourself

- Methylbenzene reacts in the same way as benzene with a mixture of concentrated nitric acid and concentrated sulfuric acid. Write a balanced equation, using condensed structural formulas for the reaction.
- When methylbenzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid, substitution occurs on C4 (with the methyl group on C1). Write the mechanism for this reaction.

10.3.4 Reduction reactions

Reduction of aldehydes, ketones and carboxylic acids

The oxidation reactions of alcohols, aldehydes and ketones that we met earlier in this topic (Subtopic 10.2.3) can be made to work in the opposite direction by using reduction reactions. Common reducing agents are lithium aluminium hydride (LiAlH_4) and sodium borohydride (NaBH_4). LiAlH_4 is the stronger reducing agent and can be used to reduce carboxylic acids, aldehydes and ketones but NaBH_4 is only strong enough to reduce aldehydes and ketones. However, NaBH_4 is much easier to use than LiAlH_4 and so is usually preferred for the reduction of aldehydes and ketones.

Aldehydes

The basic reaction is:

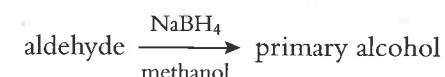


Figure 10.79 shows the reduction of ethanal.

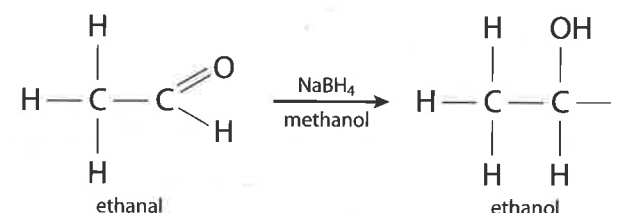


Figure 10.79 Reduction of ethanal to ethanol.

A balanced equation for the reaction can be written using $[\text{H}]$ to represent hydrogen from the reducing agent:



Ketones

The basic reaction is:

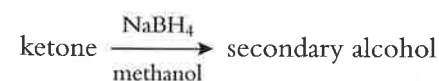


Figure 10.80 shows the reduction of propanone.

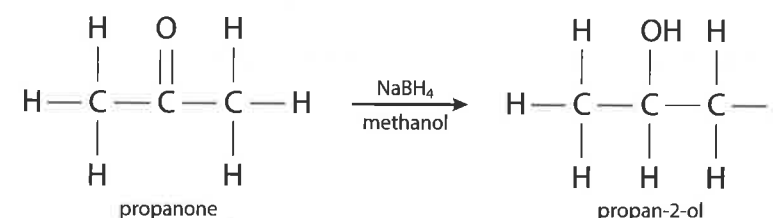


Figure 10.80 Reduction of propanone to propan-2-ol.

Learning objectives

- Describe the reduction reactions of aldehydes, ketones and carboxylic acids to form alcohols
- Describe the reduction of nitrobenzene to phenylamine (aniline)

Carboxylic acids

A stronger reducing agent (LiAlH_4) must be used for the reduction of carboxylic acids. This means that the reduction cannot be stopped at the aldehyde stage and that carboxylic acids are reduced to primary alcohols. The basic reaction is:

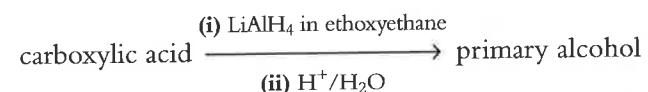


Figure 10.81 shows the reduction of ethanoic acid.

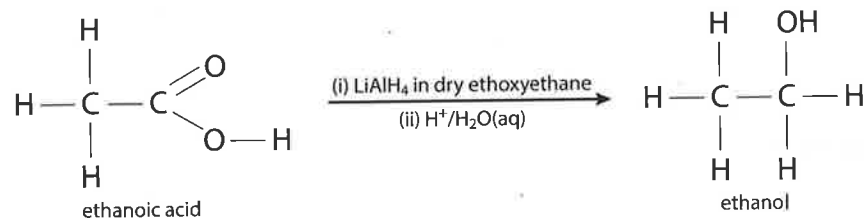
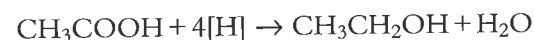


Figure 10.81 Reduction of ethanoic acid to ethanol.

This can also be written as a balanced equation using $[\text{H}]$ to represent hydrogen from the reducing agent:



If you need to make an aldehyde from a carboxylic acid, the carboxylic acid must be reduced to a primary alcohol using LiAlH_4 and then the primary alcohol must be oxidised back to an aldehyde as described on page 458 (partial oxidation with distillation).

Reduction of nitrobenzene

Nitrobenzene can be reduced to phenylamine (aniline) by heating with a reducing agent such as a mixture of tin and concentrated hydrochloric acid. This produces the protonated form of the amine $\text{C}_6\text{H}_5\text{NH}_3^+$ from which the free amine can be liberated (Figure 10.82) by treatment with a stronger base such as sodium hydroxide.

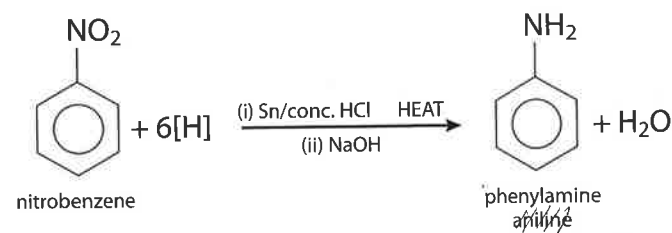
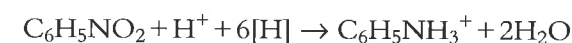
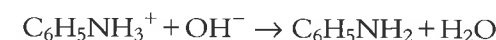


Figure 10.82 Reduction of nitrobenzene to phenylamine (aniline).

The first step could be written as:

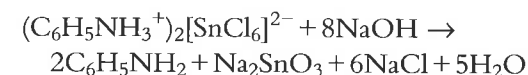


and the second as:



Extension

The product at the end of the first step is actually $(\text{C}_6\text{H}_5\text{NH}_3^+)_2[\text{SnCl}_6]^{2-}$, which reacts with sodium hydroxide according to the equation:



Nature of science

There is not really a 'scientific method' and many great discoveries have been accidental in the sense that scientists did not start out to make the thing they eventually discovered. There is, however, nothing accidental about the observational skills of the scientists involved and their skill in recognising the fact that something unusual and interesting had happened.

Phenylamine (aniline) was the chemical that sparked off the artificial dye industry. At the age of 18, William Henry Perkin was already involved in chemical research. He was given the task of making quinine (an antimalarial drug) from aniline and attempted to oxidise it using acidified potassium dichromate(VI). He ended up with a black sludge at the bottom of the flask (like many organic preparations do!). However, when he washed out the flask with ethanol he noticed a purple colour (later named mauveine or aniline purple) and had discovered, by accident, the first artificial organic dye, which was to become the basis of a huge industry. Other substances discovered by accident include PTFE (polytetrafluoroethene – used as non-stick coating) and superglue.

? Test yourself

- 38 Give the name of the organic product formed when each of the following is reduced using lithium aluminium hydride:
- propanoic acid
 - 2-methylpentanal
 - pentan-3-one
 - 3-methylbutanoic acid

Other reducing agents, such as hydrogen in the presence of a palladium or platinum catalyst, can also be used.

Exam tip

The syllabus states that you should be able to write reactions for the reduction of carboxylic acids to aldehydes, so this is worth bearing in mind in the examination.

'Aniline' is the old (non-systematic) name for phenylamine.



The A in 'BASF', the largest chemical company in the world, stands for 'anilin' (German for aniline).

Learning objectives

- Work out reaction pathways for the formation of organic compounds
- Understand that chemists often adopt a retrosynthetic approach to the synthesis of organic compounds

10.4 Synthetic routes (HL)

Reaction pathways

We can use the reactions shown in Figure 10.83 to design syntheses for organic compounds.

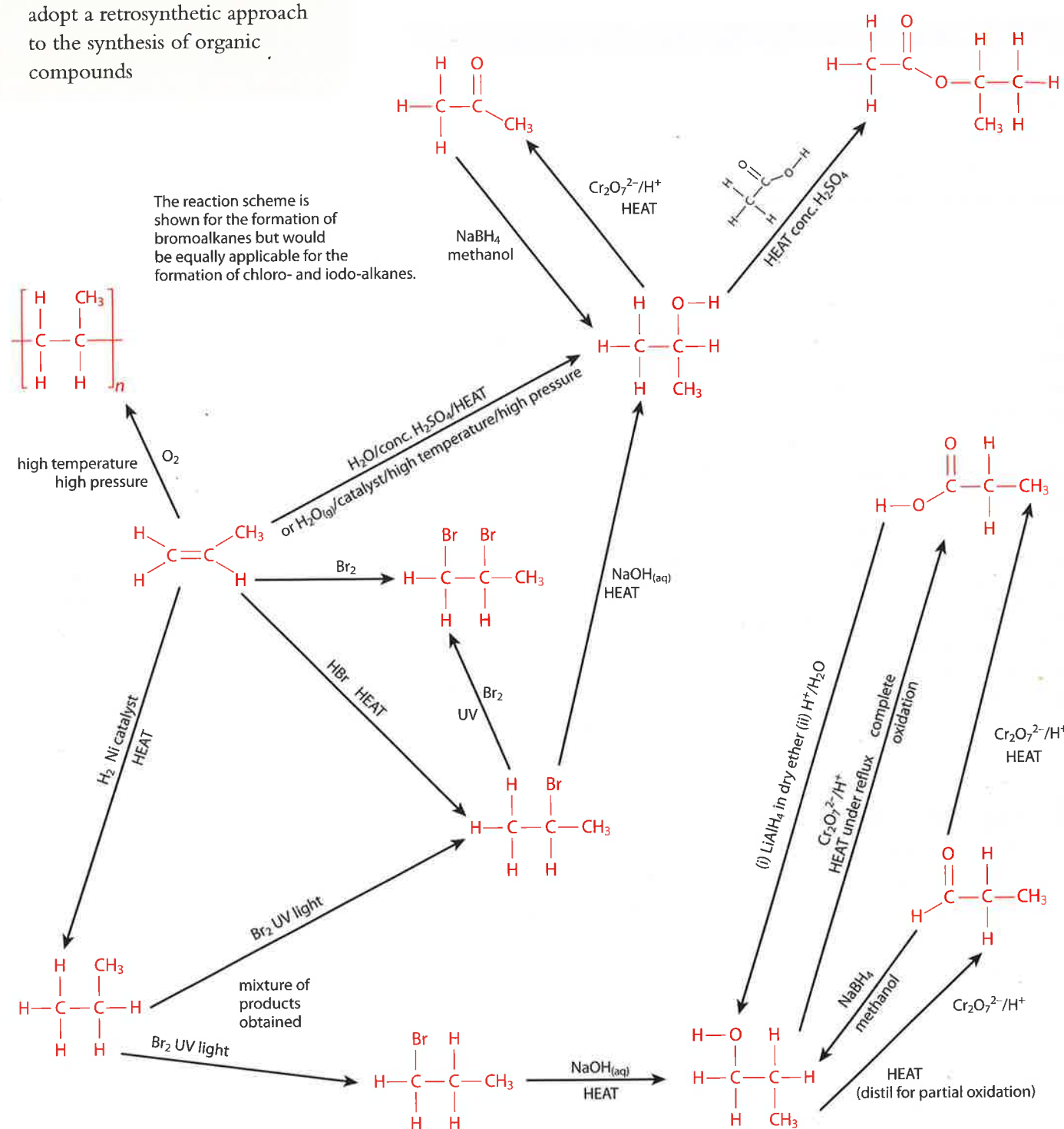
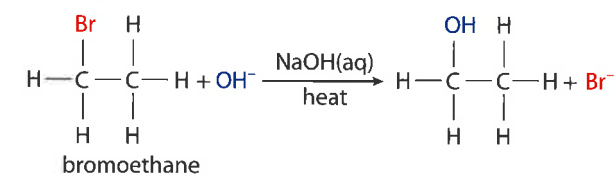
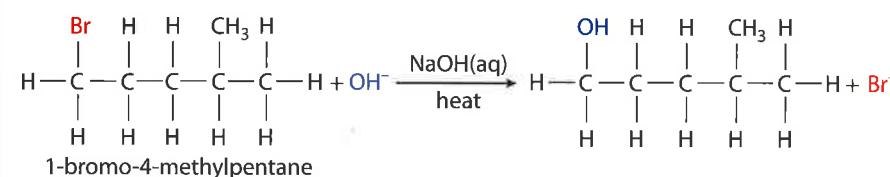


Figure 10.83 Reaction pathways.

The important thing when working out a particular reaction scheme is to concentrate on only the **functional groups** in molecules – the carbon skeleton should make very little difference to the products of a reaction. This means that 1-bromo-4-methylpentane and bromoethane react in basically the same way with aqueous sodium hydroxide to form alcohols:



When designing a synthesis for a particular organic compound, chemists often adopt a **retrosynthetic** approach. They start with the target molecule they are trying to make and work backwards, using known reactions, to get to an appropriate and readily available starting material. For example, if it is required to make butanone from an alkane, the logic could go something like this:

- butanone can be made from butan-2-ol in an oxidation reaction
- butan-2-ol can be made from 2-chlorobutane in a (nucleophilic) substitution reaction
- 2-chlorobutane can be made from butane in a (free radical) substitution reaction.

A reaction sequence like that in Figure 10.84 could, therefore, be used to make butanone.

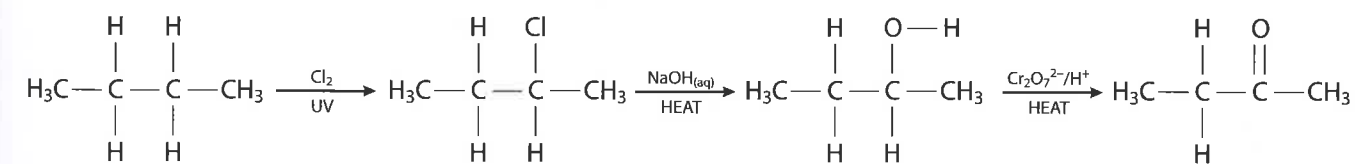
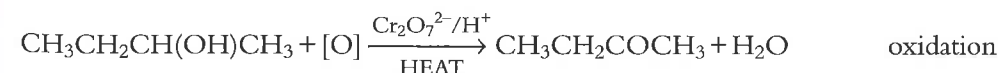
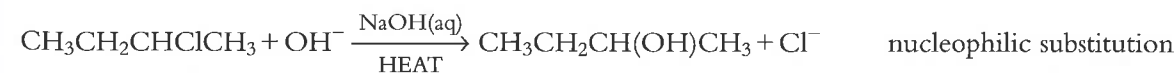


Figure 10.84 Synthesis of butanone.

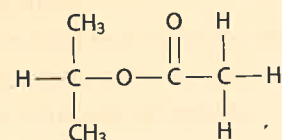
This can also be written as a series of balanced equations:



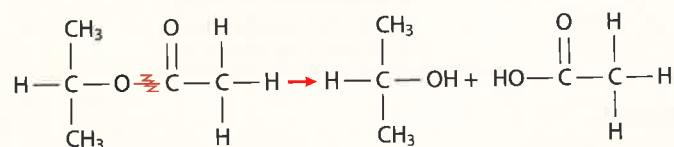
Note that free radical substitution produces a mixture of products and some 1-chlorobutane will also be formed.

Worked examples

10.2 Design a reaction pathway for the formation of the compound shown below. Use alkenes as the only organic starting materials.



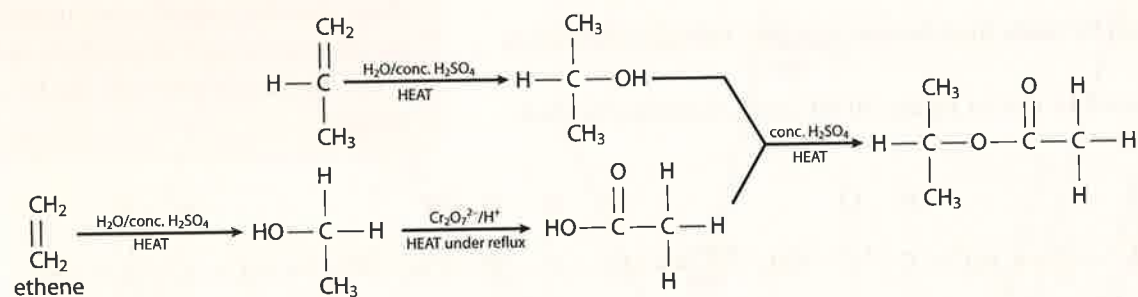
We can recognise this molecule as an ester – and therefore know that it can be made from an alcohol and a carboxylic acid. In the figure below, the right-hand part of the ester (with the C=O group) has two carbon atoms and suggests that it comes from ethanoic acid. So the left-hand part must be from an alcohol – the only alcohol that could give this arrangement of carbon atoms is propan-2-ol.



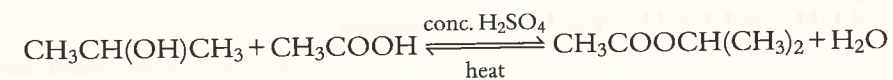
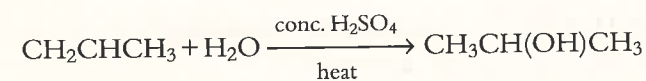
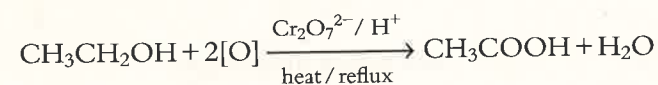
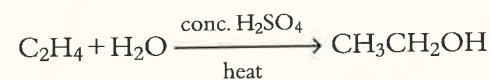
Neither of these two compounds are alkenes. Propan-2-ol can be made by the hydration of propene – so this is one of the starting compounds.

Ethanoic acid can be made using complete oxidation of ethanol, which can be made by hydration of ethene, which is the other starting compound.

The reaction sequence is shown below.

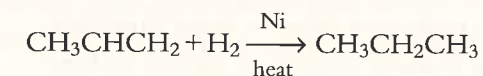


Presented as a series of balanced equations, this looks like:

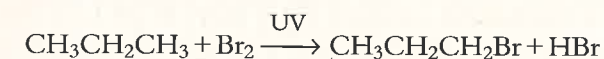


10.3 Design a reaction sequence, using balanced chemical equations, for the conversion of propene to propanoic acid.

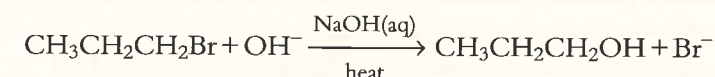
A problem here is that if water is added to propene, it will produce propan-2-ol (Markovnikov's rule), which cannot be oxidised to propanoic acid. Therefore, the alkene must first be converted to an alkane:



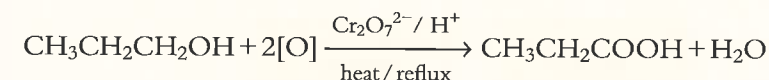
When this is reacted with bromine, a significant amount of 1-bromopropane will be formed.



This is followed by this reaction with aqueous sodium hydroxide:



Finally the oxidation of propan-1-ol:



Benzene and other aromatic compounds

So long as a particular functional group is not attached *directly* to a benzene ring, the reactions of aromatic compounds will be basically the same as the reactions met in other sections. For example, we get the reaction scheme shown in Figure 10.85 for some conversions, starting with ethylbenzene.

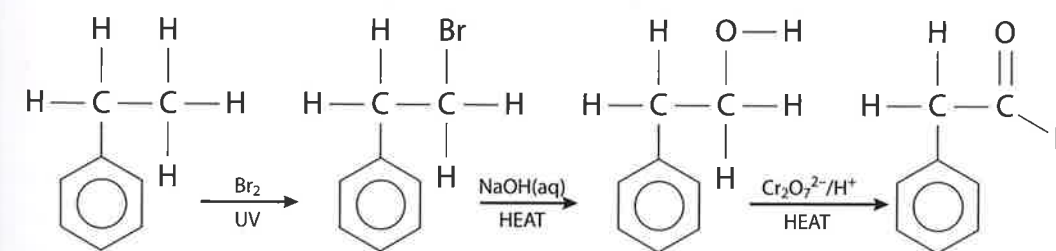


Figure 10.85 A reaction scheme starting with ethylbenzene.

Nature of science

Designing organic synthetic pathways involves a great deal of creativity and imagination – as well as detailed knowledge about organic reactions and suitable starting materials.

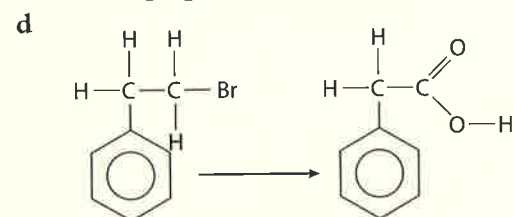
All science must be funded and commercial companies finance much research on organic synthesis to make new drugs to target important diseases. The amount of funding available is likely to depend on how many people are affected by a disease – there will be a lot more money available to do research on a disease such as malaria but less on so-called rare diseases because a commercial company is not likely to get back the money it spends on research by selling the drug if the disease only affects a small number of people. In 1983, the US government passed the Orphan Drug Act, which provides financial support to companies carrying out research to develop drugs to target rare diseases.

The principles of green chemistry (see Option D) are being used increasingly in designing organic syntheses as scientists become more aware of the environmental impact of their work.

? Test yourself

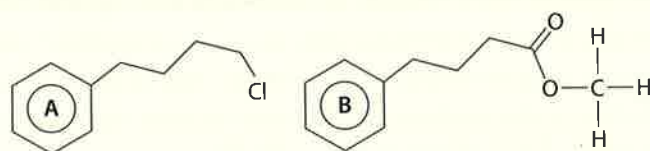
39 Draw out reaction pathways showing structural formulas and essential conditions for the following conversions:

- ethane to ethanol
- propene to propanone
- 1-chloropropane to propanoic acid



e ethene to ethyl ethanoate using ethene as the only organic starting material

40 Design a reaction sequence for the conversion of molecule A into molecule B:



41 Design a reaction sequence, using balanced chemical equations, for the synthesis of 3-methylbutan-2-one from a suitable alkene.

10.5 Stereoisomerism (HL)

Types of stereoisomerism

We have already met structural isomerism (page 441), in which molecules have the same molecular formula but the atoms are joined together differently. We will now consider **stereoisomerism**.

Stereoisomers have the same structural formula (the atoms are joined together in the same way – same connectivity) but the atoms are arranged differently in space.

The different forms of stereoisomerism are summarised in Figure 10.86.

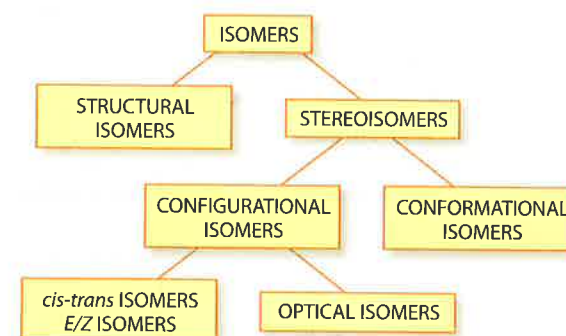


Figure 10.86 Different types of isomerism and how they are linked.

cis-trans isomerism

This type of isomerism occurs in alkenes and in cyclic (ring) compounds.

cis-trans isomerism: two compounds have the same structural formula, but the groups are arranged differently in space around a double bond or a ring.

Before we can understand *cis-trans* isomerism in alkenes, we must remind ourselves about the nature of the C=C double bond. A double bond consists of two components (Figure 10.87).

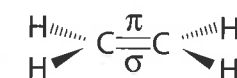


Figure 10.87 A double bond is composed of σ and π components.

Fairly free rotation is possible about a C–C single bond because the nature of the sigma bond does not restrict rotation. However, with C=C, the π component of the bond prevents the groups either side of it from rotating relative to each other (Figure 10.88). The π bond would have to be broken to allow rotation to occur, and this takes a lot of energy.

Learning objectives

- Understand what is meant by stereoisomerism
- Understand how alkenes or cycloalkanes can exist as *cis-trans* or *E/Z* isomers
- Explain what is meant by optical isomerism
- Deduce whether or not a given molecule will exhibit optical isomerism
- Explain how optical isomers can be distinguished using a polarimeter
- Understand what is meant by a racemic mixture
- Understand what is meant by conformational isomerism

The term 'geometric isomerism', which is often used for *cis-trans* isomerism, is now strongly discouraged by IUPAC.

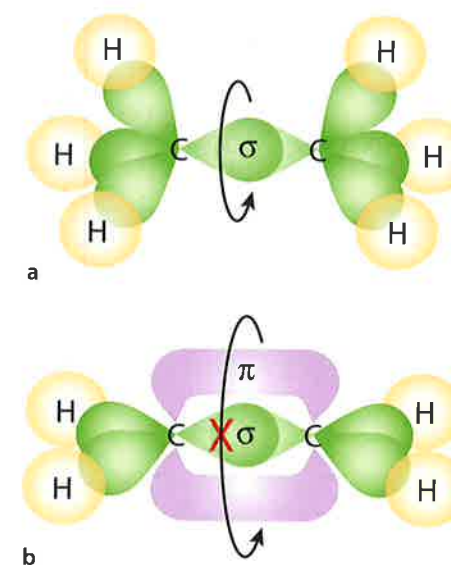


Figure 10.88 a Free rotation of groups around a C–C bond. b Restricted rotation of groups about a C=C bond.

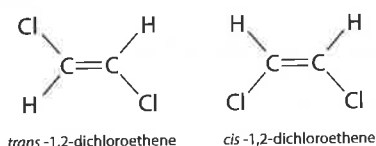


Figure 10.89 Isomers of 1,2-dichloroethene.

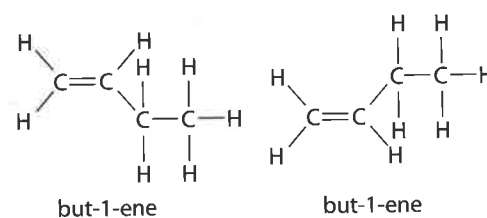
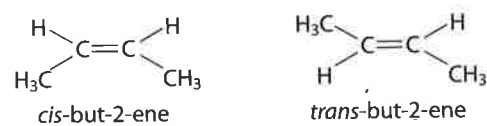


Figure 10.90 Isomers of butene.

cis: same side
trans: opposite sides

The fact that rotation of groups around a double bond is restricted gives rise to *cis-trans* isomerism. For example, two structures can be drawn for 1,2-dichloroethene (Figure 10.89).

The chlorine atoms are arranged either on the **same** side of the double bond – forming the *cis* isomer – or on **opposite** sides of the double bond – forming the *trans* isomer. These cannot be interconverted easily because the π component of the C=C bond **restricts rotation** of groups around the bond.

For a molecule to exhibit *cis-trans* isomerism, there must be two different groups on both sides of the double bond.

Figure 10.90 shows that *cis-trans* isomers are possible for but-2-ene, but not for but-1-ene.

The two molecules of but-1-ene shown in Figure 10.90 are identical – the second is simply the first turned upside down.

Other examples of molecules that do and do not exhibit *cis-trans* isomerism are shown in Table 10.22.

Compound	<i>cis-trans</i> isomers?	<i>cis</i> -isomer	<i>trans</i> -isomer
1-bromobut-1-ene	yes		
2-bromobut-1-ene	no		
3-methylpent-2-ene	yes		
2-methylpent-2-ene	no		

Table 10.22 Examples of molecules that do and do not exhibit *cis-trans* isomerism.

The *cis* and *trans* nomenclature has limited value – when there are four different groups around the C=C bond it gives no insight into the structure at all. A more general way of naming the isomers that can arise because of the lack of rotation about a C=C bond is using the *E/Z* naming system.

To do this, we give each group attached to the C=C bond a priority according to a set of rules called the Cahn-Ingold-Prelog priority rules (CIP). These give higher priority to atoms attached to the C=C bond that have a higher atomic number.

We look at each side of the C=C bond separately and assign a priority (1 or 2) to each of the atoms or groups attached. If the two groups with highest priority (labelled '1') are on the same side of a plane perpendicular to and passing through the double bond, the isomer is labelled '*Z*' (German: *zusammen* – together); if they are on opposite sides of the plane, the isomer is labelled '*E*' (German: *entgegen* – against or *entgegengesetzt* – opposite).

Consider the molecule shown in Figure 10.91. The priorities of the atoms and groups joined directly to the carbon atoms of the C=C bond are assigned – fluorine has a higher atomic number than H, therefore F has higher priority (1) than H (2). On the other side of the C=C bond, Cl has a higher priority than C. The two groups with the higher priority (labelled '1') are on the *same* side of the plane perpendicular to and through the C=C bond, so this is the *Z* isomer and it can be named (*Z*)-1-fluoro-2-chloroprop-1-ene.

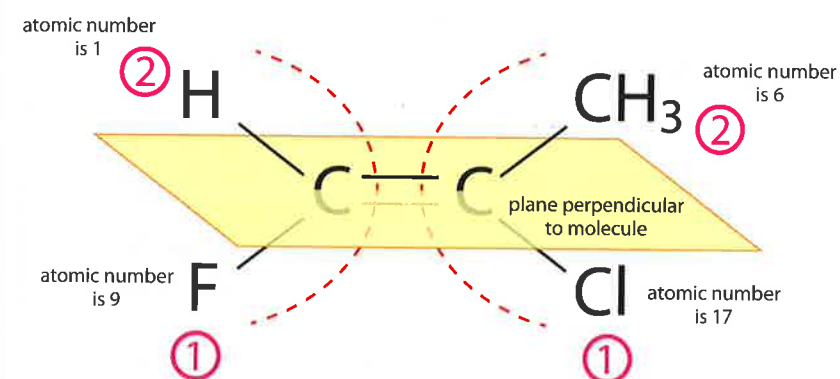


Figure 10.91 (*Z*)-1-fluoro-2-chloroprop-1-ene.

Priority of other groups

With larger groups, which have the same atom attached to the central C, we keep going along the chain until a difference between the groups is spotted. So, $-\text{CH}_2\text{CH}_3$ has a higher priority than $-\text{CH}_3$ because the first C has a another C (atomic number 6) atom attached.

In the groups shown in Figure 10.92, the group on the left has higher priority because the C with O (higher atomic number) is closer to the C=C bond.

Double-bonded atoms (Figure 10.93) count as two groups attached to an atom – so CHO has higher priority than CH_2OH because it is counted as if there are two O atoms attached to the C.

Table 10.23 shows some other molecules classified as *E* or *Z*.

<i>Z</i>	<i>E</i>
<i>Z</i>	<i>Z</i>

Table 10.23 Classification of some isomers as *E* or *Z*.

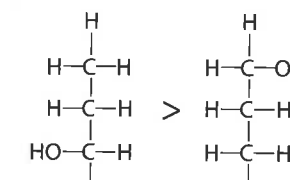


Figure 10.92 The group on the left has higher priority.

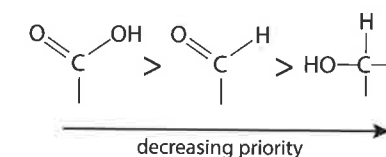


Figure 10.93 Double-bonded atoms count as two groups attached.

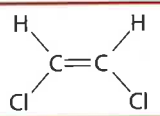
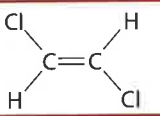
		
	<i>cis</i> -1,2-dichloroethene	<i>trans</i> -1,2-dichloroethene
<i>M_r</i>	96.94	96.94
Boiling point / °C	60.5	48.7

Table 10.24 Boiling points of a pair of isomers.

Properties of *cis-trans* isomers

Table 10.24 shows that *cis-trans* (*E/Z*) isomers have different physical properties.

The structures of *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene differ only in the orientation of their chlorine atoms around the C=C bond – Figure 10.94. This leads to the *cis* form being polar and the *trans* form being non-polar. The *trans* form is non-polar because the orientation of the chlorine atoms around the double bond means that the dipoles cancel. So there are permanent dipole-dipole interactions for the *cis* form but not for the *trans* form. Both molecules have the same relative molecular mass (and hence very similar London forces) so the difference between the boiling points is due to the permanent dipole-dipole interactions between the *cis* molecules.

cis-trans (*E/Z*) isomers may also have different chemical properties.

cis-trans isomerism in substituted cycloalkanes

A cycloalkane is a ring (cyclic) compound containing only single C–C bonds (and hydrogen). The simplest members of the homologous series are cyclopropane (C₃H₆) and cyclobutane (C₄H₈). Cycloalkanes are structural isomers of the corresponding alkene.

Two different ways of drawing these molecules are shown in Table 10.25.

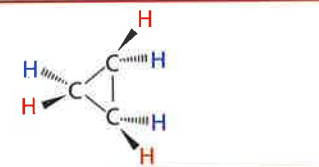
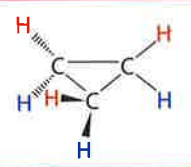
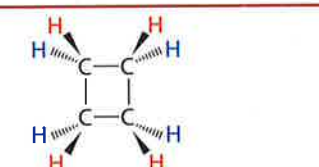
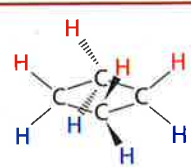
	
cyclopropane	
	
cyclobutane	

Table 10.25 Two ways of drawing cyclopropane and cyclobutane. Hydrogen atoms above the plane of the ring are red and those below are blue.

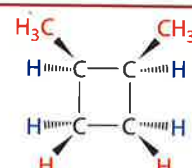
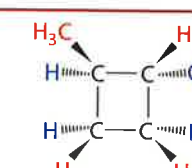
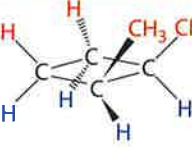
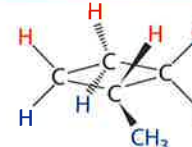
	
<i>cis</i> -1,2-dimethylcyclobutane (<i>Z</i>)-1,2-dimethylcyclobutane	<i>trans</i> -1,2-dimethylcyclobutane (<i>E</i>)-1,2-dimethylcyclobutane
	

Table 10.26 Different ways of showing the isomers of 1,2-dimethylcyclobutane.

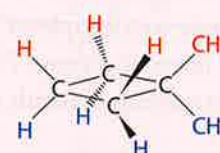
The ring structure prevents rotation of a group from above the plane of the ring to below the ring. So *cis-trans* isomers are possible in substituted cycloalkanes. Groups can be rotated from above to below the ring only if the ring is broken – this requires a lot of energy.

The condition for a cycloalkane to exhibit *cis-trans* isomerism is that at least two carbon atoms must have two different groups attached.

Take 1,2-dimethylcyclobutane as an example. Table 10.26 shows the structures in two different ways – the colours indicate the same convention as used in Table 10.25.

As before, in the *cis* form the two methyl groups are on the **same** side of the ring and in the *trans* form they are on **opposite** sides of the ring. The *E/Z* nomenclature is used in the same way as for alkenes – if the two groups with the higher priority are on the same side of the ring then it is a *Z* isomer.

Note:



is not a stereoisomer of 1,2-dimethylcyclobutane but a structural isomer. The atoms are joined together differently, with two methyl groups on the same carbon atom – so it has a different name, 1,1-dimethylcyclobutane. This molecule does not show *cis-trans* isomerism.

1,3-dimethylcyclobutane is a structural isomer of 1,1-dimethylcyclobutane and 1,2-dimethylcyclobutane and does exhibit *cis-trans* isomerism.

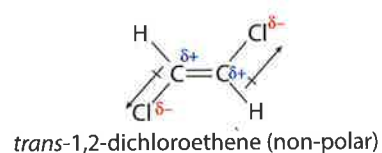
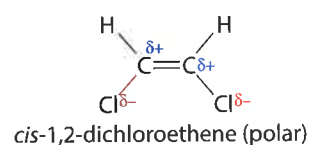


Figure 10.94 Polarity differences between similar molecules.

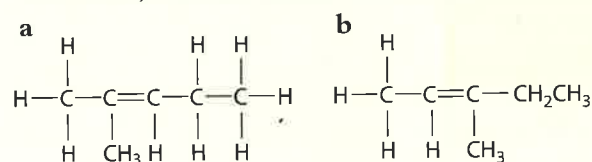
A ring containing three atoms, such as in cyclopropane, is called a three-membered ring; that in cyclobutane is a four-membered ring.

Extension

These ring compounds belong to the general group of **cyclic** compounds – those that contain a ring of carbon or other atoms. If there is another atom, such as O or N, in the ring as well as carbon atoms, the compound is described as **heterocyclic**.

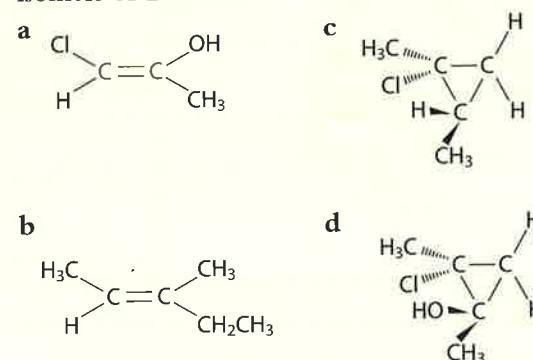
? Test yourself

- 42 Which of the following will exhibit *cis-trans* isomerism? If the molecule exhibits *cis-trans* isomerism, draw the *cis* and *trans* forms.



- c** 2,3-dimethylpent-2-ene
d 3,4-dimethylpent-2-ene
e 1,2,3-trimethylcyclopropane
f 1,3-dimethylcyclobutane

- 43 Classify each of the following isomers as *E* isomers or *Z* isomers.



Conformational isomers

Conformational isomers are forms of the same molecule that have different conformations because of rotation about a σ bond. For example, 1,2-dichloroethane can exist in different conformations according to how the chlorine atoms are arranged relative to each other. Two different conformations of 1,2-dichloroethane are shown in Figure 10.95.

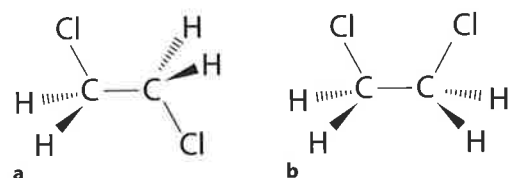


Figure 10.95 Different conformations of 1,2-dichloroethane.

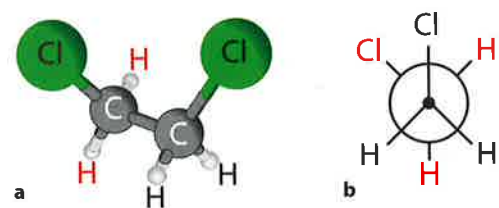


Figure 10.96 **a** Ball and stick model of a conformation of 1,2-dichloroethane; **b** Newman projection of 1,2-dichloroethane – the atoms at the back are shown in red.

Molecule 10.95a has a lower potential energy than molecule 10.95b because the chlorine atoms are further apart (and there is therefore less repulsion between them). There is a (relatively low) barrier to rotation from one form to the other due to changes in repulsion between the Cl atoms as they get further apart/closer together. Another conformation is shown in two different ways in Figure 10.96.

It is important to realise that all the conformations in Figures 10.95 and 10.96 represent the same molecule and that individual conformational forms cannot be isolated because the barrier to rotation is so low. Different forms will exist simultaneously in a sample of the substance – and these forms will be constantly interconverting. The rate of interconversion between the different conformations depends on the barrier to rotation and the temperature.

A common example of conformational isomers is the chair and boat forms (Figure 10.97) of cyclohexane (C_6H_{12}).

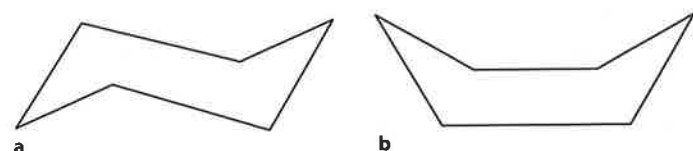


Figure 10.97 Cyclohexane: **a** chair form; **b** boat form.

Conformational isomers can be interconverted without breaking chemical bonds. Interconversion of configurational isomers requires the breaking and subsequent re-forming of chemical bonds.

Optical isomerism

Optical isomerism is another type of stereoisomerism. Butan-2-ol exhibits optical isomerism. There are two forms of this compound – they are mirror images (Figure 10.98).

Although they look identical, if we try to put one molecule ‘on top’ of the other (Figure 10.98b), it can be seen that only two of the groups can be made to correspond – the other two groups are distributed differently around the central carbon atom. Therefore the molecules are not identical but isomers of each other – we say that the two isomers are **non-superimposable**.

In order to exhibit this property of optical isomerism – that the mirror images are not superimposable – there must be **four different** groups attached to a carbon atom. If you look at butane (Figure 10.99), you can see that it has a maximum of only three different groups attached to any one carbon atom, and also that the mirror images *are* superimposable.

A carbon atom with four different groups attached to it is called a **chiral centre** (chirality centre or stereogenic unit) and molecules that exhibit optical isomerism are often described as **chiral**. We talk about the *configuration* of the chiral centre – that is the spatial arrangement of the groups at the chiral centre.

Some molecules that exhibit optical isomerism are shown in Table 10.27.

Table 10.27 Molecules that exhibit optical isomerism – the chiral centres are shown in red.

Some molecules that do *not* exhibit optical isomerism are shown in Table 10.28.

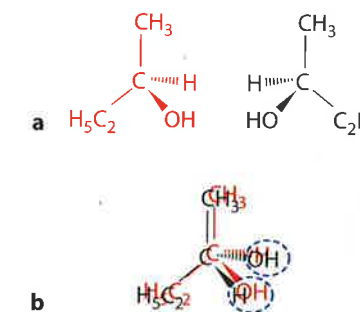


Figure 10.98 **a** Mirror image molecules; **b** non-superimposable.

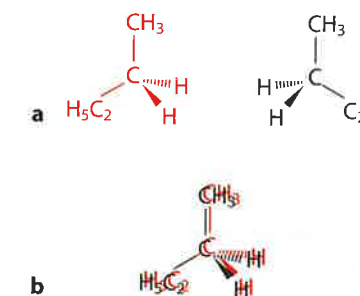


Figure 10.99 There is only one form of butane: **a** these two molecules are identical; **b** butane does not have optical isomers.

The word ‘chiral’ is derived from the Greek word for hand – your hands are non-superimposable mirror images of each other.

A carbon atom with four different atoms or groups attached is sometimes called an **asymmetric** carbon atom.



The fact that these carbon compounds exhibit optical isomerism allows us to reason that these molecules are tetrahedral. If they were square planar, optical isomers would not be possible (if you draw 2-bromobutane with a square planar structure you should be able to see that the mirror images are superimposable). This is an example of how reasoning can provide us with information about the microscopic world. Do we know or believe that these molecules are tetrahedral?

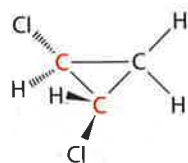
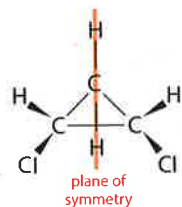


Figure 10.100 *trans*-1,2-dichlorocyclopropane



cis-1,2-dichlorocyclopropane

Figure 10.101 A molecule with a plane of symmetry.

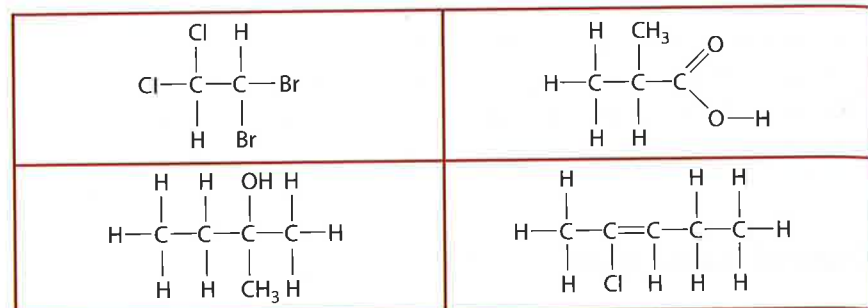


Table 10.28 Molecules that do not exhibit optical isomerism.

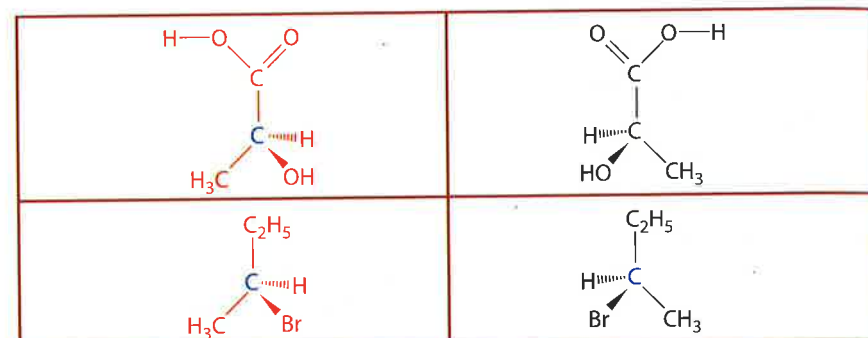


Table 10.29 The three-dimensional representation of optical isomers showing two pairs of mirror images.

To show the optical isomerism exhibited by some compounds more clearly, optical isomers are usually drawn in three dimensions, as shown in the diagrams in Table 10.28. A solid wedge indicates a bond coming out of the plane of the paper; a dashed wedge goes into the paper.

The individual optical isomers of a compound are called **enantiomers** – so, for example, the bottom row of Table 10.29 shows the two enantiomers of 2-bromobutane.

Optical isomerism and ring compounds

Optical isomerism can also occur with ring (cyclic) compounds. Figure 10.100 shows that there are two chiral centres in *trans*-1,2-dichlorocyclopropane, each shown in red.

To determine if a ring compound has optical isomers, it is necessary to look at whether or not the molecule has a plane of symmetry. If a molecule *does* have a plane of symmetry then it will *not* have optical isomers. For example, *cis*-1,2-dichlorocyclopropane has a plane of symmetry and does not exhibit optical isomerism – Figure 10.101.

If a molecule has a plane of symmetry it will *not* exhibit optical isomerism.

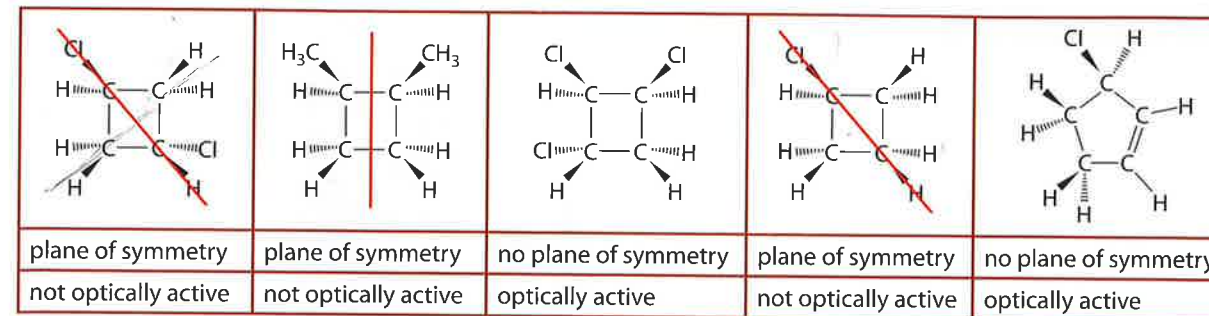


Table 10.30 Some ring compounds with optical isomers and some without.

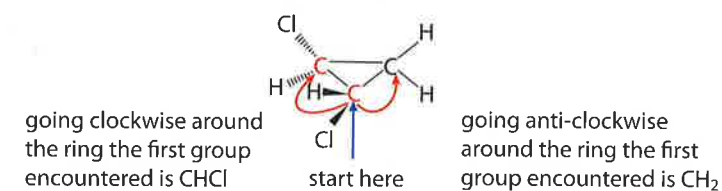


Figure 10.102 In addition to the H and Cl directly attached to the C indicated with the blue arrow, if we go clockwise around the ring, the group attached to this C is CHCl, but in the anticlockwise direction it is a CH₂ group.

The fact that the chiral centres in the molecule in Figure 10.100 are indeed carbon atoms with four different groups attached can be seen by starting at the point shown and going around the ring in two different directions (Figure 10.102).

Some ring compounds that have optical isomers and others that do not are shown in Table 10.30.

Optical isomers and plane-polarised light

The two enantiomers of an optically active compound have the property that they rotate **plane-polarised light** in opposite directions. Or, more precisely, they rotate the plane of polarisation of plane-polarised light in opposite directions.

Normal, non-polarised, light vibrates in all planes (Figure 10.103). If non-polarised light is passed through a polarising filter, plane-polarised light is produced (Figure 10.104).

If plane-polarised light is passed through samples of the two isomers of butan-2-ol, shown below, we find that one of the isomers rotates the plane of the plane-polarised light to the right (clockwise), and the other isomer rotates the plane of the plane-polarised light to the left (anticlockwise). The two enantiomers rotate the plane of the plane-polarised light by equal amounts.

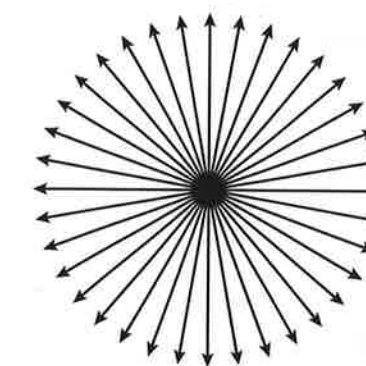


Figure 10.103 If we imagine being able to look at the vibrations in a beam of non-polarised light coming towards us, then it could be represented as shown here.

Optical isomers rotate the plane of plane-polarised light in opposite directions.

Extension

There are various ways of labelling the two enantiomers. They may be labelled according to the direction in which they rotate plane-polarised light using $+/-$ or d/l , or they may be labelled according to the absolute configuration (the arrangement of the groups around the chiral centre) using D/L or R/S .

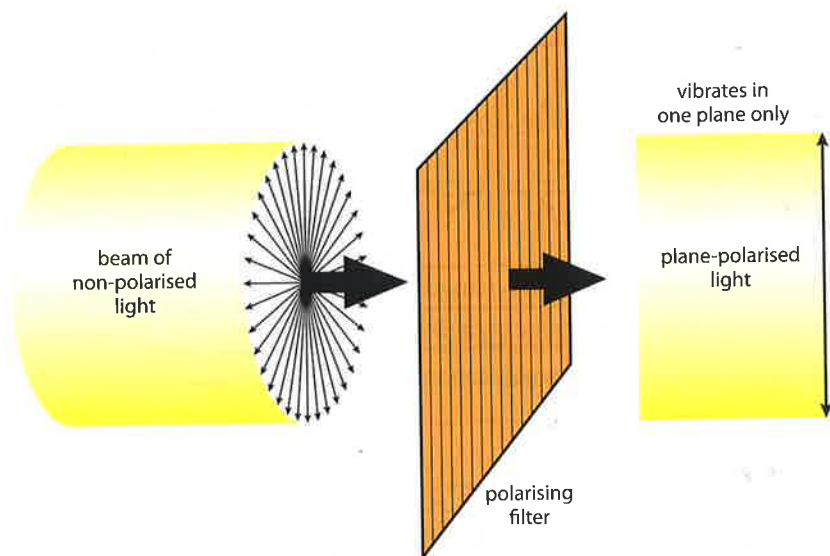


Figure 10.104 Plane-polarised light is light that vibrates in one plane only.

Extension

Which configuration corresponds to the direction in which light is rotated can be worked out only by determining the absolute configuration using X-ray crystallography and the rotation of the light using a polarimeter. We cannot just look at a particular enantiomer's three-dimensional structure and say that it rotates plane-polarised light to the right or to the left.

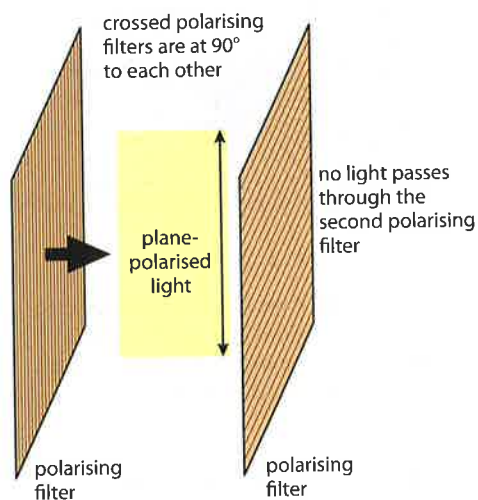


Figure 10.106 When polarising filters are crossed no light can pass through unless it has been rotated by an optically active sample between the first and second filter.

Using a polarimeter to determine the direction in which light is rotated

A simple polarimeter consists of a source of light (usually a sodium lamp producing one specific wavelength), two polarising filters, a sample tube and a scale to measure the degree of rotation of the plane-polarised light (Figure 10.105).

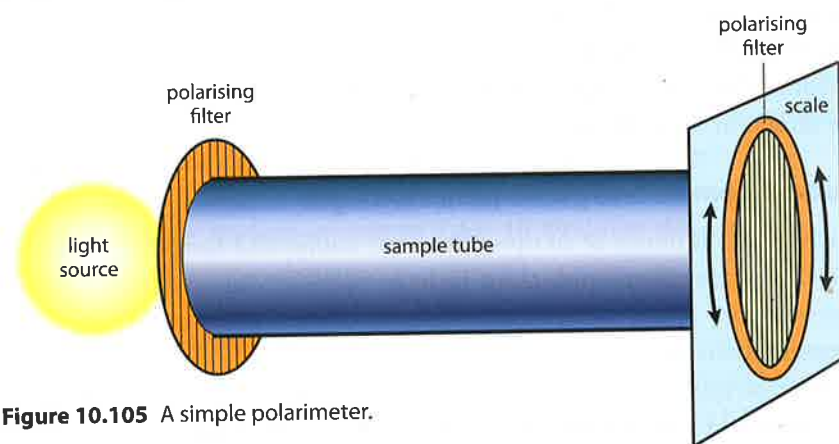


Figure 10.105 A simple polarimeter.

The solvent in which the test substance is to be dissolved is placed in the sample tube, and the second polarising filter is rotated until no light can be seen. At this point the polarising filters are exactly crossed (Figure 10.106). The solvent is then replaced by the sample dissolved in the solvent and the polarising filter rotated again until no light can be seen. The angle through which the light is rotated by the sample is the difference between the readings with and without the sample.

It is possible to distinguish between optical isomers of a particular substance using a polarimeter – one enantiomer rotates the plane-polarised light clockwise and the other rotates it in the opposite direction.

Racemic mixtures

An equimolar mixture of the two enantiomers of a chiral compound is called a **racemic mixture** (or racemate). A racemic mixture has no effect on plane-polarised light (is optically inactive) because the rotation effects of the two enantiomers cancel each other out.

Because the enantiomers are equally stable, reactions that produce molecules containing a chiral carbon atom will usually produce a racemic mixture – the resulting reaction mixture will have no effect on plane-polarised light.

When attempting to make one specific enantiomer of an optically active compound, either the synthetic route has to be carefully designed to produce this isomer (stereospecific synthesis) or the racemic mixture may be resolved into its different enantiomers.

An example of a stereospecific reaction is the S_N2 nucleophilic substitution reaction of 2-bromobutane with aqueous sodium hydroxide (Figure 10.107). If the reaction is carried out with just one enantiomer of 2-bromobutane, we will be able to predict which enantiomer of the product will be made.

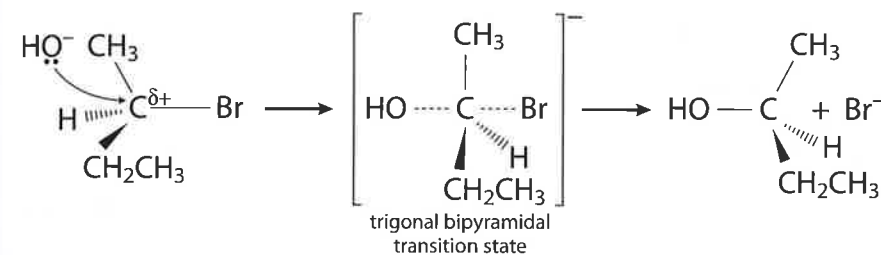


Figure 10.107 Inversion of configuration during an S_N2 reaction.

The product formed is basically the mirror image of the starting material (ignoring the fact that one molecule contains Br and the other OH). Therefore the reaction occurs with inversion of the configuration at the chiral centre.

The S_N1 mechanism is not stereospecific (page 469) and produces a racemic mixture if the product has a chiral centre.

Diastereomers

Diastereomers are stereoisomers that are not mirror images of each other – so *cis-trans* isomers are diastereomers. Diastereomers can also arise when more than one chiral centre is present in a molecule.

There are two chiral centres in the molecule shown in Figure 10.108. The compounds are mirror images of each other and are enantiomers.

However, in Figure 10.109 the two compounds are stereoisomers (same structural formula) but are not mirror images of each other, and are therefore diastereomers.

Physical properties (except the direction of rotation of the plane of plane-polarised light) such as melting point, boiling point and solubility are identical in enantiomers, but not for diastereomers. The chemical properties of enantiomers are identical for reactions with compounds that are not optically active. Diastereomers may have different chemical properties.

Exam tip

If the product of a reaction has a chiral centre and you are asked why it is optically inactive – the answer is 'because a racemic mixture is formed'.

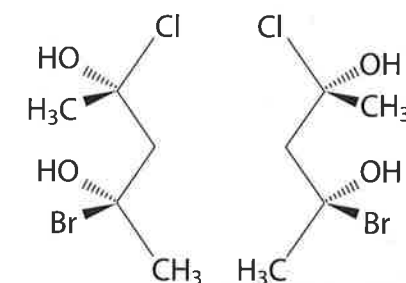


Figure 10.108 Skeletal structures of two enantiomers.

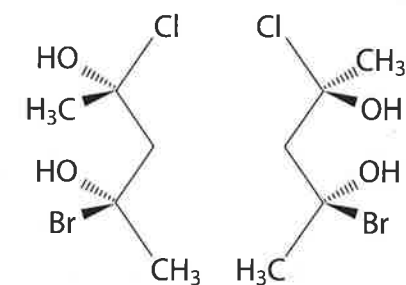


Figure 10.109 Skeletal structures of two diastereomers.



The sedative called thalidomide was introduced in the late 1950s and was used in various countries throughout the world – it was thought to be safe with very few side-effects. As well as being a sedative, it was also effective at relieving sickness and so was widely given to pregnant women in the first three months of pregnancy to alleviate morning sickness. The result was devastating, with thousands of children being born with missing or malformed limbs, and a number dying in infancy. This tragedy could have been avoided if the drug had been evaluated for teratogenicity (toxicity to the foetus) before it was marketed.

Thalidomide was given as a mixture of enantiomers (racemic mixture) but one of the enantiomers (the

S-enantiomer) was responsible for producing the teratogenic effect and caused limb deformities in the foetus (Figure 10.110).

Giving the single enantiomer would not have helped in the case of thalidomide because the enantiomers interconvert in the body producing the racemic mixture.

Nowadays, if a new drug is going to be marketed as the racemic mixture, testing must be carried out on each enantiomer separately and also on the racemic mixture. Pharmaceutical companies now tend to either synthesise or separate out the active single enantiomer of a drug and develop this instead of the racemic mixture. Different countries have different standards for approval of drugs – thalidomide was not licensed for sale in the US.

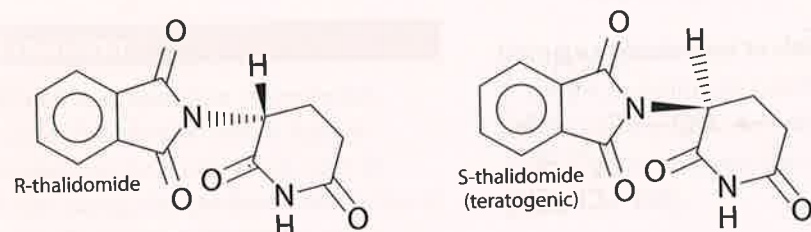


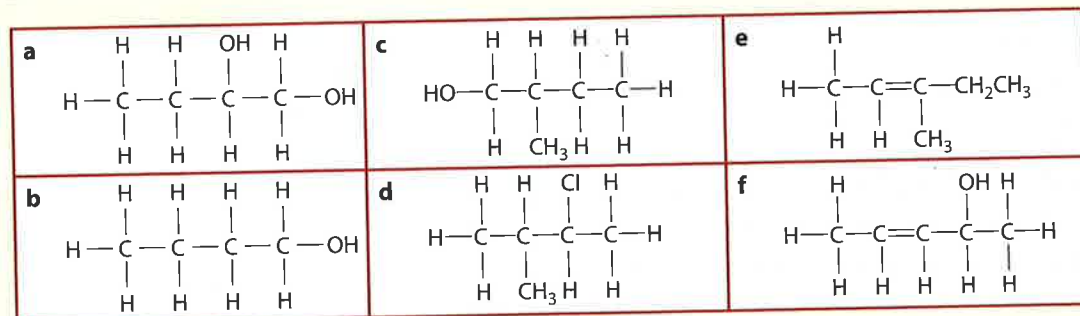
Figure 10.110 Enantiomers of thalidomide.

Nature of science

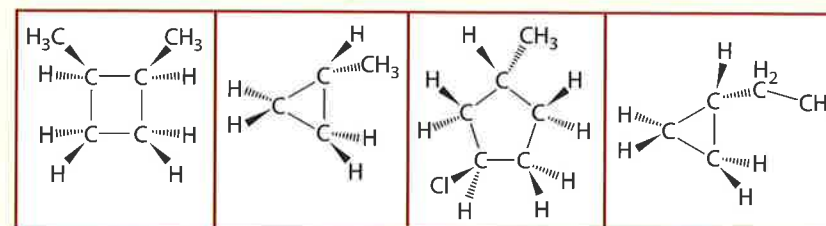
A great deal of Chemistry can be applied in other areas of science. The three dimensional shape of a molecule and stereochemistry are extremely important to reactions going on in the body and a knowledge of this is critical in some areas of biochemistry and other biological sciences.

? Test yourself

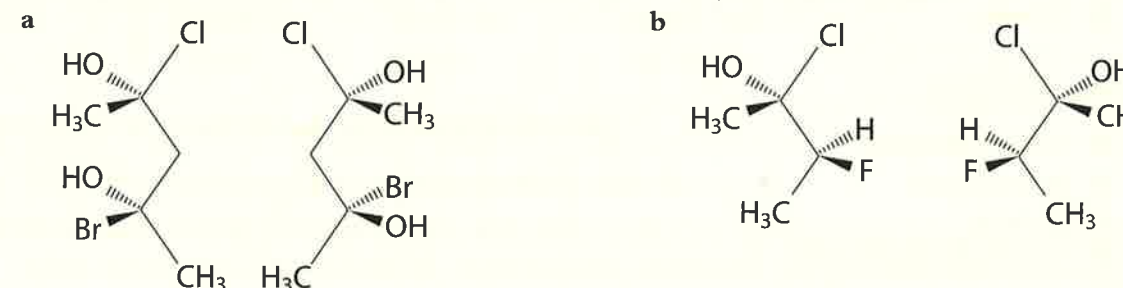
44 Which of the following molecules exhibit optical isomerism? For those that do, identify the chiral centre and draw three-dimensional diagrams showing the optical isomers.



45 Identify which of the following molecules is/are optically active:



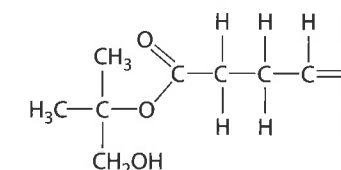
46 Identify which of the following are pairs of enantiomers or pairs of diastereomers:



Exam-style questions

1 The functional groups present in this molecule are:

- A hydroxyl, ester, alkenyl
- B ketone, carboxy, alkenyl
- C ester, aldehyde, alkenyl
- D alkenyl, ketone, hydroxyl



2 Which of the following is not a possible product when ethane reacts with chlorine in the presence of UV light?

- A HCl
- B CH₃CH₂Cl
- C H₂
- D CH₃CH₂CH₂CH₃

3 The product made when but-2-ene reacts with bromine is:

- A CH₃CHBrCH₂CH₃
- B CH₃CHBrCHBrCH₃
- C CH₃CBr₂CH₂CH₃
- D CH₃CHBrCH₂CH₂Br

4 The condensed structural formulas of three alcohols are shown below:

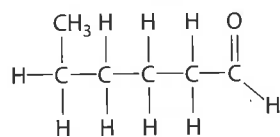
- I $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- II $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- III $(\text{CH}_3)_3\text{COH}$

Which would be oxidised by heating with acidified potassium dichromate(VI)?

- A I, II and III
- B I only
- C I and II only
- D III only

5 The name of this molecule is:

- A 5-methylpentanal
- B hexan-1-one
- C hexanal
- D 1-methylpentan-5-one

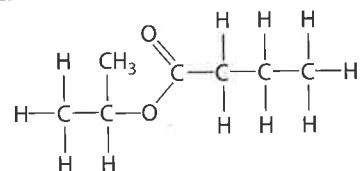


6 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ reacts with aqueous sodium hydroxide. The name of the product formed and the type of reaction are:

- | product | type of reaction |
|--------------|----------------------------|
| A butanal | oxidation |
| B butan-1-ol | electrophilic substitution |
| C butan-2-ol | electrophilic addition |
| D butan-1-ol | nucleophilic substitution |

7 The ester shown could be formed from the reaction between:

- A butanoic acid and propan-1-ol
- B propanoic acid and butan-2-ol
- C butanoic acid and propan-2-ol
- D butanoic acid and ethanol



HL 8 Which of the following substitution reactions is likely to occur most rapidly?

- A $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$
- B $(\text{CH}_3)_3\text{CCl} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Cl}^-$
- C $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH} + \text{Br}^-$
- D $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH} + \text{Cl}^-$

HL 9 Which of the following will exist as optical isomers?

- A 1-bromobutane
- B but-2-ene
- C pentan-2-ol
- D pentan-3-ol

HL 10 Butan-2-ol can be formed in each of the following reactions:

- I reduction of compound X with NaBH_4
- II heating compound Y with aqueous sodium hydroxide
- III heating Z with concentrated sulfuric acid

X, Y and Z could be:

- | | X | Y | Z |
|---|---------------|----------------|------------|
| A | butanoic acid | 2-chlorobutane | butane |
| B | butanone | 2-chlorobutane | but-1-ene |
| C | butanone | but-2-ene | butan-1-ol |
| D | butanal | butane | but-2-ene |

11 Four of the structural isomers of $\text{C}_4\text{H}_{10}\text{O}$ are alcohols.

- a Draw the structures and give the names of these alcohols. [4]
- b Two of the alcohols can be oxidised to carboxylic acids. Give the name and formula of a suitable oxidising agent, the structures of the carboxylic acids formed and describe any colour change that occurs. [6]
- c Draw and name an isomer of $\text{C}_4\text{H}_{10}\text{O}$ that is not an alcohol. [2]

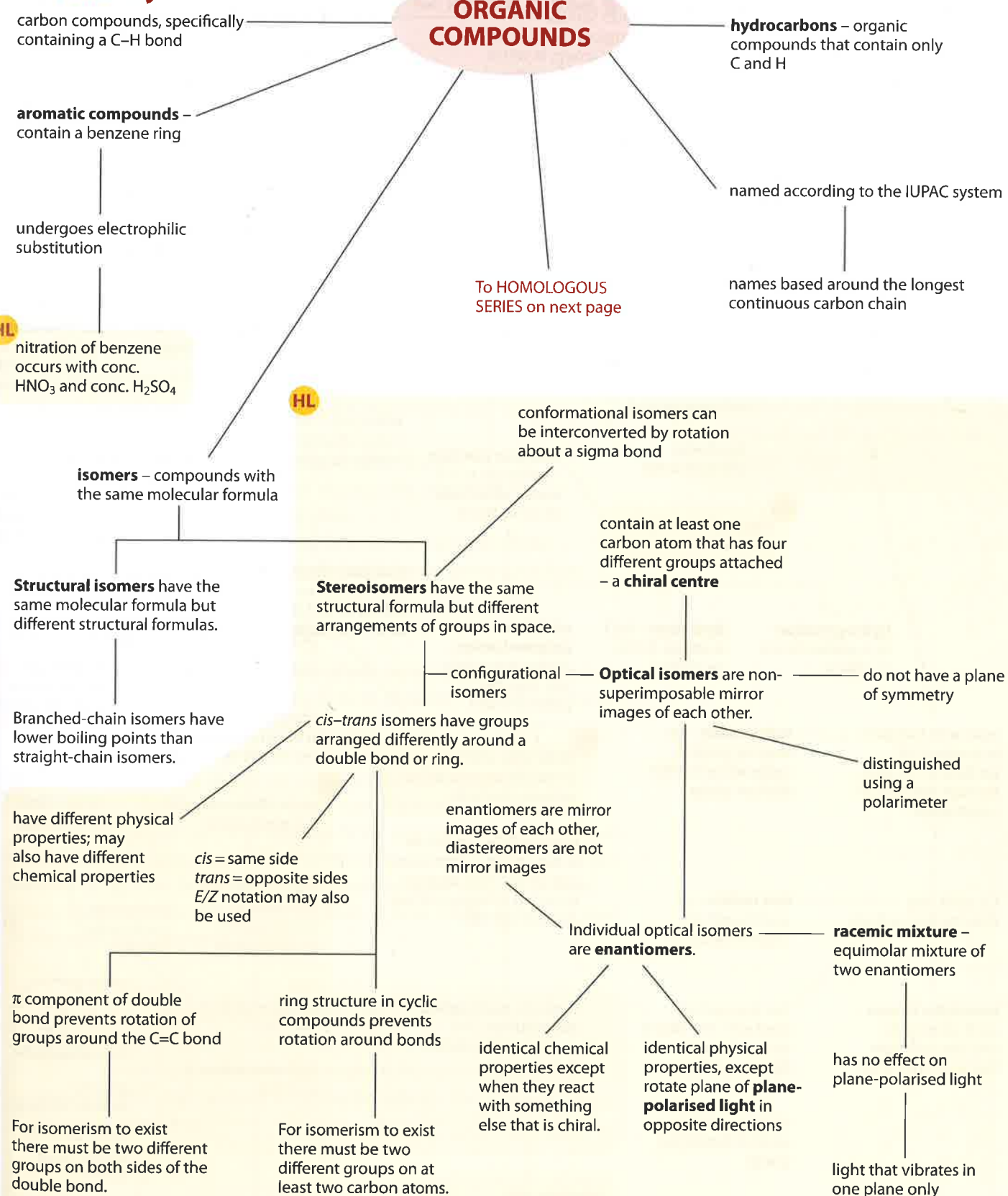
12 Ethane can react with chlorine in the presence of UV light to form chloroethane.

- a Write an equation for this reaction. [1]
- b i State the name of the mechanism by which this reaction occurs. [1]
- ii Use the mechanism of this reaction to explain the terms 'homolytic fission', 'free radical' and 'termination step'. [4]
- c Chloroethane reacts with aqueous sodium hydroxide.
 - i Write an equation for the reaction that occurs. [1]
 - ii Draw the mechanism for this reaction. [3]

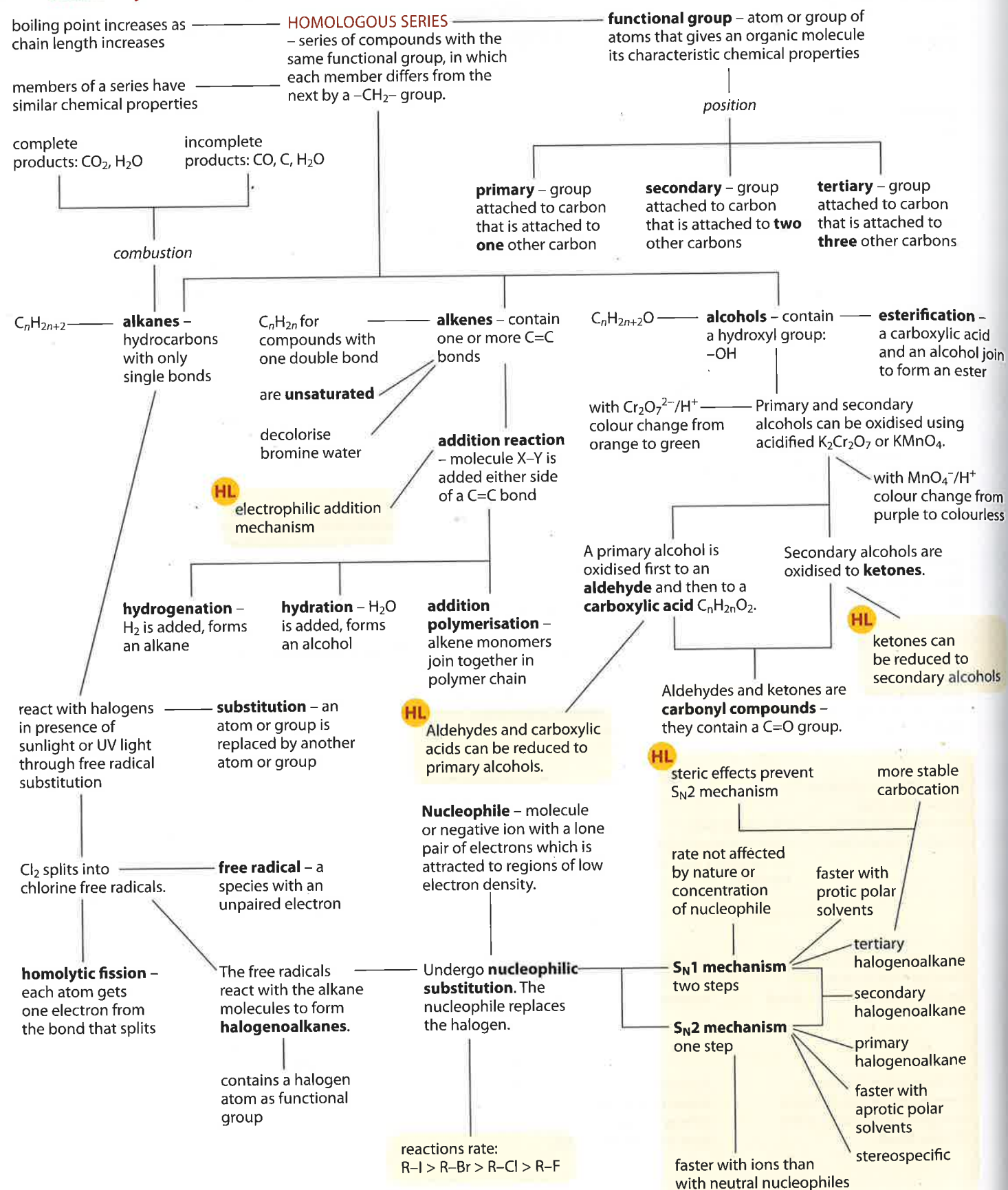
- 13 a Describe a chemical test that can be used to distinguish between butane and but-2-ene. [3]
- b Draw the structure of the compound formed when but-2-ene reacts with hydrogen bromide under appropriate conditions. [1]
- c But-2-ene can undergo polymerisation under suitable conditions. Draw three repeating units of the polymer formed. [2]
- HL d But-2-ene can be converted to butanone in a two-step reaction sequence. Draw out the reaction sequence showing all structures and giving essential conditions. [5]

- 14 An organic compound has the percentage composition 48.6% carbon, 8.2% hydrogen, 43.2% oxygen. The relative molecular mass of the compound is approximately 74. [3]
- Determine the empirical formula and the molecular formula of the compound. [3]
 - Two of the isomers of this compound are esters. Draw out full structural formulas and name these compounds. [4]
 - Write an equation for the formation of **one** of the esters from a carboxylic acid and an alcohol. [2]
 - A third isomer of this compound reacts with magnesium to form hydrogen gas. Draw the structure of this isomer and write an equation for the reaction with magnesium. [3]
- HL 15 This question is about 2-bromobutane. [3]
- 2-bromobutane exhibits optical isomerism. Explain what structural feature of 2-bromobutane allows it to exhibit optical isomerism and draw clear diagrams showing the optical isomers. [3]
 - 2-bromobutane can react with sodium hydroxide via an S_N2 mechanism. Explain what is meant by the 'N' in S_N2 . [1]
 - Explain why the S_N2 reaction of 2-bromobutane with sodium hydroxide is described as 'stereospecific'. [2]
 - Explain whether you would expect 1-bromobutane or 2-bromobutane to react more quickly with sodium hydroxide via an S_N2 mechanism. [2]
- HL 16 a Draw the full structural formula of 2-methylpent-2-ene. [1]
- Draw the full structural formula of the major product formed when 2-methylpent-2-ene reacts with hydrogen bromide in the dark. [2]
 - Write the mechanism for this reaction and explain the formation of the major product. [5]
 - The major product of the reaction in part **b i** reacts with sodium hydroxide via an S_N1 mechanism to form the alcohol, **X**. Write the mechanism for the formation of **X**. [3]
 - Explain whether **X** can be oxidised or not when it is heated with acidified potassium dichromate(VI). [1]

Summary



Summary – continued



Measurement and data processing 11

11.1 Uncertainties and errors in measurements and results

11.1.1 Uncertainties in measurements

Qualitative and quantitative data

Qualitative data are non-numerical data. These would normally be observations made during an experiment. For instance, when determining the empirical formula of magnesium oxide by burning magnesium in air you might make the following observations:

- the piece of magnesium is grey and not very shiny
- the electronic balance fluctuated as the magnesium was weighed
- the crucible was dirty
- the magnesium burned with a bright, white flame
- white smoke escaped as the lid of the crucible was lifted.

These are all pieces of qualitative data.

Quantitative data are numerical data. So, for example, all the measurements of mass made during the experiment above constitute quantitative data.

Measurements in science

Although in mathematics it is possible to have pure numbers and to write a number to any number of decimal places, in chemistry we are concerned with real quantities obtained by making measurements in a laboratory.

It is not possible to measure the actual, or true, value of a particular quantity. The true mass of a piece of magnesium ribbon could be 0.257 846 368 246 89 g, but we have no way of actually measuring that. The best we can ever get is an estimate. If we put the piece of magnesium on an electronic balance that gives values to one decimal place, we might measure 0.3 g. If we had a balance that could measure to three decimal places, then we might get 0.258 g. Neither of these values is the true mass of the piece of magnesium ribbon.



Consider the following argument.

Experimental data can never provide a true value for a quantity. The knowledge we get from science is ultimately obtained from experimental data. The knowledge we obtain from science is never true.

Learning objectives

- Understand the difference between quantitative and qualitative data
- Understand the difference between random uncertainties and systematic errors
- Understand the difference between precision and accuracy
- Understand how to quote values with uncertainties
- Understand the difference between significant figures and decimal places