

ORGANIC CHEMISTRY

10

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10.1 INTRODUCTION

- 10.1.1 Describe the features of a homologous series.
- 10.1.2 Predict and explain the trends in boiling points of members of a homologous series.
- 10.1.13 Discuss the volatility and solubility in water of compounds containing the functional groups listed in AS 10.1.9.

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Organic chemistry is the chemistry of carbon compounds (excluding compounds such as metal carbonates and oxides). Organic compounds constitute a major component of energy sources (petroleum, coal, natural gas), food (proteins, fats, carbohydrates, vitamins, enzymes, hormones, steroids), drugs (anaesthetics, antiseptics, antibiotics) and materials such as fibres, fabrics, plastics, paints, dyes, soaps, detergents, explosives etc.

Carbon is in group 4/14 of the periodic table and it always forms covalent bonds. As carbon has four electrons in its

valence level ($2s^2 2p^2$) it forms four covalent bonds. When these are all single bonds, they have a tetrahedral arrangement. In organic molecules carbon always forms four bonds, oxygen two, hydrogen and the halogens one (refer Section 4.2)

Carbon atoms can combine with each other and with other atoms (especially H and O) to form millions of compounds. Compounds of this kind are the basis of all known life, hence the term 'organic'. The existence of such a large number of stable compounds is partly due to the strength and stability of the C—C and C—H bonds (348 and 412 kJ mol^{-1} respectively). The former ensure that carbon can form long chains (a process known as catenation) and rings of carbon atoms; the latter that these structures are relatively stable and unreactive. Multiple bonds can also be formed between carbon atoms, but the presence of these usually leads to an increase in chemical reactivity. Similarly **functional groups** containing other atoms, such as oxygen, nitrogen and the halogens, can be attached to the hydrocarbon chain and result in greater reactivity. The reactions of these functional groups are the dominant feature of organic chemistry. Organic compounds may therefore be usefully regarded as comprising a hydrocarbon skeleton to which **functional groups** are inserted and/or attached:

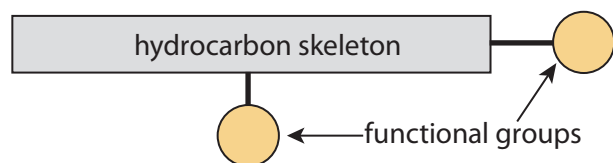


FIGURE 1001 Diagrammatic representation of an organic molecule

CORE

The ability of carbon atoms to form chains leads to the existence of a series of compounds that have the same functional group (and hence similar chemical properties) and only differ from each other by the presence of an additional carbon atom and its two associated hydrogen atoms in the molecule (which causes the physical properties to change in a regular manner). A series of compounds related in this way is said to form an **homologous series**. The alkanes are the simplest example of such a series, but others include the alkenes, the alcohols and the carboxylic acids. These series can be thought of as different ‘families’ of organic compounds. In these homologous series:

- successive compounds differ from each other by a $-\text{CH}_2-$ unit (known as a methylene group)
- the compounds can all be represented by a general formula (in the case of the alkanes $\text{C}_n\text{H}_{2n+2}$; if $n = 3$, then the formula is C_3H_8)
- the compounds have similar chemical properties
- successive compounds have physical properties that vary in a regular manner as the number of carbon atoms present increases.

The point about **chemical properties** is best illustrated by the sections that follow, on different homologous series. The changes in **physical properties** are a result of the

changes that occur in the strength of van der Waals’ forces with increasing molar mass and in some cases a change in molecular polarity. The simplest illustration of the effect of chain length on physical properties is the variation of the boiling point of the alkanes with the number of carbon atoms in the chain, as illustrated in Figure 1002.

This curve is initially quite steep because, for small molecules, the addition of an extra carbon has a proportionally larger effect on the molar mass (for example, from CH_4 to C_2H_6 there is an increase of 97.5%) and hence on the strength of the van der Waals’ forces. As the length of the chain increases, the percentage change in molar mass becomes progressively smaller (there is a 10.9% increase in molar mass from C_9H_{20} to $\text{C}_{10}\text{H}_{22}$) and so the curve flattens. Similar regular variation would be found in graphs of other physical properties, such as density and viscosity, against the number of carbon atoms.

The physical properties, especially the melting and boiling point of a compound, depend on the intermolecular forces present. All other factors being unchanged, the greater the molar mass of a molecule the stronger the intermolecular forces, hence the trend in the boiling points of the alkanes illustrated below. Some functional groups (such as $>\delta^+\text{C}=\text{O}\delta^-$, in aldehydes and ketones, and the presence of halogens) give rise to polarity within molecules, and this results in dipole-dipole forces and hence slightly higher melting and boiling points than would otherwise be expected. Other functional groups, such as alcohol ($-\text{OH}$), carboxylic acid ($-\text{COOH}$), amine ($-\text{NH}_2$) and amide ($-\text{CONH}_2$) give rise to hydrogen bonding between the molecules. Compounds containing these tend to have significantly higher melting and boiling points than non-polar or polar organic compounds of similar molar masses.

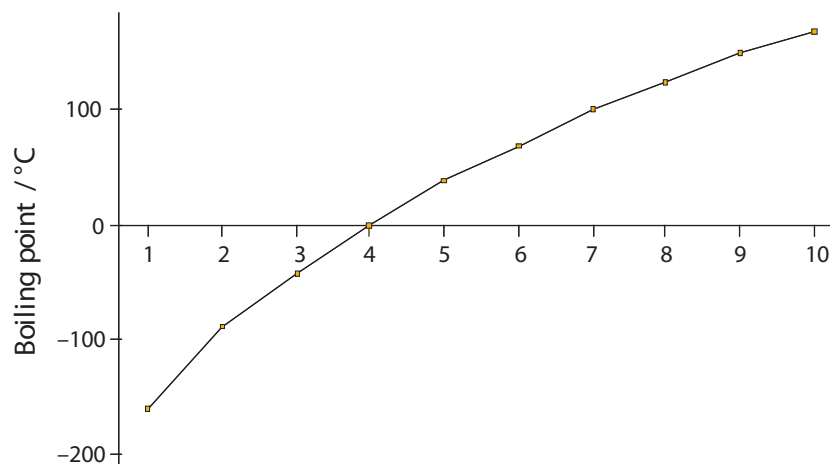


Figure 1002 Boiling points variations

These points are illustrated by the examples below:

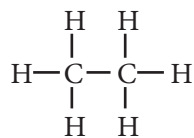


Figure 1003 Ethane
 $M_r = 30$ Non-polar b.p. = -89°C

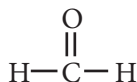


Figure 1004 Methanal
 $M_r = 30$ Polar b.p. = -21°C

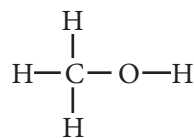


Figure 1005 Methanol
 $M_r = 32$ Highly polar b.p. = 65°C

Most organic compounds are non-polar and hence tend to be insoluble in water owing to the strong hydrogen bonds between the water molecules. If however the functional groups can hydrogen bond to the water (that is those that hydrogen bond to themselves, plus those containing the $>\text{C}=\text{O}$ group which can form hydrogen bonds to water), then the substance will be water soluble, as long as the hydrocarbon chain is relatively short. As the carbon chain increases there is a gradual decrease in the solubility as is the case with the alcohols. Thus, ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, is water miscible (mixes in all proportions), but hexan-1-ol, $\text{CH}_3(\text{CH}_2)_5\text{OH}$, dissolves only slightly in water. Some functional groups interact with the water and hence affect the pH of the resulting solution. Carboxylic acids, for example behave as weak acids and so reduce the pH. Amines act as weak bases in a similar manner to ammonia and so increase the pH.

10.1.3 Distinguish between empirical, molecular and structural formulas.

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In organic chemistry it is particularly important to distinguish carefully between **empirical formula**, **molecular formula**, **structural formula** and **full structural formula**. The full structural formula (also referred to as

graphic formula and displayed formula) shows all the atoms and bonds. For example the full structural formula for butanoic acid is:

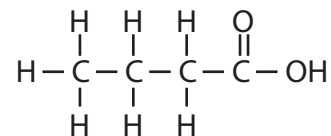
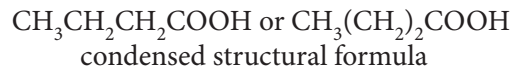



Figure 1006 Structural formula for butanoic acid

A structural formula indicates in an unambiguous manner how the atoms are arranged in the molecule. A condensed structural formula, that can usually be written on a single line, is one in which the bonds are omitted, side chains put in brackets and repeated identical groups collected together. Again using butanoic acid as the example:



As noted previously, the molecular formula gives the actual number of each type of atom in the molecule and the empirical formula the simplest whole number ratio of these. For butanoic acid these are:



Note that an alkyl group ($\text{C}_n\text{H}_{2n+1}$, like an alkane with one H removed) can be represented by R. Thus alcohols (which contain the hydroxyl group $-\text{OH}$) can be represented as ROH. Similarly the benzene ring can be represented as  so that phenol (a benzene ring with an $-\text{OH}$ attached) is represented as $\text{HO}-\text{C}_6\text{H}_5$.

10.1.4 Describe structural isomers as compounds with the same molecular formula but with different arrangements of atoms.

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Isomers are different compounds that have the same molecular formula. Different compounds have different physical properties (melting point, boiling point etc.). They may also have very different chemical properties depending on the type of isomerism present. Isomers may be divided into:

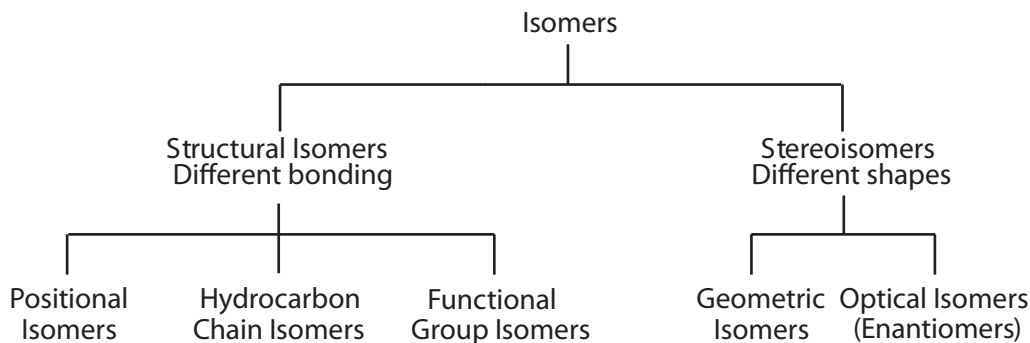


Figure 1007 The relationship of different types of isomers

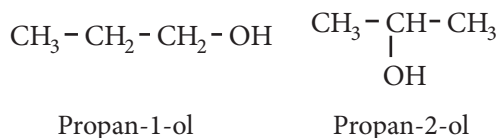
- **structural isomers**, in which the atoms are joined in a different order so that they have different structural formulae.

and

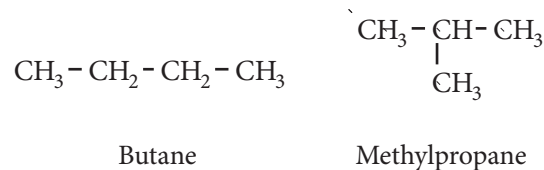
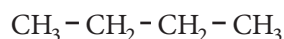
- **stereoisomers**, in which the order that the atoms are joined together is the same, but the molecules have a different arrangement of atoms in space and hence different three dimensional shapes.

It is useful to subdivide structural isomers into positional isomers, hydrocarbon chain isomers and functional group isomers. Similarly stereoisomers can be divided into geometrical isomers and optical isomers (also called enantiomers) and these are dealt with in more detail later. The relationship between the different types of isomerism is illustrated in Figure 1007.

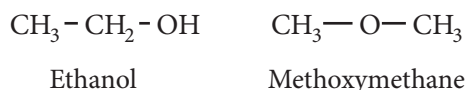
Positional isomers have the same hydrocarbon skeleton and the same functional group; it is just that the functional group is joined to a different part of the skeleton. A simple example of this type of isomerism is propan-1-ol and propan-2-ol:



Hydrocarbon chain isomers have, as the name would imply, different hydrocarbon skeletons that the functional group is attached to. Butane and methylpropane illustrate this type of isomerism:

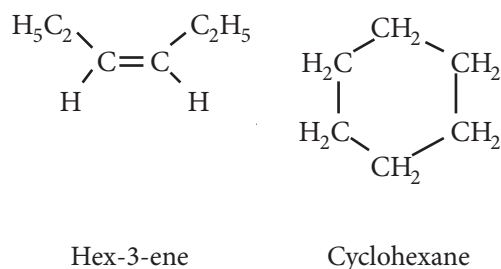


Because of their nature, some functional groups will usually have isomers containing another functional group. For example alcohols usually have an alkoxyalkane that is isomeric to them, hence ethanol has an isomer methoxymethane:

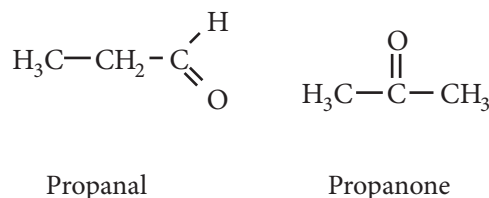


Other common pairs of functional groups that display functional group isomerism with each other are:

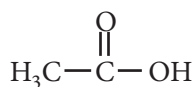
Alkene and Cycloalkane



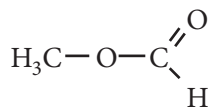
Aldehyde and Ketone



Carboxylic acid and Ester



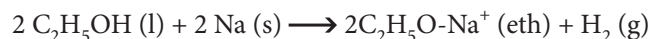
Ethanoic Acid



Methyl methanoate

In the case of positional and hydrocarbon chain isomers the functional group, which usually dictates the reactivity of the molecule, is unchanged therefore they have quite similar chemical properties. With functional group isomerism the change in the functional group can have a profound effect on both the physical and chemical properties of the molecule. In the previous example ethanol is a liquid (at room temperature and pressure) that will react with sodium to release hydrogen. Sodium

ethoxide is obtained as a white solid if excess ethanol is evaporated.



Methoxymethane (at room temperature and pressure) is a gas, since there is no hydrogen bonding, and it does not react with sodium because it has no hydroxyl group. Similarly methyl methanoate is a sweet smelling liquid that forms neutral solutions, whereas ethanoic acid has a sharp smell (vinegar) and forms acidic solutions.

TOK The importance of chemical models

The different types of formulas referred to in this chapter are certainly employed for different purposes. "Empirical" means "by experiment" and that's exactly what the empirical formula is – the result of a microanalysis experiment in which all of the carbon in the compound is converted into carbon dioxide and all the hydrogen into water, so the relative amounts of carbon, hydrogen and oxygen can be calculated, but on its own it is not of much further use. Combine it however with some information about how heavy each molecule is and we can then deduce some much more interesting information; how many atoms of each element are present in every molecule. That then allows us to test our theories of chemical bonding to work out the structural formulae showing how atoms can join together. Sometimes this can really stretch the mind and require creative thought, like Kekulé's dream.

This question also started me thinking about the words "formula" and "model" – do they mean the same thing and if not how do they differ? Both transfer information, but models (like the Bohr model of the atom) are also used to help with our "understanding" (whatever exactly that is) of the world and maybe that is a facet we do not seek in a formula. When I look, even at a full structural formula, I do not think that it helps my "understanding", it just conveys "information" about how the atoms are joined in the molecule and hence its probable shape. Now that leads us back to "models", though perhaps a slightly different use of the word – I'll leave you to judge. We get an even better idea of the shape using molecular models of different types. These are rather like different maps, each show some things clearly and other things less well, "Ball and stick" models for example give a clear idea of shape and what bonds are present, but the atoms always seem to be a long way apart. "Space filling" models more accurately reflect bond lengths as well as the different sizes of the atoms involved. Actually the concept of atomic size is an interesting one considering that we envisage the outer regions of an atom as just a cloud of electron density. How do we know where it ends? It's a bit like asking where does the Earth's atmosphere end; it doesn't really it just sort of fades away to nothing.

10.1.9 Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: alcohol, aldehyde, ketone, carboxylic acid and halide.

10.1.10 Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: alcohol, aldehyde, ketone, carboxylic acid and halide.

10.1.11 Identify the following functional groups when present in structural formulas: amino (NH_2), benzene ring (C_6H_6), esters (RCOOR).

10.1.12 Identify primary, secondary and tertiary carbon atoms in alcohols and halogenoalkanes.

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THE IUPAC SYSTEM

There is a systematic scheme for naming organic compounds known as the IUPAC (International Union of Pure and Applied Chemists) system, but many compounds also have 'trivial' names used before the introduction of this system, hence a large number of organic compounds have two names. In this book IUPAC names will be used consistent with the names used in the IB syllabus.

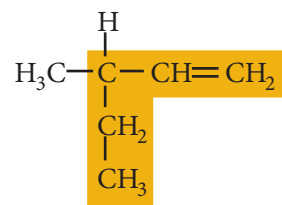
From the point of view of IUPAC naming, organic compounds are considered to comprise a hydrocarbon 'backbone' to which side chains and functional groups are attached. The backbone is considered to be the longest continuous chain of carbon atoms in the molecule and this supplies the stem of the name. The first six of these are given in Figure 1008:

No. of C atoms	Stem	Side chain
1	meth	Methyl
2	eth	Ethyl
3	prop	Propyl

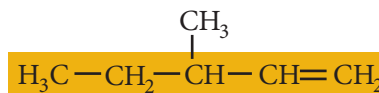
4	but	Butyl
5	pent	Pentyl
6	hex	Hexyl
Benzene ring	benz	Phenyl

Figure 1008 The naming of hydrocarbon chains

Note that it pays to inspect the formula carefully as the most obvious carbon chain is not always the longest one; $\text{CH}_3-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}=\text{CH}_2$ has a principal chain 5 carbons long, not 4 carbons long as shown below:

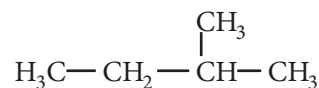
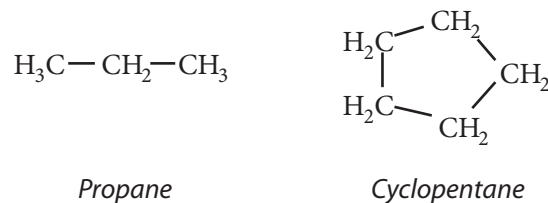


which is the same as



The prefix 'cyclo' can also be added to indicate that the carbon atoms are arranged in a ring. Hydrocarbon side chains may be attached to this longest chain and they are named in a similar manner. Another cyclic hydrocarbon structure that is often found in organic compounds is the **benzene ring**, C_6H_6 , which in condensed formulas may be abbreviated to C_6H_6 .

If the compound is an alkane where no functional groups are present, the ending '-ane' is added to the stem. Hence:



Methylbutane

Figure 1009

20.1 INTRODUCTION (AHL)

20.1.1 Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester, nitrile.

20.1.2 Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester, nitrile.

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The functional groups present in the molecule are indicated by prefixes or suffixes attached to the stem. These and a specific example of each class of compound are given in Figure 1010. In some cases a prefix is used if another **functional group** is already providing the ending; these alternatives are shown in brackets. There are also, in many cases, two ways of writing the functional group depending on whether a full structural formula or a condensed structural formula is being written. In formulas written

Name	Functional group	Prefix/suffix	Example
Alkane	None	-ane	CH ₄ ; methane
Alkene	C=C	-ene	CH ₂ =CH ₂ ; ethene
Alcohol	—O—H or —OH	-anol (or hydroxy-)	CH ₃ CH ₂ OH; ethanol
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \\ \text{or} \\ -\text{CHO} \end{array}$	-anal	CH ₃ CHO; ethanal
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \text{ or } \text{CO} \end{array}$	-anone	CH ₃ COCH ₃ ; propanone
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{H} \text{ or } \text{COOH} \end{array}$	-anoic acid	CH ₃ COOH; ethanoic acid
Halogenoalkane (chloro, bromo, or iodoalkane)	X (i.e. Cl, Br, I)	Halogeno- (fluoro-, chloro-, bromo-, or iodo-)	CH ₃ CH ₂ Cl; chloroethane
Amine	$\begin{array}{c} \text{H} \\ \\ -\text{N}-\text{H} \text{ or } \text{NH}_2 \end{array}$	-ylamine (or amino-)	CH ₃ CH ₂ NH ₂ ; ethylamine
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N} \begin{array}{l} \text{H} \\ \text{H} \end{array} \text{ or } \text{CONH}_2 \end{array}$	-anamide	CH ₃ CONH ₂ ; ethanamide
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \text{ or } \text{CO}-\text{O}- \end{array}$	The naming of esters is covered in section 20.4,	CH ₃ —CO—O—CH ₃ Methyl ethanoate
Nitrile	—C≡N or -CN	-anenitrile (or cyano-)	CH ₃ —CN Ethanenitrile (cyanomethane)

AHL

Figure 1010 The naming of functional groups table
(Note that the shaded groups are only required by Higher Level students).

this latter way, brackets are used to denote side chains, for example methylbutane would be $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$.

The naming of esters is slightly different in that they are named as if they were salts of the carboxylic acid, as explained in Section 20.4.

- If there is more than one functional group or side chain present then a principal functional group defines the ending and the other functional groups and side chains are indicated as prefixes, arranged in alphabetical order:

e.g. $\text{HO}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CHO}$ is 3-hydroxy-2-methylpropanal ("h" comes before "m"; note CHO must be a terminal group and the COOH group is the same)

- A double or triple bond may be indicated by changing the first vowel in the ending.

e.g. $\text{HO}-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{COOH}$ is 4-hydroxy-3-methylbut-2-enoic acid

- If there are a number of identical side chains or substituents, then this is indicated by placing the prefixes di- (2), tri- (3), tetra- (4) immediately in front of the prefix/suffix.

e.g. $\text{Cl}_3\text{C}-\text{COOH}$ is trichloroethanoic acid

- If there is more than one possible position for the side chain or functional group to attach itself, then this is indicated by numbers identifying the carbon atoms in the principal chain. If there is a functional group which must occur at the end of a carbon chain (such as COOH), then the carbon in this group is taken as the first carbon in the chain.

e.g. $\text{CH}_3-\text{CH}_2-\text{CHCl}-\text{COOH}$ is 2-chlorobutanoic acid

In other cases, the numbering starts from the end of the chain which gives the lowest sum of numbers for the substituents present.

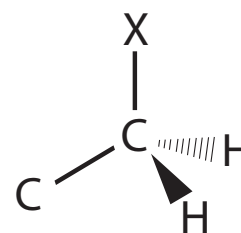
e.g. $\text{CH}_3-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{OH}$ is 2-chlorobutan-1-ol, not 3-chlorobutan-4-ol

Note that numbering of a side chain or functional group is ignored when there are no alternatives. For example as the aldehyde CH_3CHO is propanal, not propan-1-al, similarly $(\text{CH}_3)_3\text{CH}$ is just methylpropane (the 2- numbering for methyl can be ignored as it can only be in the 2-position; if it were in the 1-position it would be butane). However,

the name 'propanol' is ambiguous as it could be referring to propan-1-ol or propan-2-ol.

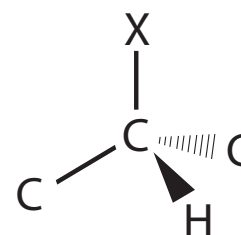
Comprehensive IUPAC nomenclature is a very complex subject, but this brief summary should enable you to cope with most of the compounds commonly encountered.

Organic compounds often contain functional groups bonded on to different types of carbon chains. These can often be usefully distinguished using the terms **primary**, **secondary** and **tertiary**. Primary means that the carbon that the functional group is joined to is bonded to only one other carbon atom, secondary means that it is bonded to two other carbon atoms and tertiary three other carbon atoms. This is illustrated in Figure 1011 where X represents the functional group.



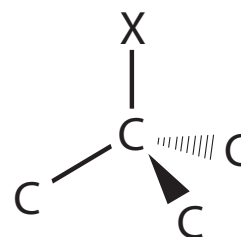
Primary

e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$



Secondary

e.g. $\text{CH}_3\text{CH}_2\text{CHClCH}_3$



Tertiary

e.g. $(\text{CH}_3)_3\text{CCl}$

Figure 1011 Illustrating primary, secondary and tertiary structures

Exercise 20.1

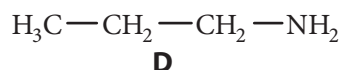
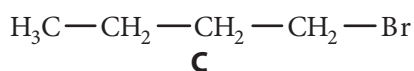
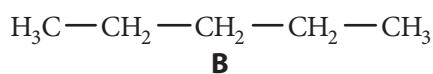
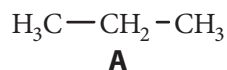
1. Which of the following is correct about the number of bonds formed by atoms of different elements in organic compounds?

	Carbon	Hydrogen	Oxygen
A	4	2	2
B	4	1	2
C	4	1	3
D	3	2	3

2. The alcohols, methanol, ethanol, propanol, butanol etc., form a homologous series. This means that they:

- A have similar chemical properties, but gradually changing physical properties.
 B have similar physical properties, but gradually changing chemical properties.
 C have the same molecular formula, but different physical properties.
 D have similar physical properties and the same structural formula.

These structural formulae are required for questions 3 & 4:



3. Which one of the above compounds would have the lowest boiling point?
4. Which one of the above compounds would be the most soluble in water?
5. Which one of the following lists the alkanes in order of decreasing boiling point?

- A Octane, Methane, Butane, Ethane
 B Methane, Ethane, Propane, Butane
 C Hexane, Octane, Propane, Methane
 D Hexane, Pentane, Propane, Ethane

6. Which one of the following formulae could represent more than one compound?

- A C_3H_8
 B $\text{CH}_3\text{CH}=\text{CH}_2$
 C $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
 D C_4H_{10}

7. How many isomers are there of the molecular formula $\text{C}_3\text{H}_7\text{Cl}$?

- A 2
 B 3
 C 4
 D 8

8. To which series of compounds does the molecule belong?



- A Ketone
 B Alcohol
 C Carboxylic acid
 D Aldehyde

9. Which of the following is the structure of but-1-ylamine?

- A $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$
 B $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$
 C $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}_2$
 D $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}_2$

10. What is the correct name of $\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{CHO}$?

- A 2-chlorobutanal
 B 4-chlorobutanal
 C 2-chloropentanal
 D 4-chloropentanal

11. The molecular formulae of a group of closely related molecules are given below.



- a) What name is given to a group of compounds related in this way?
- b) Write a general formula for this group of compounds.

- c) How would you expect the boiling points of these compounds to change with increasing numbers of carbon atoms? Explain.
- d) Compared to alkanes of a similar molar mass, would you expect these compounds to be
- more or less soluble in water.
 - more or less volatile.
- Explain your answers.
- e) CH_3NO_2 can be reduced to CH_3NH_2 by reacting it with hydrogen over a nickel catalyst. What product would you expect when $\text{C}_5\text{H}_{11}\text{NO}_2$ was treated in the same way? On what do you base your prediction?

10.1.5 Deduce structural formulas for the isomers of the non-cyclic alkanes up to C_6 .

10.1.6 Apply IUPAC rules for naming the isomers of the non-cyclic alkanes up to C_6 .

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Hydrocarbons are compounds containing only carbon and hydrogen. The simplest homologous series of this type is that comprising the straight chain **alkanes**. The first six members of this series, along with their names and structural formulae are given in Figure 1014.

No. of C atoms	Molecular Formula	Name	Structural formula
1	CH_4	Methane	
2	C_2H_6	Ethane	
3	C_3H_8	Propane	
4	C_4H_{10}	Butane	
5	C_5H_{12}	Pentane	
6	C_6H_{14}	Hexane	

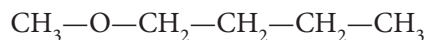
Figure 1014 The straight chain alkanes

The compounds shown in Figure 1014 are known as the straight chain alkanes because isomers of these compounds exist in which the carbon atoms are not joined in a single chain. The simplest example of such **isomerism** is butane and methylpropane which both have the molecular formula C_4H_{10} . Similarly three isomers exist with the formula C_5H_{12} . The names and structural formulae of these compounds are shown in Figure 1015 below (Note that C_6H_{14} has 5 isomers).

12. Draw structural formulae of the following compounds:

- Pentane
- 3-ethylhexane
- Bromoethane
- 2-methylbut-1-ene
- 3,3-dichloro-2-methylbutanoic acid

13. The structural formula of 1-methoxybutane is

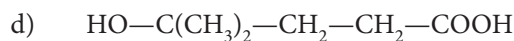
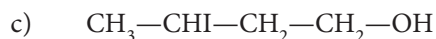
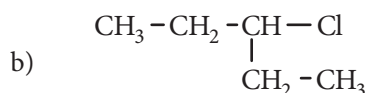
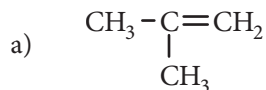


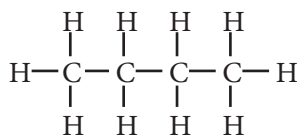
Draw structural isomers of this compound that illustrate:

- positional isomerism
- hydrocarbon chain isomerism
- functional group isomerism

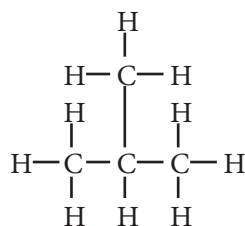
14. Write abbreviated structural formulae and name all the structural isomers of the compound with molecular formula C_6H_{14} .

15. Name the following compounds:

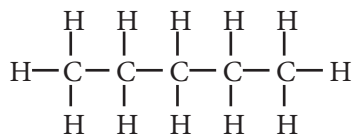




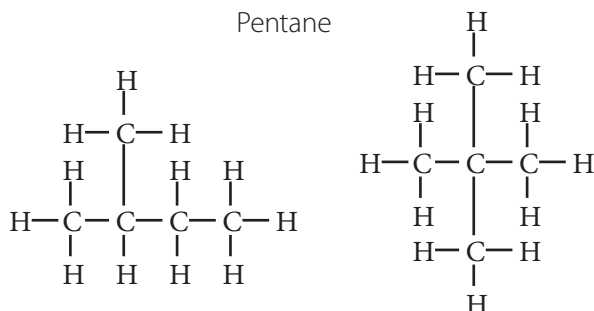
Butane



Methylpropane



Pentane



Methylbutane

Dimethylpropane

Figure 1015 Isomers of C_4H_{10} and C_5H_{12}

10.2 ALKANES

10.2.1 Explain the low reactivity of alkanes in terms of bond enthalpies and bond polarity.

10.2.2 Describe, using equations, the complete and incomplete combustion of alkanes.

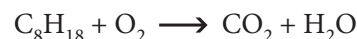
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The most familiar reaction of the alkanes is **combustion**. Like almost all organic compounds, the alkanes are flammable and oxidise when burnt in the air to form carbon dioxide and water if sufficient oxygen is present. The combustion of organic compounds is a highly exothermic process and is one of the most common sources of energy in society. Equations for these reactions often involve quite large coefficients, but balancing them is easy provided the following procedure is adopted:

1. All carbon atoms are converted to carbon dioxide fixing this coefficient
2. All hydrogen atoms are converted to water, fixing a second coefficient

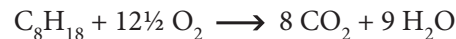
3. The number of oxygen molecules on the left must be adjusted to balance the oxygen

Consider applying this to the complete combustion of octane (C_8H_{18}), a major component of gasoline:



1. There are 8 carbon atoms so these must form 8 carbon dioxide molecules.
2. There are 18 hydrogen atoms so these must form 9 water molecules.
3. There are now 25 oxygen atoms on the right hand side, requiring $12\frac{1}{2}$ O_2 molecules.

The final equation is therefore:



This form is acceptable, but the ' $\frac{1}{2}$ ' can be eliminated by doubling all the coefficients.

Gasoline and many other fuels very rarely burn in this way. If the supply of air/oxygen is limited, as is the case in an automobile engine, then **incomplete combustion** occurs, so some of the carbon in the fuel, rather than forming carbon dioxide, is converted to carbon monoxide (CO, a colourless, odourless, highly toxic gas) or the element carbon itself (hence black smoke). Note that the hydrogen is still converted to water. These products, along with other minor products of hydrocarbon combustion and the residue of the lead compounds still added to some gasolines, are a major source of air pollution in large cities. Many countries now require the installation of catalytic converters which ensure that the combustion process is more nearly complete. For more details of these pollution problems, refer to Option D.

10.2.3 Describe, using equations, the reactions of methane and ethane with chlorine and bromine.

10.2.4 Explain the reactions of methane and ethane with chlorine and bromine in terms of a free-radical mechanism.

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Alkanes can also react with chlorine or bromine in a **substitution reaction**, to give an initial product in which one hydrogen atom is replaced by the halogen. Usually these reactions are brought about by exposure to ultraviolet light or sunlight, though they will also occur without light

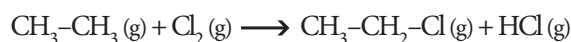
TOK The importance of IUPAC names

Communicating what exactly we are talking about quickly and effectively is important in any subject, hence names. It also depends on who you are talking to. For example when you are talking to other people in your class “Charlie” is an effective way to refer to a particular individual. It is however not very specific. If you said “Charlie” to your mother for example she probably wouldn’t know who you were talking about. To her “Charlie” is probably the name of the security guard at the hospital where she works. You would then have to go into a longer explanation – joined the school from Finland last term / has ginger hair / did a solo in the school concert / father drives a Ferrari etc. It’s useful not to have to go through all of that each time you want to tell a friend about something that took place during the last lesson, so names have their uses and pitfalls. Chemistry has the same problems; names that are unique and universal. For example in one research group TCP might be trichlorophenol and in another it might be tetrachloropropyne. The IUPAC system tries to tidy this and goes one step further because it should allow us to draw the structure of an organic compound from its name. Is it worth it? Why don’t we just draw the structure? In a

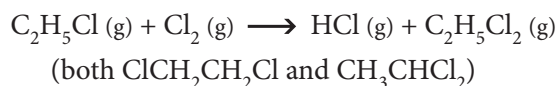
few cases it might be quicker (compare HOOC-COOH with ethanedioic acid, 9:15 characters), but in most cases the reverse would be true and complex ring structures are really difficult to do in the middle of text! Nevertheless alanine is a lot simpler to write than 2-aminopropanoic acid and *p*-xylene is simpler than 1,4-dimethylbenzene, which is probably why IUPAC names have never really caught on with biochemists and industrial chemists.

An IUPAC equivalent with humans might be to have a system that looks at facial characteristics so you can draw somebody from their name? For example: {gender / hair colour / hair length / eye colour / nose / chin} - I’m sure my children used to have a game that was based on this idea – what was it called? Anyway, on this system I might be {male-brown-neck length-brown-medium-bearded} - though it would be strange to have to change your name if you altered your hairstyle! The advantage is you now have some idea what I look like, but it requires a lot more writing than “John” and it’s hardly unique. How many characteristics would I have to list until my name was unique?

at very high temperatures. Taking ethane and chlorine as an example:



Note that the inorganic product is the hydrogen halide (in the above case HCl) and not hydrogen (H_2). These substitution reactions can replace more than one hydrogen, so that some of the chloroethane produced above will react with more chlorine to produce dichloroethanes. These substitutions also occur in a random manner so that the product will be a mixture of both 1,1-dichloroethane and 1,2-dichloroethane:



Further substitution of hydrogen atoms by chlorine can take place eventually yielding, with a large excess of chlorine, hexachloroethane (C_2Cl_6)

The reaction of an alkane, such as methane, with a halogen is a **free radical chain reaction**. This process can be split up into three distinct stages, **initiation** which produces the radicals (reactive species with unpaired electrons), **propagation** which forms most of the product and in which the radicals are reformed (that is one radical is used

up but another formed) and **termination** which consumes radicals. As a result the initiation stage occurring once can cause the propagation steps to occur many times before the radicals are consumed in a termination step. The details of such a process are given below using the reaction of methane with chlorine as an example.

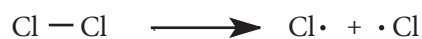


Figure 1016 - Initiation

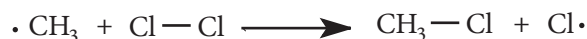


Figure 1017 - Propagation



Figure 1018 - Termination

It is traces of this final product, ethane that give a clue as to the nature of the reaction mechanism. Note that the hydrogen atom ($\text{H}\cdot$) does not occur at any stage in the mechanism. The mechanism of the reaction with ethane is very similar except that it involves the ethyl radical ($\text{CH}_3\text{CH}_2\cdot$) rather than the methyl radical and traces of butane (C_4H_{10}) are found in the product from the combination of these in a termination step.

Bromine reacts in an almost identical manner to chlorine. Because of its brown colour the speed of reaction with bromine is easily followed and if a mixture of an alkane and bromine is placed in sunlight the brown colour slowly fades, but there is no reaction in the dark.

10.3 ALKENES

10.1.7 Deduce structural formulas for the isomers of the straight-chain alkenes up to C_6 .

10.1.8 Apply IUPAC rules for naming the isomers of the straight-chain alkenes up to C_6 .

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The alkanes are said to be **saturated hydrocarbons** because they contain only single carbon-carbon bonds, those with multiple bonds are called **unsaturated**

hydrocarbons. The simplest compounds of this type are the **alkenes**, which contain a carbon-carbon double bond. The **alkynes**, containing $\text{C}\equiv\text{C}$ triple bonds, are also unsaturated hydrocarbons. The general formula for the alkene homologous series is C_nH_{2n} (note that this is also the general formula of the cycloalkanes) and the structural formulae and names of the simplest isomers of the first five members of the series are given in Figure 1019.

Though double bonds are stronger than single bonds, they are not twice as strong ($\text{C}=\text{C}$ 612 kJ mol^{-1} , $\text{C}-\text{C}$ 348 kJ mol^{-1}). This means that it is energetically favourable for a double bond to be converted into two single bonds. The activation energy for these reactions is also relatively low, owing to the high electron density in the double bond. This means that alkenes are considerably more reactive than alkanes and are an important starting point in the synthesis of other organic compounds. As a result alkenes, usually formed by the cracking of fractions of petroleum, are very important intermediates in the economically important **petrochemicals** industry.

No. of C atoms	Molecular formula	Name	Structural formula
2	C_2H_4	Ethene	
3	C_3H_6	Propene	
4	C_4H_8	But-1-ene	
5	C_5H_{10}	Pent-1-ene	
6	C_6H_{12}	Hex-1-ene	

Figure 1019 Straight chain terminal alkenes

10.3.1 Describe, using equations, the reactions of alkenes with hydrogen and halogens.

10.3.2 Describe, using equations, the reactions of symmetrical alkenes with hydrogen halides and water.

10.3.3 Distinguish between alkanes and alkenes using bromine water.

10.3.4 Outline the polymerization of alkenes.

10.3.5 Outline the economic importance of the reactions of alkenes.

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A reaction in which the double bond of an alkene is converted to a single bond and two new bonds are formed to the species it reacts with is known as an **addition reaction** and they are typical of alkenes and alkynes. A number of important addition reactions are illustrated in Figure 1020:

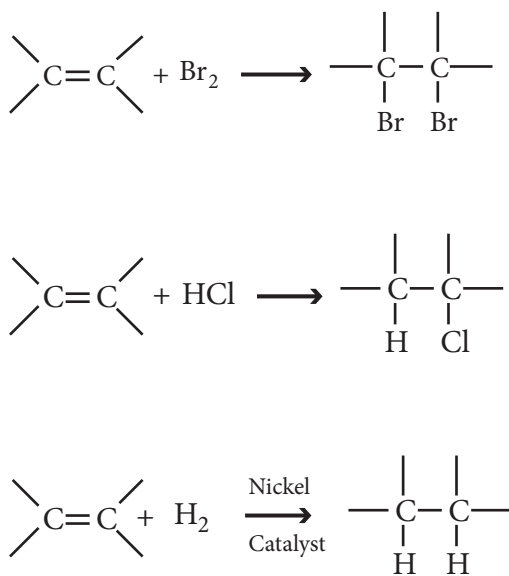
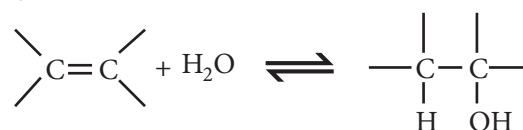


Figure 1020 Common addition reactions

The usual test for the presence of a carbon–carbon double or triple bond is to add bromine water to the compound. If a double or triple bond is present, the bromine water changes colour from yellow–brown to colourless. This reaction, shown in Figure 1020a, which also occurs with chlorine and iodine, takes place spontaneously at room temperature and pressure. A similar spontaneous reaction occurs between alkenes and hydrogen halides such as hydrogen chloride and this is shown in Figure 1020b. With hydrogen, the activation energy is slightly higher, but if a gaseous mixture of an alkene and hydrogen is passed over a heated nickel catalyst, an addition reaction to form an alkane occurs as shown in Figure 1020c. This reaction is

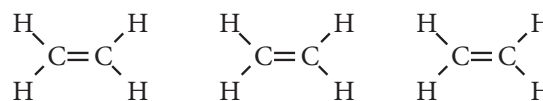
the basis of the conversion of vegetable oils, which contain a number of C=C double bonds, into margarine, which has fewer double bonds and hence a higher melting point.

With water (in the form of superheated steam), the addition reaction is reversible. At a temperature of $\sim 300^\circ\text{C}$ and a high pressure (~ 7 atm) the equilibrium shown is driven to the right (Le Chatelier's principle) and this provides the basis for the industrial manufacture of ethanol. **Ethanol** is used in large quantities by industry both as a solvent and as an intermediate in the manufacture of other compounds, hence this is a very commercially important process. At atmospheric pressure the equilibrium lies to the left and alkenes are formed by the dehydration of alcohols. The reaction in both directions is catalysed by either acids (usually H_2SO_4 or H_3PO_4) or heated aluminium oxide, Al_2O_3 .

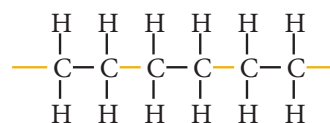


Polymers are long chain molecules that are formed by the joining together of a large number of repeating units, called **monomers**, by a process of **polymerisation**. Polymers, can be made artificially and these are usually referred to as plastics, but there are also a great number of naturally occurring polymers.

One type of polymerisation reaction is known as addition polymerisation. In this the monomers contain double bonds and in the addition reaction new bonds (shown coloured below) form between these monomer units. The simplest polymerisation reaction of this type is that of ethene when heated under pressure with a catalyst to form **polyethene**, commonly known as 'polythene'.



Ethene monomers



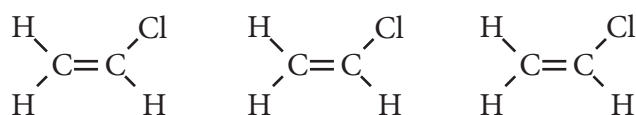
Polyethene polymer

Figure 1021 The addition polymerisation of ethene to form polyethene

This may also be represented by the equation below in which the repeating unit is shown in square brackets.



Two other common addition polymers are poly(chloroethene), better known as PVC (short for its old name of PolyVinyl Chloride), formed by the polymerisation of chloroethene



Chloroethene monomers

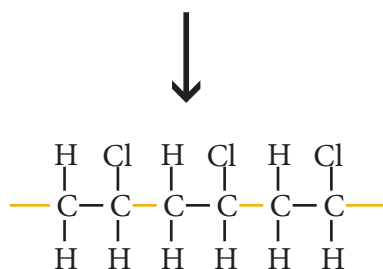
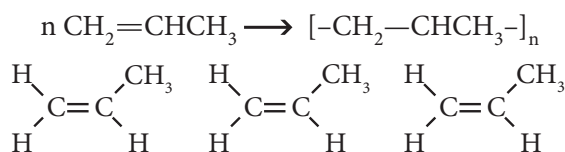
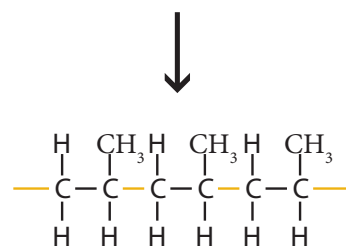


Figure 1022 Polymerisation of chloroethene to form poly(chloroethene)

and polypropene, formed by the polymerisation of propene:



Propene monomers



Polypropene polymer

Figure 1023 Polymerisation of propene to form polypropene

All of these polymers are produced in very high tonnages for the manufacture of a wide variety of products, hence these polymerisation reactions are economically very important. Polymers are discussed in greater detail in the Chemistry in Industry and Technology Option, Chapter 14.

Exercise 10.3

CORE

- It is found that natural gas from a particular source decolourises bromine water. From this it can be concluded that
 - the gas contains some unsaturated hydrocarbons.
 - the gas contains only unsaturated hydrocarbons.
 - the gas is an alkene.
 - the gas contains some saturated hydrocarbons.
- What is the formula of the organic product of the reaction between propene and bromine?
 - $\text{Br}-\text{CH}_2-\text{CH}=\text{CH}_2$
 - $\text{CH}_3-\text{CH}_2-\text{CHBr}_2$
 - $\text{CH}_3-\text{CHBr}-\text{CH}_2\text{Br}$
 - $\text{Br}-\text{CH}_2-\text{CBr}=\text{CH}_2$
- Which one of the following molecular formulae does not represent an alkane?
 - C_3H_6
 - C_6H_{14}
 - C_8H_{18}
 - $\text{C}_{12}\text{H}_{26}$
- When propane undergoes complete combustion in air, for each mole of propane burnt, how many moles of oxygen are consumed and how many moles of water are formed?

	Moles of oxygen	Moles of water
A	3	8
B	5	8
C	3	4
D	5	4

5. Which one of the following would you not expect to find in the exhaust gases of a normal car?
- Nitrogen
 - Hydrogen
 - Water vapour
 - Carbon monoxide
6. A free radical is any chemical species that:
- is very reactive.
 - results from the breaking of a covalent bond.
 - is formed by the action of UV light on a molecule.
 - contains unpaired electrons.
7. a) Draw the structural formula of pent-2-ene.
 b) Write a balanced chemical equation for the complete combustion of pent-2-ene.
 c) What is produced during the reaction, other than the chemical products?
 d) If the supply of oxygen was reduced, what other chemical product might result from the combustion?
 e) Give one reason why the production of this substance is undesirable.
 f) Draw a structural isomer, other than pent-1-ene, and name the compound.
8. a) Name and write the structural formula of the organic product formed when ethene reacts with hydrogen bromide.
 b) To what class of reactions does this belong?
 c) What reagents and conditions are required for the conversion shown below?

$$\text{CH}_3-\text{CH}=\text{CH}_2 \longrightarrow \text{CH}_3-\text{CH}_2-\text{CH}_3$$

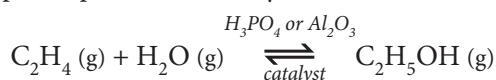
 d) What test could you carry out on both the starting material and the product that would show that this reaction had occurred?
 e) What conditions are required for an alkene to react with steam?
 f) Name the alkene $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$.
 g) Write the structural formula of the product formed when this alkene reacts with steam.
9. Most plastics are polymers formed from monomers produced from crude oil.
- Explain what is meant by the terms in *italics*.
 - Polythene, which may be produced by heating ethene ($\text{CH}_2=\text{CH}_2$) at a very high pressure, can be represented by the formula $[-\text{CH}_2\text{CH}_2-]_n$. Give the equivalent formulae for P.V.C. (polyvinyl chloride; polychloroethene) and also give the formula of the monomer that it is made from.
 - Propene too can be polymerised to form the polymer "Polypropylene", used in ropes and knitwear. Write the structural formula of a section of "Polypropylene" containing three propene units.

10.4 ALCOHOLS

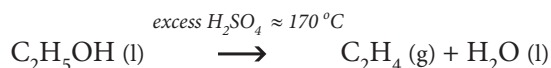
The simplest group of organic compounds containing oxygen are the **alcohols**, which contain the hydroxyl (—OH) group. The best known of this group of compounds is **ethanol** (C₂H₅OH), the ‘alcohol’ in alcoholic drinks. For the production of alcoholic drinks ethanol is formed by the fermentation of sugars such as glucose, a slow process requiring warm, anaerobic (meaning in the absence of oxygen) conditions:



This reaction is brought about by enzymes (biochemical catalysts) produced by yeast (a microorganism) that grows in the fermenting liquid. This produces only ~15% ethanol, but pure ethanol may be produced by distillation. Ethanol for industrial purposes is usually produced by the addition reaction of ethene with steam over a phosphoric acid catalyst at high pressure. If an alcohol is passed over the acid catalyst or a heated aluminium oxide catalyst at atmospheric pressure it is dehydrated to an alkene:



In the laboratory the dehydration reaction is more usually performed by heating the alcohol with a dehydrating agent such as concentrated sulfuric or phosphoric acid. Using ethanol as the example:

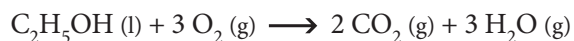


The mechanism of this dehydration is discussed in more detail later on.

10.4.1 Describe, using equations, the complete combustion of alcohols.

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Alcohols, like most other organic compounds, burn readily in air to form carbon dioxide and water, hence they are useful fuels. An equation for this reaction is given below, using ethanol as the example:



As with all such combustion reactions, carbon monoxide or even carbon can be produced if the supply of air is restricted, hydrogen however is never a product of combustion.

10.4.2 Describe, using equations, the oxidation reactions of alcohols.

10.4.3 Determine the products formed by the oxidation of primary and secondary alcohols.

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Alcohols may be subdivided into three classes according to the number of carbon atoms attached to the same carbon atom as the the hydroxyl group, —OH, group:

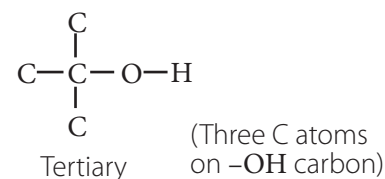
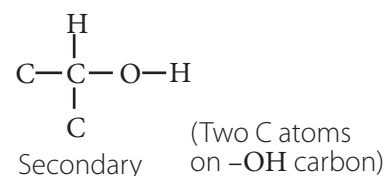
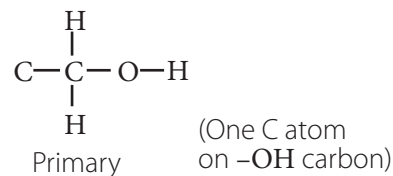


Figure 1024 Groups of alcohols (page 383)

The hydrogen atoms attached to the same carbon as the —OH group are readily **oxidised** and so these three classes of alcohols behave in rather different ways when they react with oxidising agents such as acidified potassium dichromate(VI). Tertiary alcohols do not have any reactive hydrogen atoms and are not readily oxidised. Secondary alcohols have one reactive hydrogen and so undergo one stage of oxidation to yield ketones. Primary alcohols have two readily oxidised hydrogen atoms and so the oxidation occurs in two stages producing firstly **aldehydes** and then, on further oxidation, carboxylic acids. This is summarised in Figure 1025.

Both aldehydes and alcohols are polar, however, alcohols have higher boiling points as these experience hydrogen bonding in addition to dipole-dipole forces. Thus, in practice to obtain the aldehyde, the alcohol is added to the boiling oxidising agent so that as soon as the more volatile aldehyde is formed, it **distils** off (see Figure 1026a) before it can be further oxidised. In order to obtain the carboxylic acid a more concentrated solution of the oxidising agent is used and the mixture is refluxed so that the aldehyde

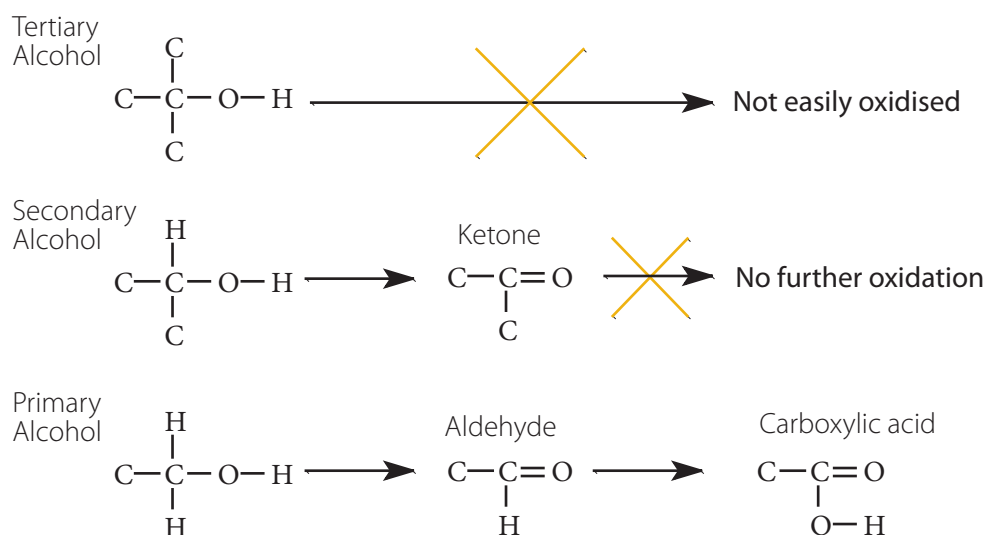
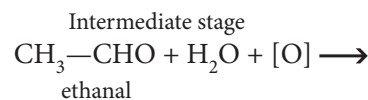
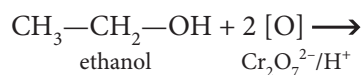


Figure 1025 The oxidation of alcohols

cannot escape further oxidation (see Figure 11.8b). Heating under **reflux** allows us to carry out a reaction at the boiling point of the solvent without any loss of the solvent. The vapour from the boiling solvent turns back to a liquid in the vertical condenser and drips back into the flask (see Figure 1026b).

If dichromate(VI) is used as the oxidising agent, then the orange dichromate(VI) ion ($\text{Cr}_2\text{O}_7^{2-}$) undergoes a colour change to the green chromium(III) ion (Cr^{3+}). The balanced equation is rather complex (though writing one is a good test of understanding of half equations) and so in such reactions the convention has arisen to indicate the oxygen from the oxidising agent as an oxygen atom in

square brackets. Hence the oxidation of ethanol to its final product, ethanoic acid, can be written as:



Other oxidising agents, such as the permanganate(VII) ion in acidified solution, may also be used, but care must be

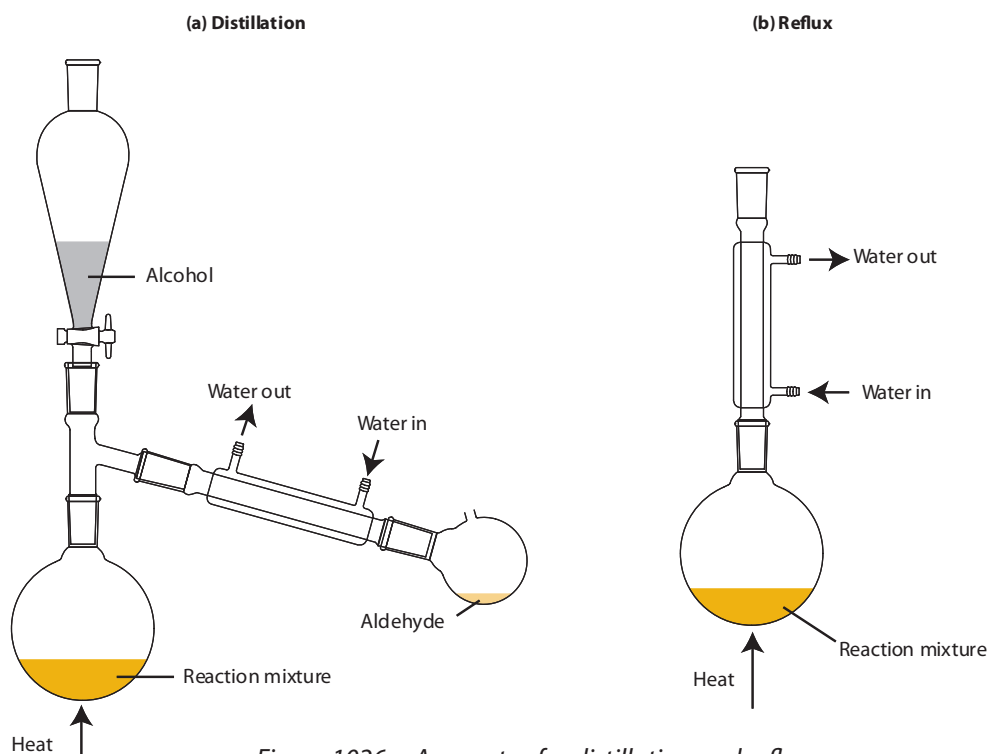


Figure 1026 Apparatus for distillation and reflux

taken as this more powerful reagent can also oxidise other functional groups (e.g. $>C=C<$). Ethanoic acid is also produced by bacterial oxidation when alcoholic drinks are left exposed to the air, producing vinegar. Carboxylic acids, as their name suggests, act as weak acids in aqueous solution.

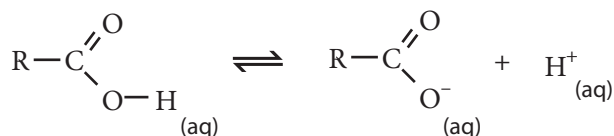


Figure 1027

Exercise 10.4

- When ethanol is oxidised to ethanoic acid by heating with acidified potassium dichromate(VI):
 - the ethanol is reduced and the colour changes from orange to green.
 - the ethanol is reduced and the colour changes from green to orange.
 - the ethanol is oxidised and the colour changes from green to orange.
 - the ethanol is oxidised and the colour changes from orange to green.
- When propan-1-ol is burnt in a plentiful supply of air, how many molecules of oxygen are consumed for each molecule of propanol?
 - $4\frac{1}{2}$
 - 5
 - 9
 - 10
- Propan-1-ol can be oxidised to propanoic acid in the same way as ethanol to ethanoic acid.
 - What reagents would you use for this oxidation?
 - What colour change would you expect to observe during the reaction?
 - How would you expect the product to react with sodium carbonate?

10.5 HALOGENOALKANES

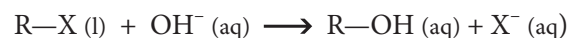
10.5.1 Describe, using equations, the substitution reactions of halogenoalkanes with sodium hydroxide.

10.5.2 Explain the substitution reactions of halogenoalkanes with sodium hydroxide in terms of S_N1 and S_N2 mechanisms.

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CORE

In **halogenoalkanes**, the polarity of the carbon–halogen bond means that the carbon atom carries a slight positive charge. Because of this it is susceptible to attack by **nucleophiles** (reagents that attack at a centre of positive charge by donating an electron pair), and this means that halogenoalkanes are considerably more reactive than the alkanes, undergoing **nucleophilic substitution** reactions, in which the halogen atom is readily replaced by other atoms or groups of atoms. For example when they are warmed with an aqueous alkali halogenoalkanes undergo hydrolysis to form an alcohol:



Warming 1-bromobutane with aqueous sodium hydroxide will therefore produce butan-1-ol:



There are two distinct mechanisms by which nucleophilic substitution reactions occur. A mechanism is a model of how a reaction occurs through series of steps). The first of these is known as S_N1 . In this mechanism there is a slow, rate determining, unimolecular (hence the 1), heterolytic fission of the carbon–halogen bond to yield an intermediate electron deficient carbocation. This then reacts rapidly with the hydroxide ion to yield the final product.

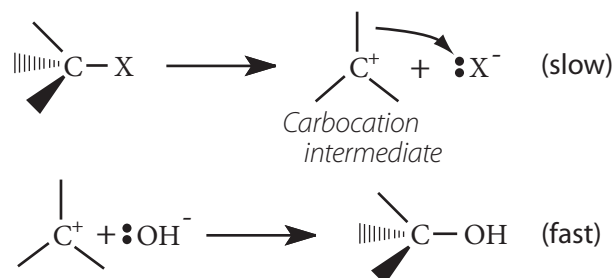


Figure 1028 Nucleophilic substitution by an S_N1 mechanism

Experimentally, the rate expression for this reaction is found to be:

$$\text{rate} = k \cdot [\text{R-X}]$$

that is it is first order with respect to halogenoalkane and independent of (zero order in) the concentration of the hydroxide ion.

The second mechanism is known as $\text{S}_{\text{N}}2$. In this mechanism, the bimolecular (hence the 2) attack of the hydroxide ion on the halogenoalkane molecule is rate determining. The reaction passes through a transition state (or activated complex) in which the bond to the hydroxide ion is starting to form at the same time as the bond to the halogen breaks, hence the substitution occurs in one concerted step:

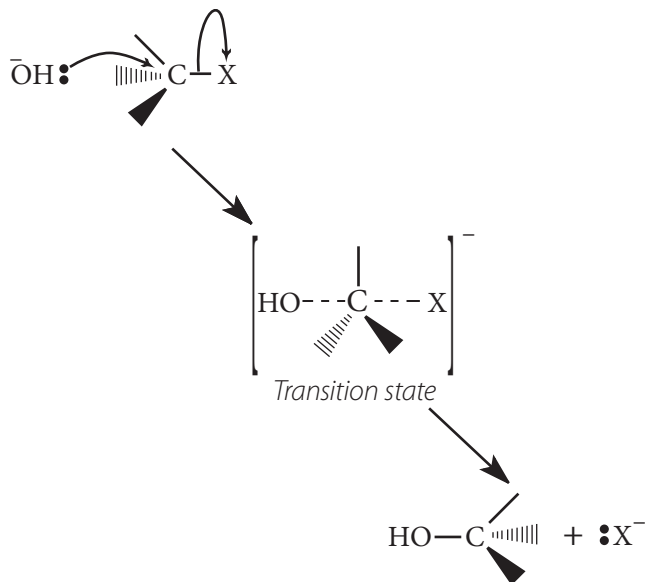


Figure 1029 Nucleophilic substitution by a $\text{S}_{\text{N}}2$ mechanism

Reactions that occur by this mechanism are found to be first order with respect to both $[\text{RX}]$ & $[\text{OH}]$, hence second order overall:

$$\text{rate} = k[\text{R-X}]^1[\text{OH}]^1$$

Like alcohols, halogenoalkanes can be divided into primary, secondary and tertiary according to the number of groups bonded to the same carbon as the halogen:

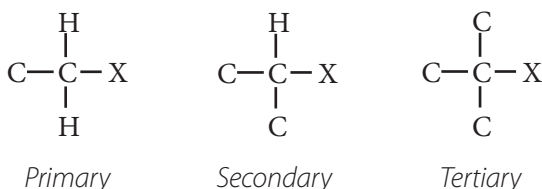


Figure 1030 Classes of halogenoalkanes

With primary halogenoalkanes (for example $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$) reaction with nucleophiles, such as the hydroxide ion, usually occurs by the $\text{S}_{\text{N}}2$ mechanism, whereas with tertiary halogenoalkanes (for example $(\text{CH}_3)_3\text{CCl}$) it usually occurs by the $\text{S}_{\text{N}}1$ mechanism. With secondary halogenoalkanes (such as $\text{CH}_3\text{CH}_2\text{CHClCH}_3$) both mechanisms can occur.

Exercise 10.5

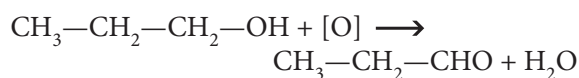
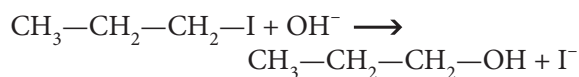
- When 2-iodopropane ($\text{CH}_3\text{CHICH}_3$) is warmed with aqueous potassium hydroxide the major organic product is:
 - CH_3COCH_3
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 - $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- Which one of the following compounds would be **most** likely to react with aqueous sodium hydroxide by an $\text{S}_{\text{N}}2$ mechanism?
 - $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
 - $\text{CH}_3\text{C}(\text{CH}_3)\text{BrCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_3$
- Which one of the following is **not** true about a reaction between an aqueous alkali and a halogenoalkane that occurs by an $\text{S}_{\text{N}}1$ mechanism?
 - The product will be an alcohol
 - The hydroxide ion bonds to the carbon at the same time as the halogen breaks free
 - The reaction occurs through the formation of a carbocation intermediate.
 - The mechanism involves the heterolytic fission of the carbon-halogen bond.
- Write a balanced equation for the reaction between iodoethane and aqueous sodium hydroxide, then describe the mechanism of the reaction indicating the movements of the valence electrons.
- Write the mechanism for the alkaline hydrolysis of 3-chloro-3-ethylpentane and use this to explain the meaning of the terms *heterolytic fission* and *carbocation intermediate*.

10.6 REACTION PATHWAYS

10.6.1 Deduce reaction pathways given the starting materials and the product.

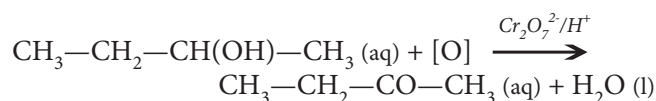
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Often in organic chemistry the desired product cannot be produced from the available starting material in a single step. In these cases the reaction must be carried out in a number of steps, referred to as the reaction pathway. For example if you wanted to convert 1-iodopropane into propanal you could not achieve this in a single step, so you must consider what substances can be easily converted to aldehydes (alcohols can) and whether you can form such a compound directly from the available starting material (in this case “yes”; if the answer is “no” then the pathway would involve more than 2 steps. The conversion can therefore be brought about by firstly hydrolysing 1-iodopropane to propan-1-ol and then oxidising this to propanal:

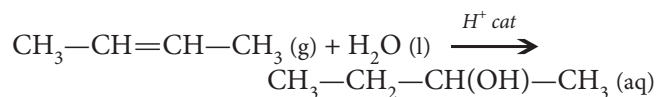


It is also important to know the conditions required to bring these reactions about and this can be found either from the relevant sections of this chapter or from the summary table at the end of this section.

Another example of a conversion that cannot be directly carried out is the preparation of butanone from but-2-ene. In the scheme in Figure 1031 the only reaction to produce a ketone is the oxidation of an alcohol. In fact it must be a secondary alcohol, as a primary alcohol gives an aldehyde then a carboxylic acid. Butanone must therefore be produced by the oxidation of butan-2-ol. This reaction can be brought about by heating the alcohol with acidified potassium dichromate(VI):



The scheme in Figure 1031 shows that it is possible to convert an alkene to an alcohol. This can be brought about by reacting the alkene with water in the presence of an acid catalyst, so that the reaction with but-2-ene will be:



Note that it is important to use but-2-ene as but-1-ene could also produce some of the primary alcohol (butan-1-ol), which would oxidise to the aldehyde, not the ketone.

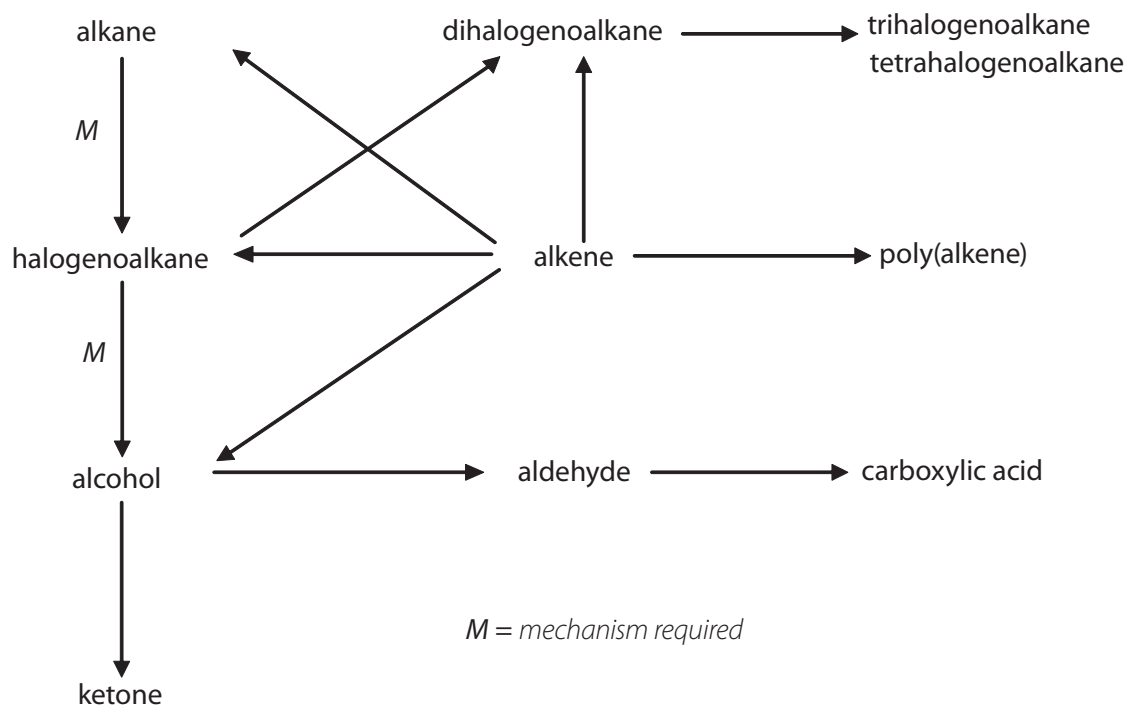
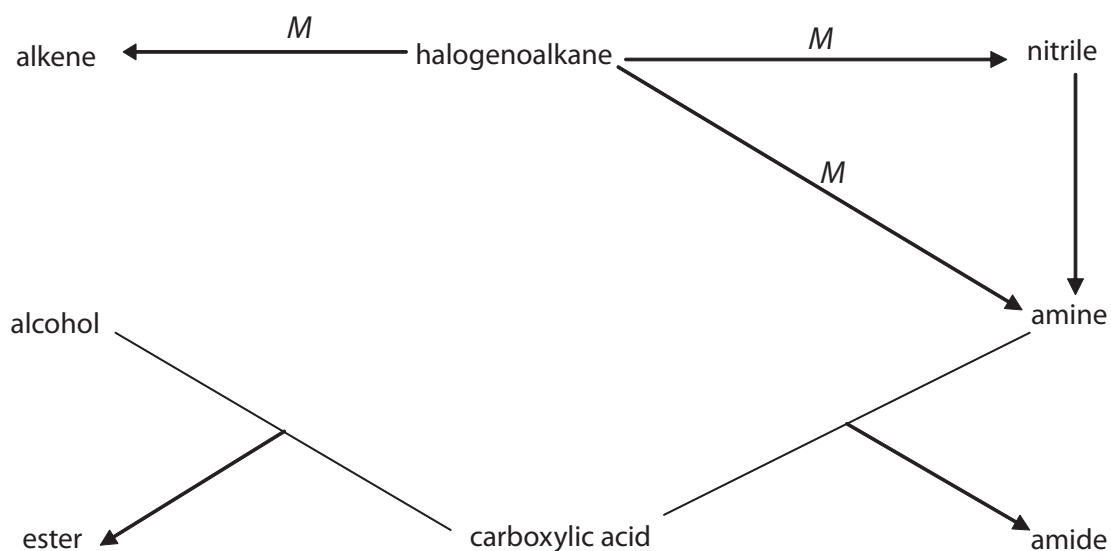


Figure 1031 Standard Level Reaction Pathways



M = mechanism required

Figure 1032 Higher Level Reaction Pathways

AHL

HIGHER LEVEL

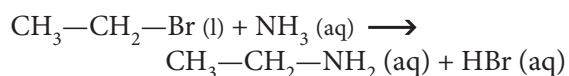
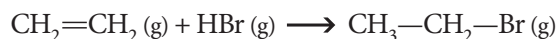
Exercise 10.5

20.5 REACTION PATHWAYS (AHL)

20.5.1 Deduce reaction pathways given the starting materials and the product.

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An example of a more advanced conversion of this type would be the formation of ethylamine from ethene. Here the alkene could be converted to a halogenoalkane, which could then be converted to an amine, (refer to Figure 1032)



Again the conditions required to bring these reactions about and this can be found either from the relevant sections of this chapter or from the summary table provided.

(* indicates HL question)

- Which one of the following would be a suitable intermediate in the conversion of methane to methanol?
 - CH_3Cl
 - CH_2Cl_2
 - CHCl_3
 - CCl_4
- An alkene can be converted to a ketone via
 - an aldehyde.
 - an alcohol.
 - a halogenoalkane.
 - an alkane.
- Which one of the following cannot be produced by the oxidation of an alcohol?
 - An aldehyde.
 - A ketone.
 - A carboxylic acid.
 - An alkane.

4*. Which one two compounds can react to form an amide?

- A An alcohol and a carboxylic acid.
- B An amine and an alcohol.
- C A halogenoalkane and an amine.
- D An amine and a carboxylic acid.

5*. Which of the following reactions does not require a catalyst?

- A A nitrile reacting with hydrogen
- B An alcohol reacting with a carboxylic acid
- C A halogenoalkane reacting with aqueous sodium hydroxide
- D An alkene reacting with water.

6. Indicate by means of balanced equations how you could convert 2-chlorobutane to butanone. Give the reagents and conditions for the reactions that you give.

7*. Given just ethanol, how could you produce an ester? Name the ester and outline the reagents and conditions required for all of the reactions you describe.

HIGHER LEVEL

20.2 NUCLEOPHILIC SUBSTITUTION REACTIONS (AHL)

20.2.1 Explain why the hydroxide ion is a better nucleophile than water.

20.2.2 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on the identity of the halogen.

20.2.3 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on whether the halogenoalkane is primary, secondary or tertiary.

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AHL

The reaction of **halogenoalkanes** with the hydroxide ion is just one example of a class of reactions known as **nucleophilic substitution** reactions. As outlined above these can occur by two different mechanisms, S_N1 and S_N2 . In the S_N1 mechanism, the slow heterolytic fission of the carbon-halogen bond to form a carbocation intermediate is the rate determining step. The intermediate then reacts rapidly with the nucleophile (Nu^-) to form the final product. Note that the intermediate has a finite existence and occurs at a potential energy minimum on Figure 1033.

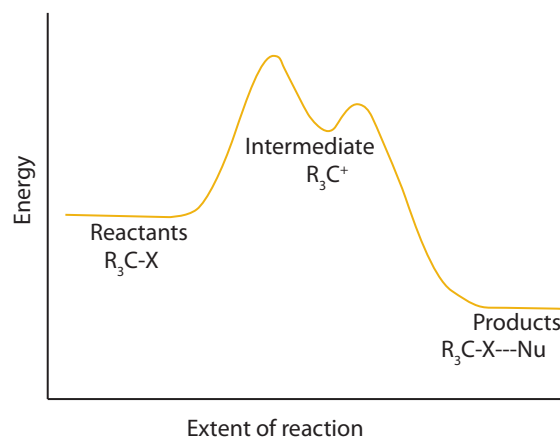


Figure 1033 Energy profile of a S_N1 reaction

In the S_N2 mechanism the breaking of the carbon-halogen bond occurs simultaneously with the formation of the new bond to the nucleophile. The point at which both are half completed is known as the transition state and it occurs at a potential energy maximum on the energy level diagram in Figure 1034.

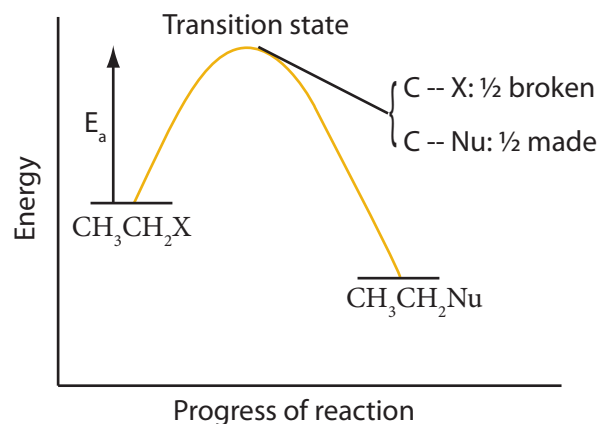


Figure 1034 Energy profile of a S_N2 reaction

The rate at which these reactions occur depends on the nature of both the nucleophile and the halogenoalkanes. For example some species are described as being stronger nucleophiles because they more readily attack a carbon with a partial positive charge. The hydroxide ion, for example, is a stronger nucleophile than the water molecule because it is negatively charged and hence attracted to the partial positive charge on the carbon attached to the halogen. As a result S_N2 hydrolysis reactions occur far more rapidly in aqueous alkali than in neutral solution.

The nature of the halogen also affects the rate of reaction. There are two factors. Firstly, as the halogen changes from chlorine to iodine, the polarity of the carbon-halogen bond decreases and this would be expected to decrease the rate of reaction going from chlorine to iodine because the partial positive charge on the carbon would become smaller. Secondly, the strength of the carbon-halogen bond decreases going from chlorine to iodine and it would be expected to have the opposite effect. In practice it is found that the rate of hydrolysis is greater for iodoalkanes than it is for chloroalkanes, implying that the bond strength is the dominant factor: see Figure 1035.

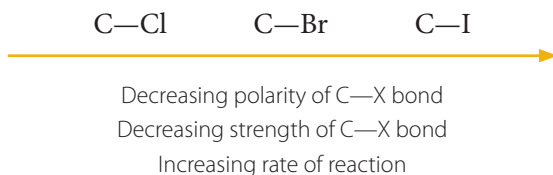


Figure 1035 Effect of the halogen on the rate of nucleophilic substitution

Tertiary halogenoalkanes (R_3C-X) usually react by an S_N1 mechanism, whereas primary halogenoalkanes (RCH_2-X) usually react by an S_N2 mechanism. This is a result of a number of factors:

- Tertiary carbocations are relatively stable because of the inductive effect of the alkyl groups, which reduces the charge on the central carbon, so stabilising the carbocation intermediate required for S_N1 .
- The change from tetrahedral to trigonal planar geometry when the carbocation is formed increases the bond angle from 109° to 120° . In tertiary halogenoalkanes this allows the alkyl groups to move further apart, so stabilising the carbocation by reducing steric stress.
- In the S_N2 mechanism, the nucleophile usually attacks the central carbon from the direction opposite to the halogen. In tertiary compounds bulky alkyl groups hinder such an attack.

Secondary halogenoalkanes (R_2CH-X) can react by either or both mechanisms. Because S_N1 reactions generally occur faster than S_N2 reactions it is found that, all other factors being equal, the rate of hydrolysis of halogenoalkanes decreases in the order



Note that halogenated aromatic compounds, in which the halogen is bonded directly on to the benzene ring, are much less reactive than other halogenoalkanes. The main reasons for this are:

- the carbon-halogen bond is stronger and more difficult to break because one of the lone electron pairs on the halogen atom interacts with the delocalised σ -bond of the benzene ring giving the carbon-halogen bond partial double bond characteristics.
- attack from the opposite side to the carbon-halogen bond is blocked by the electron rich benzene ring.
- the partial charge on the carbon bonded to the halogen is reduced because of adjustments in the mobile electrons of the delocalised σ -bond.

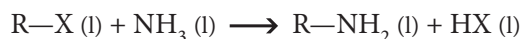
20.2.4 Describe, using equations, the substitution reactions of halogenoalkanes with ammonia and potassium cyanide.

20.2.5 Explain the reactions of primary halogenoalkanes with ammonia and potassium cyanide in terms of the S_N2 mechanism.

20.2.6 Describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst.

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Besides the hydroxide ion, a variety of other molecules and ions can behave as nucleophiles and participate in nucleophilic substitution reactions with halogenoalkanes. Two examples of these are the reaction with ammonia to form a **primary amine** and reaction with the cyanide ion to form a **nitrile**:



With a primary halogenoalkane this will occur by an S_N2 mechanism as shown in Figure 1036.

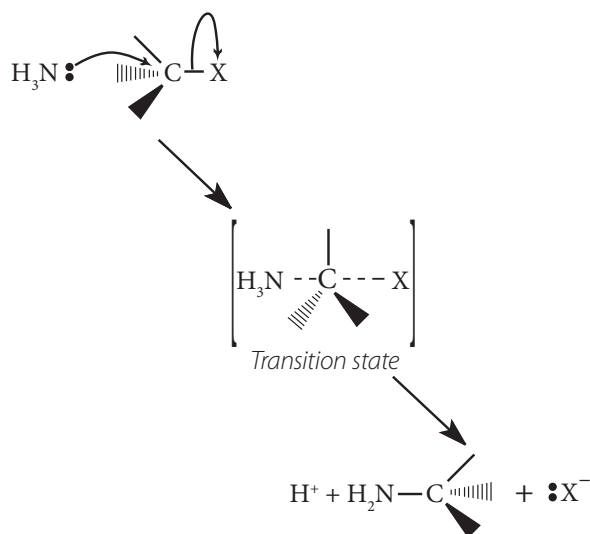


Figure 1036 The S_N2 mechanism for the formation of a primary amine from a halogenoalkane

Note that the product above is the cation formed from the amine and it must lose a hydrogen ion to form the amine itself. Similarly the reaction of a primary halogenoalkane with the cyanide ion to form a nitrile will occur by an S_N2 mechanism as shown in Figure 1037.

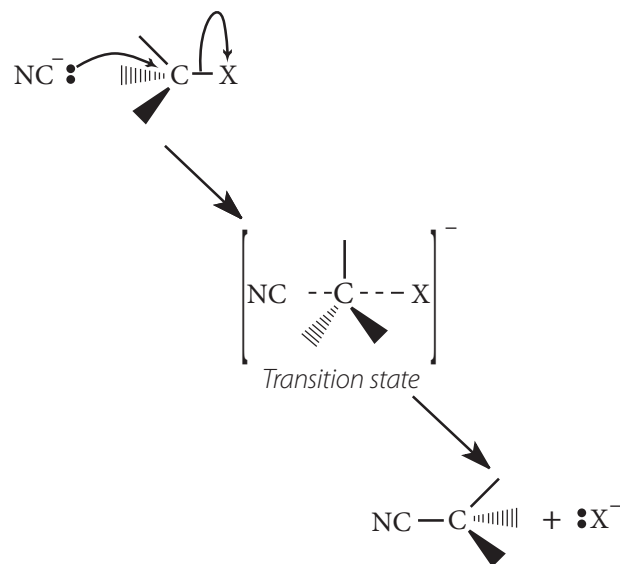


Figure 1037 The S_N2 mechanism for the formation of a nitrile from a halogenoalkane

In forming this product a new carbon-carbon bond has been formed and hence it is a useful way to lengthen the hydrocarbon chain of a molecule. The triple bond in the nitrile may be readily reduced, using hydrogen and a nickel catalyst to form a primary amine, but note that this amine contains one more carbon atom than the one formed by direct reaction with ammonia.



Exercise 20.2

- When a halogenoalkane reacts with ammonia, the product is:
 - a nitrile
 - an amine
 - a carboxylic acid
 - an amide
- Which one of the following isomers would hydrolyse the most rapidly with aqueous sodium hydroxide?
 - $CH_3-CH(CH_3)-CH_2-Br$
 - $(CH_3)_3C-Br$
 - $CH_3-CH_2-CH_2-CH_2-Br$
 - $CH_3-CHBr-CH_2-CH_3$
- Which one of the following does not undergo a nucleophilic substitution reaction with iodomethane?
 - $CH_3-CH(CH_3)-CH_2-Br$
 - $(CH_3)_3C-Br$
 - $CH_3-CH_2-CH_2-CH_2-Br$
 - $CH_3-CHBr-CH_2-CH_3$

- A Ammonia
 B Water
 C Bromide
 D Hydroxide

4. a) Write a balanced equation for the conversion of 1-chlorobutane to but-1-ylamine.
 b) What mechanism would this occur by?
 c) Draw this mechanism and use it to explain what is meant by the terms nucleophile and a transition state.
 d) Would you expect the reaction using 1-bromobutane to be more rapid or less rapid? Explain your reasoning.
5. a) Draw the structural formula of ethanenitrile and give the hybridisation of the two carbon atoms involved.
 b) Write a balanced equation for the formation of this compound from bromomethane and draw the mechanism for this reaction so as to show the movement of electrons.
 c) Ethanenitrile will react with hydrogen under suitable conditions. Write a balanced equation for this reaction, naming both the catalyst required and the product.

When a bromoalkane is warmed with dilute aqueous alkali it undergoes a substitution reaction to produce the corresponding alcohol. If however it is added to a hot, concentrated solution of an alkali in ethanol it undergoes an **elimination reaction** to form an **alkene** as shown in Figure 1038.

In the case of the elimination reaction, the hydroxide ion reacts with the ethanol to produce the ethoxide ion as follows:



This is a stronger base and weaker nucleophile than the hydroxide ion and so favours the elimination reaction, as does the higher temperature and concentration. The ethoxide ion acts as a base and removes the hydrogen ion from the carbon next to the halogen as shown in Figure 1039.

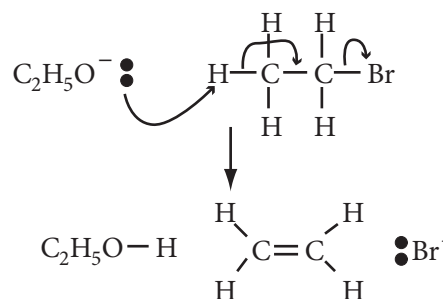


Figure 1039 Mechanism of the elimination reaction of a bromoalkane

The overall reaction is therefore the elimination of hydrogen bromide from the bromoalkane. Note that if the halogen is in the middle, rather than at the end of the hydrocarbon chain then the elimination can occur in more than one direction, hence a mixture of products may result. Hence, as shown in Figure 1040 below, two different alkenes are produced when 2-bromobutane is heated with alcoholic solution of potassium hydroxide:

20.3 ELIMINATION REACTIONS (AHL)

20.3.1 Describe, using equations, the elimination of HBr from bromoalkanes.

20.3.2 Describe and explain the mechanism for the elimination of HBr from bromoalkanes.

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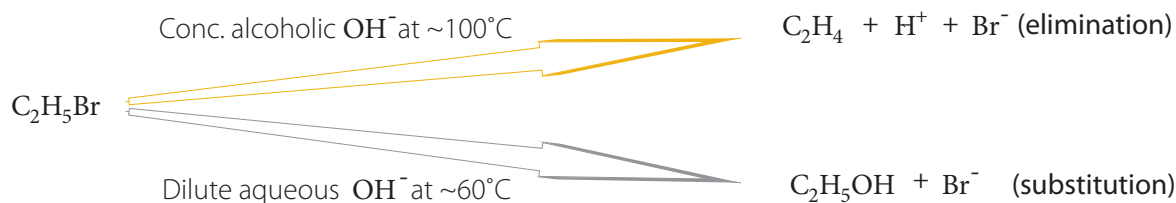


Figure 1038 The competition of elimination and substitution reactions in bromoalkanes

Exercise 20.3

1. When 1-bromobutane is added to the following solutions of potassium hydroxide, which would give the greatest yield of but-1-ene?

	Solvent	Concentration	Temperature
A	Ethanol	5 mol dm ⁻³	70°C
B	Ethanol	0.5 mol dm ⁻³	40°C
C	Water	5 mol dm ⁻³	40°C
D	Water	0.5 mol dm ⁻³	70°C

2. In the elimination reaction of 1-bromoethane to produce ethene, the hydroxide ion acts as:

- A a nucleophile.
 B an oxidising agent.
 C a reducing agent.
 D a base.

3. When 3-bromopentane undergoes an elimination reaction the product will be

- A pent-1-ene only.
 B pent-2-ene only.
 C a mixture of pent-1-ene and pent-2-ene.
 D a mixture of pent-1-ene and pentan-3-ol.

4. Explain how varying the reaction conditions can affect the product of the reaction between 1-bromopropane and sodium hydroxide.

5. 2-bromohexane is added to a concentrated boiling solution of potassium hydroxide in ethanol.

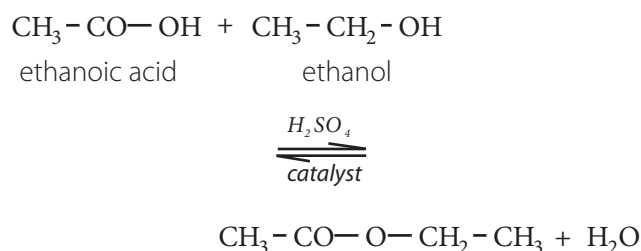
- a) What class of reactions does this belong to?
 b) Draw the mechanism by which this reaction occurs.
 c) Explain why two different products can be obtained and name these products.
 d) How would the product change if the halogenoalkane were warmed with dilute aqueous alkali?

20.4 CONDENSATION REACTIONS (AHL)

20.4.1 Describe, using equations, the reactions of alcohols with carboxylic acids to form esters, and state the uses of esters.

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When **alcohols** are heated with **carboxylic acids** in the presence of concentrated sulfuric acid, they produce sweet smelling compounds called **esters**. Because of their aroma and taste, esters are often incorporated into artificial perfumes and flavours. They are also used as solvents and plasticisers. A simple reaction of this type is that of ethanol with ethanoic acid to form ethyl ethanoate:



In these reactions, known as **esterification reactions**, the small amount of sulfuric acid has two functions. Firstly, and most importantly, the hydrogen ions act as a catalyst to increase the rate of the reaction and secondly it reacts with the water formed to shift the position of the equilibrium to the right hand side (Le Chatelier's principle) ensuring a good yield of product. Note that unlike the acid and alcohol, an ester does not contain an -OH group and so is much more limited in its ability to hydrogen bond to water molecules, hence esters tend to be insoluble in water.

It can be seen that the naming of esters is rather different from that of other organic compounds. They are named as if they were salts of the alcohol and the acid; the alcohol provides the first half of the name (alkyl) and the organic acid provides the second half of the name (alkanoate). In naming an ester it is important to remember that the -CO- group is part of the carboxylic acid. The molecule below is therefore methyl propanoate (not propyl methanoate), because it can be considered as being formed from methanol and propanoic acid.

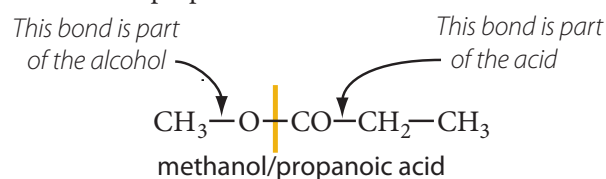
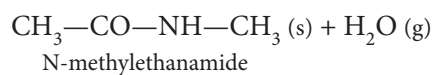
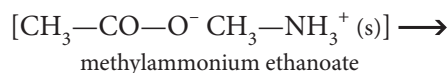
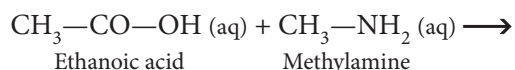


Figure 1041 Naming of an ester

20.4.2 Describe, using equations, the reactions of amines with carboxylic acids.

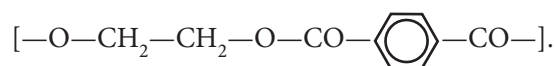
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Ammonia and primary amines initially react with carboxylic acids to form a salt of the acid, but if this is heated it dehydrates to form an **amide**. If ethanoic acid is reacted with methylamine, and the initially formed methylammonium ethanoate is heated, then N-methylethanamide is formed:



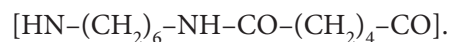
polymers, two different functional groups are required and for each new bond between the monomer units (shown coloured below), a small molecule (often water) is produced. Each monomer must also have two functional groups. This can involve two different functional groups on the same monomer or more frequently, as in the examples below, two different monomers which have two identical groups on them. One group of condensation polymers are the **polyesters**, so called because the bonding depends on the reaction of an alcohol with a carboxylic acid to form an ester. The best known example of this polymer is **Terylene**, formed by the reaction of benzene-1,4-dicarboxylic acid with ethane-1,2-diol, as shown in Figure 1042(a)

The repeating unit in Terylene is therefore



Another group of condensation polymers is the **polyamides**, so called because the bonding depends on the reaction of an amine group with a carboxylic acid to form an amide. These polymers are better known as **nylon**, though there are actually a whole range of nylons. One of the most common is nylon 6,6, formed by the polymerisation of hexanedioic acid with hexane-1,6-diamine (See Figure 1042(b)).

The repeating unit in this is therefore



Both polyesters and nylons are used in large quantities for the production of fibres to convert into cloth for garments, hence the above reactions are of major economic importance in most developed countries.

20.4.3 Deduce the structures of the polymers formed in the reactions of alcohols with carboxylic acids.

20.4.4 Deduce the structures of the polymers formed in the reactions of amines with carboxylic acids.

20.4.5 Outline the economic importance of condensation reactions.

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The two reactions discussed above are made use of in polymers known as **condensation polymers**. In these

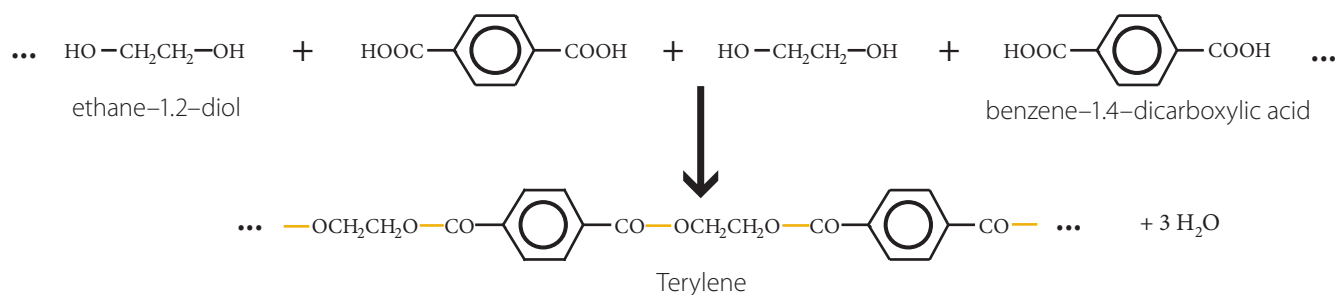


Figure 1042(a) The polymerisation reaction forming a polyester - Terylene

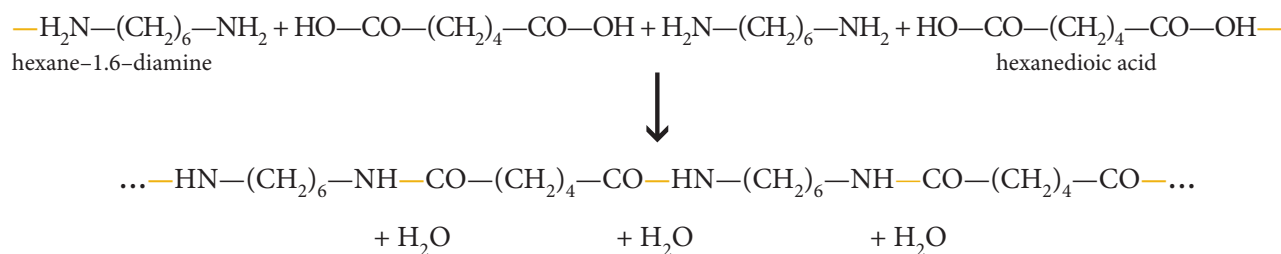


Figure 1042(b) The polymerisation reaction forming Nylon 6.6

Exercise 20.4

- Which one of the following is not necessarily a characteristic of condensation polymers?
 - It involves two different monomers.
 - A small molecule is formed for each new bond between the monomers.
 - Each monomer must have two functional groups.
 - The reaction to form the bond between the monomers involves two different functional groups.
- The molecule $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CO-CH}_3$ is called
 - prop-1-yl methanoate.
 - prop-1-yl ethanoate.
 - ethyl propanoate.
 - methyl butanoate.
- Which one of the following could not be a monomer for a condensation polymer?
 - $\text{HO-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CO-OH}$
 - $\text{HO-C}_6\text{H}_4\text{-CO-OH}$
 - $\text{HO-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$
 - $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CO-NH}_2$
- Write a balanced equation for the reaction that you would expect to occur when the initial product formed between butanoic acid and ethylamine is strongly heated and give the full structural formula of the organic product.
- What reagents would you require to prepare a sample of methyl butanoate?
 - Write a balanced equation for the reaction that occurs giving structural formulae for all organic compounds.
 - Apart from the reactants what else would be required if the reaction were to produce a good yield of the product?
 - Predict one property of methyl butanoate.

20.6 STEREOISOMERISM (AHL)

20.6.1 Describe stereoisomers as compounds with the same structural formula but with different arrangements of atoms in space.

20.6.2 Describe and explain geometrical isomerism in non-cyclic alkenes.

20.6.3 Describe and explain geometrical isomerism in C_3 and C_4 cycloalkanes.

20.6.4 Explain the difference in the physical and chemical properties of geometrical isomers.

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AHL

Stereoisomers are molecules, in which the order that the atoms are joined in is the same (hence they are isomers with the same structural formula), but the molecules have a different arrangement of atoms in space and hence different three dimensional shapes. Stereoisomers can be sub-divided into **geometrical isomers** and **optical isomers** (or **enantiomers**).

GEOMETRIC ISOMERISM

It is possible for a molecule to rotate freely around a single (σ -)bond so that, for example, the two CH_3 groups in ethane can rotate relative to each other. Atoms joined by a double bond are however not free to rotate. This is because the π -bond in the double bond involves two regions of high electron density on opposite sides of σ -the bond, hence rotation would involve breaking this π -bond. As a consequence in a molecule containing a double bond, if the form produced by rotating one end of the bond by 180° is not identical to the original, then there can be two separate forms of the molecule. See Figure 1043.

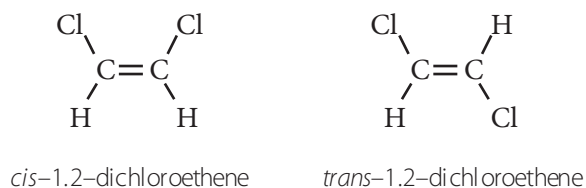


Figure 1043 Geometric isomerism in alkenes

These isomers are known as geometric isomers and the forms of 1,2-dichloroethene ($\text{ClCH}=\text{CHCl}$) is a typical example. The isomer in which the groups or substituents are on the same side of the double bond is known as the *cis*-isomer, the one with them on opposite sides is the *trans*-isomer.

Frequently, as in this case, the *cis*-isomer will be polar whilst the more symmetrical *trans*-isomer will not. This affects physical properties such as the boiling points, the *cis*-isomer above for example boils at 60°C , whereas the *trans*-isomer boils at 48°C . Thus, geometric isomers have different physical properties such as polarity (dipole moment), boiling point, melting point, and solubility, etc. They can therefore be separated by methods such as fractional distillation, chromatography, etc.

Usually the chemical properties are similar, but in some cases the proximity of the functional groups allows interaction in the *cis*-isomer more easily than in the *trans*-isomer. For example *cis*-butenedioic acid dehydrates at under 200°C to form the anhydride (see below), whilst the *trans*-isomer sublimates unchanged at $\sim 200^\circ\text{C}$. Dehydration of the *trans*-isomer requires a much higher temperature so as to achieve the activation energy required for rotation about the double bond and hence the product has the same form as the *cis*-isomer as shown in Figure 1044

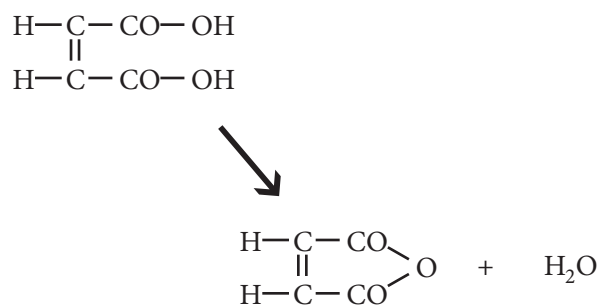
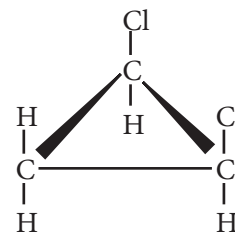


Figure 1044 The dehydration reaction of butenedioic acid

Cycloalkanes also display geometrical isomerism because being part of a ring prevents rotation of carbon-carbon single bonds as well, so for example, 1,2-dichlorocyclopropane can exist as both *cis*- and *trans*-isomers:

cis-1,2-dichlorocyclopropane



trans-1,2-dichlorocyclopropane

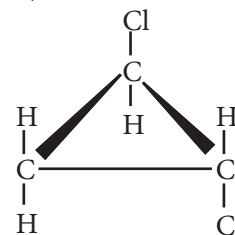


Figure 1045 Geometric isomerism in cycloalkanes

OPTICAL ISOMERISM

- 20.6.5 Describe and explain optical isomerism in simple organic molecules.
- 20.6.6 Outline the use of a polarimeter in distinguishing between optical isomers.
- 20.6.7 Compare the physical and chemical properties of enantiomers.

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If a carbon atom has four different groups attached to it then there are two different ways in which these groups can be arranged around this carbon atom, which is known as an **asymmetric carbon atom**, or a **chiral centre** (from the Greek word for 'hand'). The two forms of such a chiral molecule, known as **optical isomers** (or enantiomers), are mirror images of each other, but cannot be superimposed on each other (like a pair of gloves). This is illustrated below using butan-2-ol as an example. The asymmetric carbon atom is marked with * in Figure 1046.

Note that all four groups must be different for this to occur so that propan-2-ol ($\text{CH}_3\text{-CHOH-CH}_3$) does not exist as a pair of optical isomers. Because these molecules are so similar, there is very little difference in their physical and chemical properties. In fact the only difference in the properties of these compounds is in their interaction with plane polarised light.

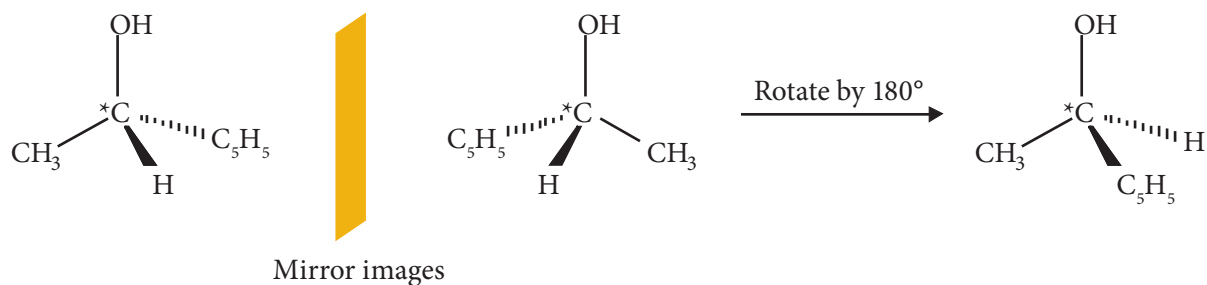


Figure 1046 Optical isomerism

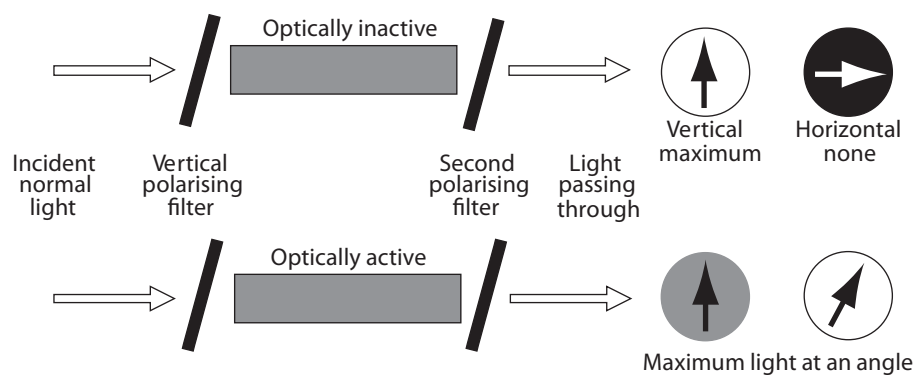


Figure 1047 Illustrating the effect of optically active compounds

TOK Belief or truth?

'The existence of optical isomers provided indirect evidence of a tetrahedrally bonded carbon atom. This is an example of the power of reasoning in allowing us access to the molecular scale. Do we know or believe those carbon atoms are tetrahedrally coordinated?'

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Knowledge and belief; the relationship between these is the basis of so many issues in TOK. One of the most common definitions of knowledge (though strongly challenged about 50 years ago by Edmund Gettier) is that knowledge is "Justified True Belief". Taking this as a starting point, the difference between knowledge and belief therefore lies in Truth and Justification. How do we know what is true? On truth test is "correspondence"; that something is true if it corresponds with reality, but can we consider atoms and molecules part of reality in the way that this book is? A second test is "coherence"; that something is true if it fits in, and does not contradict, other ideas we consider true. Now this might be a little more hopeful. What of justification? This is a far more personal thing. Even before the days of space flight, most people still accepted that the world was a sphere in spite of our observations, especially when in the middle of the ocean, that it looks pretty flat. This was because we accepted the many justifications for this, though inevitably there were still those who were not convinced.

I suppose that the strength of a justification lies in whether we can think of any alternatives to explain observations that we agree upon. In this case that there are two substances, identical in every way except for the effect they have on the plane of polarisation of polarised light. One explanation for this is the familiar one given in this chapter. The real test is to come up with an alternative explanation, which preferably also explains a few other phenomena as well (the way that relativity did), and does not contradict other evidence relating to the tetrahedral arrangement of bonds in carbon, such as x-ray diffraction data about the structure of diamond. In other words it's back to Popper again – our confidence in any theory depends only on our attempts to refute it (see TOK Box in Chapter 5). It probably follows that our knowledge of the universe is constrained only by our inability to imagine better theories than the ones we currently have.

Plane polarised light can be considered to be light in which the oscillation of the wave is restricted to one plane, say the vertical. This can be achieved by passing the light through a **polarising filter**. If the light is now passed through a second polarising filter orientated in the same direction (vertical) then there is virtually 100% transmission (see Figure 1045). If the second polarising filter has its axis at right angles to the first (horizontal) then no light will pass. A pure optical isomer placed between the two filters will rotate the plane of polarisation in one direction (say clockwise) so that maximum transmission is no longer when the second filter is aligned with the first one. The second optical isomer will rotate the plane of polarisation by exactly the same amount (assuming equal concentration), but in the opposite direction (anticlockwise). Substances that affect polarised light in this way are said to be **optically active**. An instrument containing two polarising filters that can be rotated relative to each other, separated by a compartment in which the plane polarised light passes through a liquid, allowing the angle through which the plane of polarisation is rotated is called a **polarimeter**. See Figure 1047.

Apart from this the physical properties of optical isomers are identical. Chemically, the behaviour of the optical isomers is identical unless the reaction also involves another pure optical isomer. Chemical reactions that produce an asymmetric (chiral) carbon atom in a molecule usually give rise to a mixture containing exactly equal amounts of the two optical isomers. Such a mixture is known as a **racemic mixture**. The effects of the two optical isomers in a racemic mixture cancel each other out and so it is not optically active. In contrast almost all natural products, produced by enzyme catalysed biochemical processes, result in just one pure optical isomer and hence produce optically active material. Natural turpentine (produced from pine tree resin) can, for example, be differentiated from white spirit (a substitute produced by the chemical industry) because turpentine is optically active and will rotate the plane of polarised light, whereas white spirit will not.

TOK The use of conventions in representing three-dimensional molecules in two dimensions

Conventions, and the extent that they are a result of cultural conditioning, is a fascinating subject. The diagrams in this book have to attempt to represent three-dimensional molecules through the two-dimensional medium of the page of the book. This is a problem that graphic artists also have to contend with and as a result they developed the technique of perspective. Our drawings have attempted to draw on some of these techniques, but added a few other little conventions, such as things with dotted lines being below the plane of the book and wedge shaped lines coming out of the page. Like so many things, the concept of perspective was well known to the Greeks, but was then lost to be rediscovered and thoroughly developed in the Renaissance period. It depends on the apparent diminution of size with distance and the resulting convergence of lines. If we show two human figures in a drawing, but one is much smaller than the other we can either assume the smaller one is further away from us, or that it represents a leprechaun or some other kind of diminutive human. Usually for us the former explanation is more convincing. A consequence of this is that the constant width of a road

appears to be smaller the further away from us it goes, hence as it disappears towards the horizon the sides of the road appear to get closer together, meeting at the horizon (in theory an infinite distance away!). We have grown up with these tricks of the graphic artist and find it difficult when viewing a scene drawn using perspective, to imagine in any other way.

It is reported that when drawings incorporating perspective are shown to people of more 'primitive' cultures, they do not realise that some of the objects are supposed to be further away than others, in other words the appreciation of perspective is something that we develop by growing up in a culture where it is widely employed. Others however contest this say that the appreciation of perspective, even though not developed by all societies, is innate to humans rather than something that is culturally developed. Anyway I hope that you have all been exposed to enough Escher "impossible geometries" to be able to pick up the three-dimensional shapes that we are trying to represent.

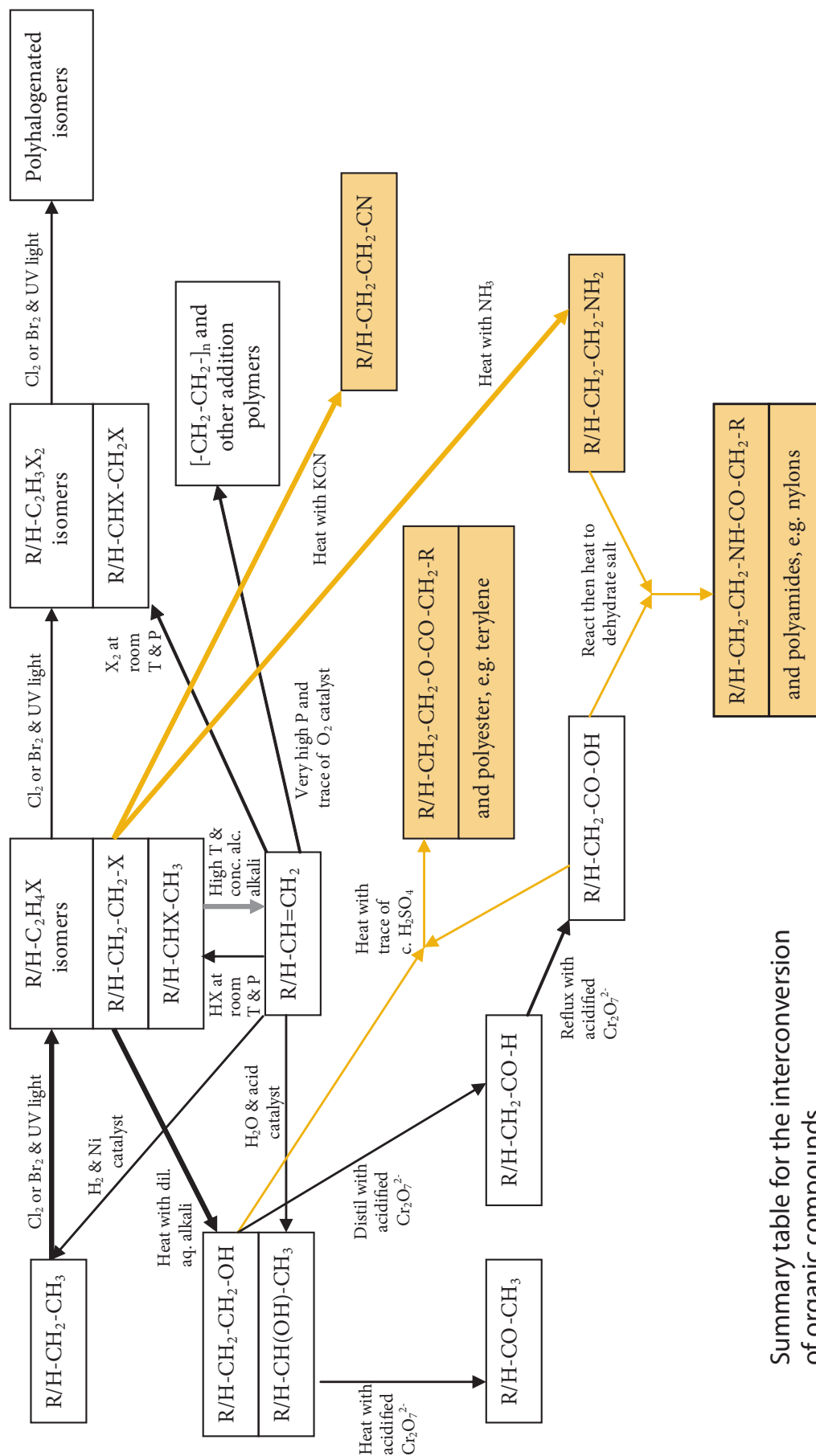


Figure 1048 A summary table for the interconversion of organic compounds

Exercise 20.6

- Which one of the following compounds will exhibit geometrical isomerism?
 - $\text{CH}_3\text{CH}=\text{CH}_2$
 - $\text{CH}_3\text{CCl}=\text{CH}_2$
 - $\text{CH}_3\text{CH}=\text{CHCl}$
 - $\text{CH}_3\text{CH}=\text{CCl}_2$
- Counting from the left hand end of the principal chain, which carbon atom in the following molecule is an asymmetric one?

$$\text{ClCH}_2-\text{C}(\text{CH}_3)_2-\text{CHCl}-\text{CHCl}_2$$
 - The first
 - The second
 - The third
 - The fourth
- Which one of the following isomeric alcohols can exist as a pair of optical isomers?
 - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
 - $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{OH}$
 - $\text{CH}_3-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$
 - $(\text{CH}_3)_3\text{C}-\text{OH}$
- 3-bromopent-1-ene can exist in many isomeric forms. Draw a full structural formula of the molecule and then draw structural formulae of isomers that only differ from it in the manner given:
 - A hydrocarbon chain isomer.
 - An optical isomer (enantiomer).
 - A positional isomer.
 - An isomer which displays geometric isomerism.
 - An isomer not containing a double bond.
- Lactic acid $[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]$ can either be extracted from sour milk, or it may be produced synthetically by the addition of water to propenoic acid $(\text{CH}_2=\text{CHCOOH})$.
 - Explain what is meant by the terms 'optically active' and 'racemic mixture'.
 - How would you expect samples from these two sources to differ.
 - In practice, how could you determine whether a sample of lactic acid was of natural or synthetic origin?
- Samples of 2-bromobutane may exhibit optical activity. Explain why.
 - 2-bromobutane may be produced by the reaction of hydrogen bromide with but-2-ene. Would you expect a sample prepared in this way to be optically active? Explain why.