Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 15

Organic chemistry - CARBONYLS, CARBOXYLIC ACIDS AND CHIRALITY

15A 1Chirality and enantiomers

DIFFERENT TYPES OF ISOMERISM

In Book 1, you learned about structural isomerism and its division into chain isomerism and position isomerism. You then considered a different type of isomerism called 'geometric isomerism', including the terms E-Z and cis-trans isomerism - this is one type of stereoisomerism.

This chapter looks at a second type of stereoisomerism - optical isomerism. Before we introduce this, it is useful to consider all the types of isomerism that you need to be familiar with, in the form of a family tree.

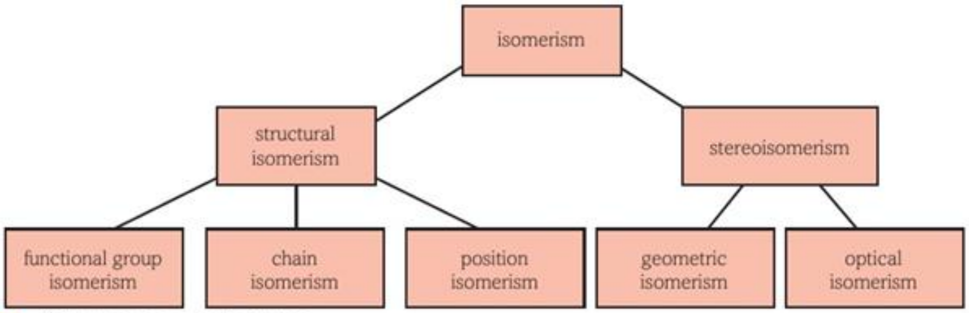


fig A The isomerism family tree.

Positional isomers differ because the same functional group is attached to different carbon atoms in the chain.

Stereoisomers have the same structural formula but differ because their atoms or groups are arranged differently in three dimensions.

Geometric isomers differ because their atoms or groups are attached at different positions on opposite sides of a C=C double bond.

OPTICAL ISOMERISM

How does optical isomerism fit into this family tree? Optical isomers are non-superimposable mirror images of each other but are otherwise the same. This needs careful explanation!

CHIRALITY

This is a term derived from the Greek word for 'hand', and could be translated as 'handedness'. Many objects, including human hands, can be described as chiral. Your hands have the same features, and you could describe both hands using the same words.

CHIRALITY IN SIMPLE MOLECULES

Understanding chirality in simple molecules requires visualizing them in 3D using models. For example, a molecule with a single carbon atom joined to four groups can be represented using ordinary lines, tapered or wedge-shaped lines, and dashed lines. This helps visualize the bond arrangements and their relationship as objects and mirror images.

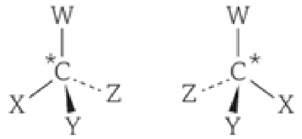


fig B This is one way to show optical isomers in 3D.

The asterisk (*) indicates that the carbon atom next to it is a chiral centre, also known as an **asymmetric** carbon atom.

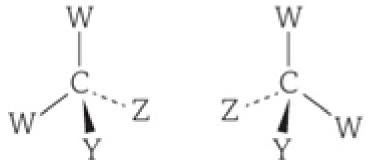
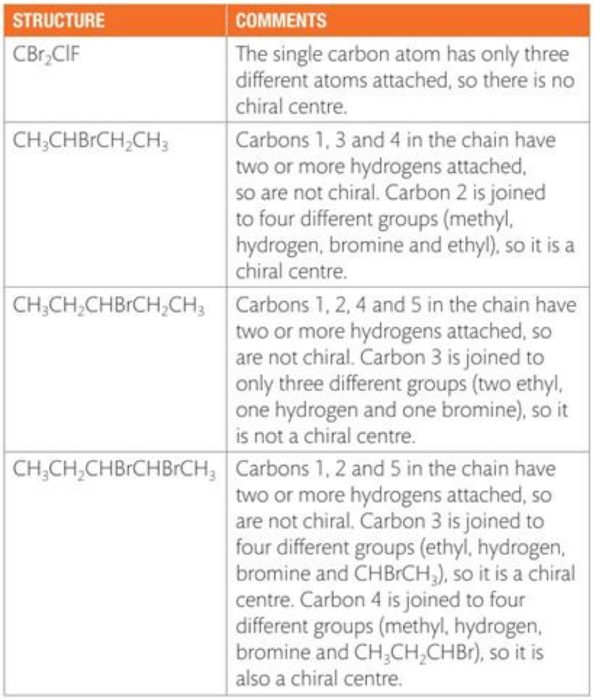


fig C These structures are not optical isomers because there are only three different groups joined to the central carbon atom.

If the attached atoms or groups are W, W, X and Y (so that two are the same) it is possible to show that they relate to each other in the same way (they are mirror images). However, there is no chirality because one can also be superimposed on the other (fig C).

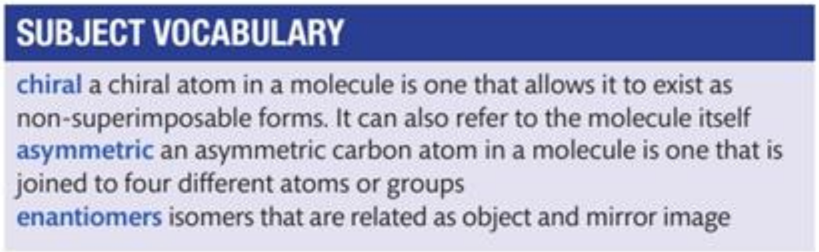
HOW TO IDENTIFY CHIRAL CENTRES IN STRUCTURAL FORMULAE

You need to be able to identify chiral centres in molecules such as the examples shown in table A. You only need to consider whether there is a carbon atom joined to four different atoms or groups.



STRUCTURE	COMMENTS
CBr_2ClF	The single carbon atom has only three different atoms attached, so there is no chiral centre.
$CH_3CHBrCH_2CH_3$	Carbons 1, 3 and 4 in the chain have two or more hydrogens attached, so are not chiral. Carbon 2 is joined to four different groups (methyl, hydrogen, bromine and ethyl), so it is a chiral centre.
$CH_3CH_2CHBrCH_2CH_3$	Carbons 1, 2, 4 and 5 in the chain have two or more hydrogens attached, so are not chiral. Carbon 3 is joined to only three different groups (two ethyl, one hydrogen and one bromine), so it is not a chiral centre.
$CH_3CH_2CHBrCHBrCH_3$	Carbons 1, 2 and 5 in the chain have two or more hydrogens attached, so are not chiral. Carbon 3 is joined to four different groups (ethyl, hydrogen, bromine and $CHBrCH_3$), so it is a chiral centre. Carbon 4 is joined to four different groups (methyl, hydrogen, bromine and CH_3CH_2CHBr), so it is also a chiral centre.

If a molecule has a chiral centre, then it can exist as optical isomers - each one is known as an **enantiomer**.



SUBJECT VOCABULARY

chiral a chiral atom in a molecule is one that allows it to exist as non-superimposable forms. It can also refer to the molecule itself
asymmetric an asymmetric carbon atom in a molecule is one that is joined to four different atoms or groups
enantiomers isomers that are related as object and mirror image

15A 2 Optical activity

PLANE-POLARISED LIGHT

In the previous section we looked at the causes of **optical isomerism.** Before we consider optical activity, we must have some understanding of **plane-polarised light**. One way to consider light is as electromagnetic radiation that travels as a transverse wave. This means that the oscillations exist in planes at right angles to the direction of travel. Fig A shows 'normal' **unpolarised light and plane- polarised light** with the oscillations in only one plane.

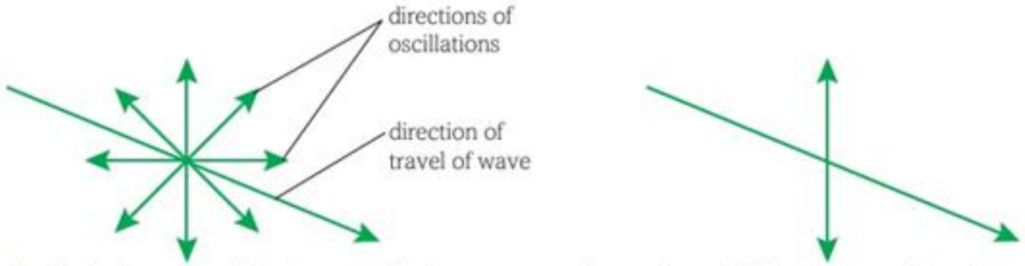


fig A In an unpolarised wave, oscillations may occur in any plane, while in a plane-polarised wave they occur in only one plane.

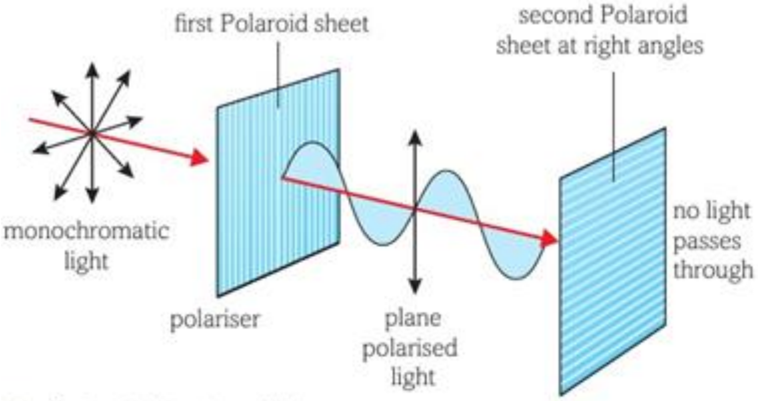


fig B Polarisation of light.

Fig B shows that the second sheet of Polaroid has horizontal lines, which means that only horizontally plane-polarised light can pass through. As the first sheet has produced vertically plane- polarised light, then no light can pass through the second sheet.

POLARIMETRY

Polarimetry is the use of a **polarimeter** to measure the amount of optical activity, if any, of a substance. Fig C shows how a polarimeter works. A monochromatic light source (light of only one colour or frequency) passes through a **polarising** filter (such as a piece of Polaroid). This is called the polariser because it converts unpolarised light into (vertically) plane-polarised light.

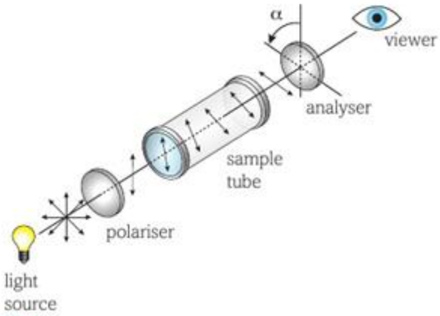


fig C You can see how the plane of polarisation of the polarised light is rotated anticlockwise as it passes through the sample tube.

The second polarising filter, known as the **analyser**, is rotated to a position where the maximum light intensity can be seen. The angle of rotation (a) is measured, and is quoted as a positive value if the rotation is clockwise and as a negative value if the rotation is anticlockwise. In fig C, the rotation, o, is approximately -90°.

PROPERTIES OF ENANTIOMERS

Two enantiomers have identical physical properties, with one exception. The enantiomers rotate the plane of polarisation of plane-polarised light by equal angles, but in opposite directions. So, if the rotation for one enantiomer is +60°, then the rotation for the other enantiomer is -60°.

Two enantiomers have identical chemical properties, with one exception - the way in which they react with enantiomers of other substances. This chemical property may be different for each enantiomer.

RACEMIC MIXTURES

What happens if a compound with a chiral centre is present as a mixture of both enantiomers? You can imagine that the dextrorotatory and laevoratatory enantiomers have equal but opposite effects on plane-polarised light. This means that the analyser does not need to be rotated to allow the maximum light intensity to be seen. Without knowing anything about the substance, it is not possible to distinguish between a substance that has no optical activity and one that has optically active enantiomers whose effects cancel out. A mixture containing equal amounts of two enantiomers is called a **racemic mixture.**

Here are the structures of the two enantiomers of tartaric acid:

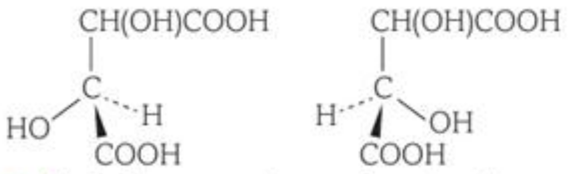
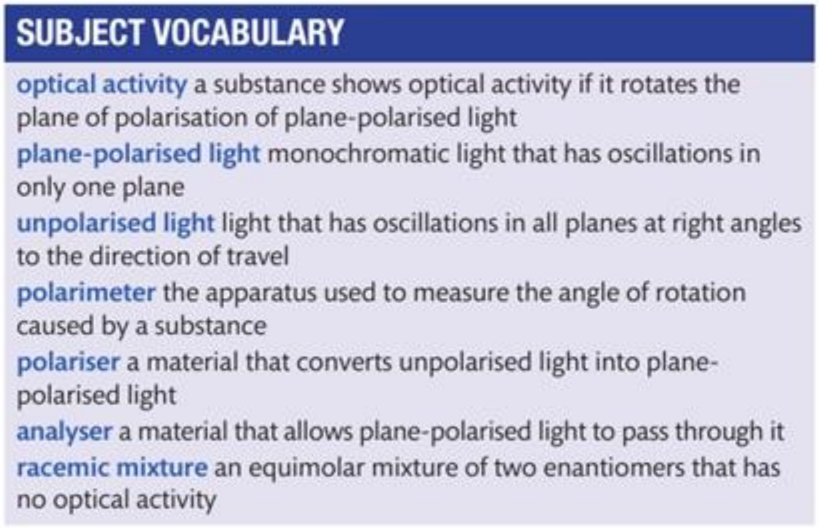


fig D The two enantiomers of tartaric acid.



SUBJECT VOCABULARY

optical activity a substance shows optical activity if it rotates the plane of polarisation of plane-polarised light

plane-polarised light monochromatic light that has oscillations in only one plane

unpolarised light light that has oscillations in all planes at right angles to the direction of travel

polarimeter the apparatus used to measure the angle of rotation caused by a substance

polariser a material that converts unpolarised light into plane-polarised light

analyser a material that allows plane-polarised light to pass through it

racemic mixture an equimolar mixture of two enantiomers that has no optical activity

15A 3 Optical activity and reaction mechanisms

NUCLEOPHILIC SUBSTITUTION IN HALOGENOALKANES

In Book 1 you learned to write mechanisms for these reactions, but this was limited. We suggested that the explanation given in Book 1 was incomplete and that there was more to come.

Now is the appropriate time to develop the explanation in greater depth. First, let us revise what you may remember from Book 1. Fig A shows how we represented the mechanism of the reaction between the primary halogenoalkane bromoethane and hydroxide ions.

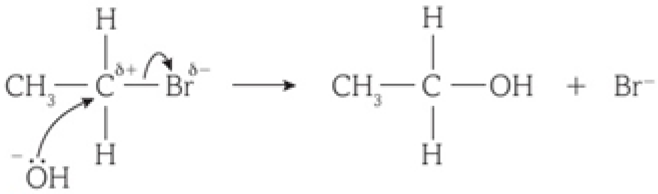


fig A This is a simple way to represent a nucleophilic substitution mechanism.

THE S_N2 MECHANISM

The individual symbols in 'S_N2' have the following meanings.

S = substitution N = nucleophilic 2 = **bimolecular**

The term 'bimolecular' means that there are two species involved in the rate-determining step - in this example, the OH-ion and the halogenoalkane.

Bimolecular reactions were considered in Topic 11 in this book. In this topic, we are going to revisit the mechanism provided in Book 1, by looking at it in more detail. Here is the mechanism for a primary halogenoalkane that is also an enantiomer.

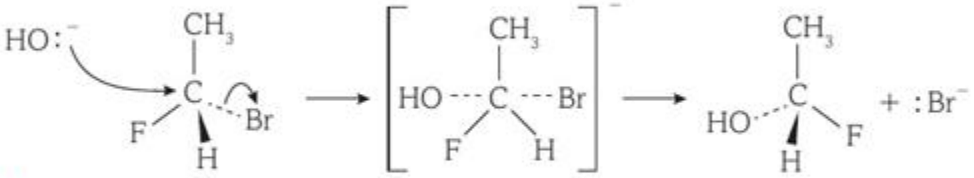


fig B This is the S_N2 mechanism showing the transition state.

EVIDENCE FROM OPTICAL ACTIVITY

If the reaction actually occurs according to the SN2 mechanism, then the optical activity of the product is different from that of the reactant. (This is because of the inversion that occurs.) If the reactant is dextrorotatory, then the product will be laevorotatory, and vice versa. So, by measuring the optical activity of the original halogenoalkane and the alcohol formed, we can show whether the reaction has occurred by the SN2 mechanism.

THE S_N1 MECHANISM

The individual symbols in 'S_N1' have the following meanings.

S = substitution N = nucleophilic 1 = **unimolecular**

The term 'unimolecular' means that only one species is involved in the rate-determining step - in this example, just the halogenoalkane. In fig C we have used the same halogenoalkane as for the SN2 mechanism so that you can focus on the differences between the two mechanisms.

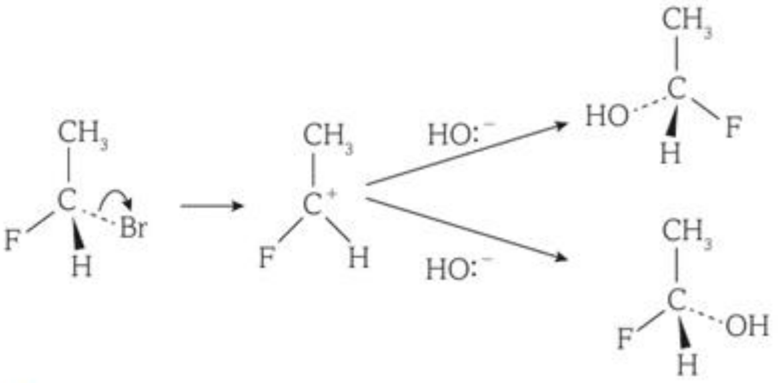


fig C In the S_N1 mechanism, the planar carbocation can be attacked from the left or from the right, giving a pair of enantiomers.

EVIDENCE FROM OPTICAL ACTIVITY

If the reaction actually occurs according to the SN1 mechanism, then the optical activity of the product is different from that of the reactant. Whether the reactant is dextrorotatory or laevorotatory, the product has no optical activity. So, by measuring the optical activity of the original halogenoalkane and the alcohol formed, we can show whether the reaction has occurred by this mechanism.

WHICH MECHANISM?

In general, the main mechanism for primary halogenoalkanes is S_N2, and for tertiary halogenoalkanes is S_N1. For secondary halogenoalkanes, both mechanisms can occur, although the main one depends on the actual halogenoalkane and the conditions.

SUBJECT VOCABULARY

bimolecular (mechanism) a mechanism in which two species are reacting in the rate-determining step

unimolecular (mechanism) a mechanism in which only one species is reacting in the rate-determining step

15B 1 Carbonyl compounds and their physical properties

NOMENCLATURE

We met carbonyl compounds briefly in Book 1, but only as the products of the oxidation of alcohols.
The carbonyl group (C=O) is a carbon atom joined by a double bond to an oxygen atom. Many types of compounds contain this group (such as carboxylic acids, which contain COOH), but only two types are classified as carbonyl compounds - these are aldehydes and ketones.

ALDEHYDES

A carbonyl compound is described as an aldehyde if there is a hydrogen atom joined to the carbonyl group. The naming system uses the suffix -al, and the carbon chain is named in the same way as an alkane. If locants are used, then the carbon of the carbonyl group is carbon 1 in the chain. Table A shows some examples.

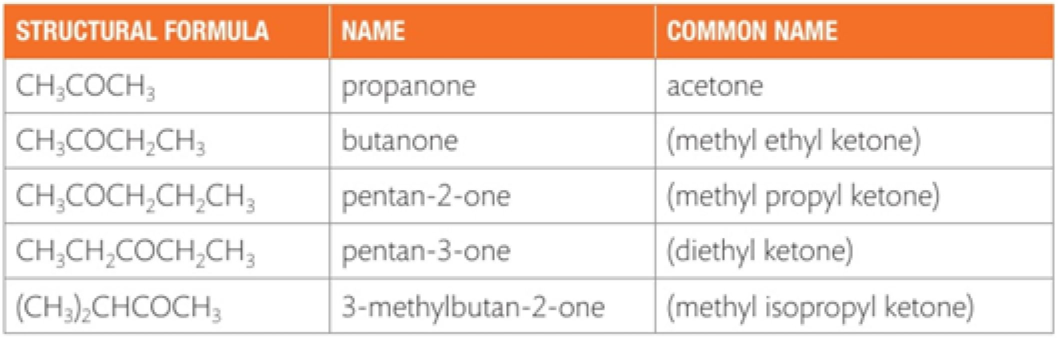
STRUCTURAL FORMULA	NAME	COMMON NAME
HCHO	methanal	formaldehyde
CH_3CHO	ethanal	acetaldehyde
CH_3CH_2CHO	propanal	(propionaldehyde)
$(CH_3)_2CHCHO$	methylpropanal	(isobutyraldehyde)
$CH_3CH_2CH_2CHO$	butanal	(butyraldehyde)
C_6H_5CHO	benzenecarbaldehyde	benzaldehyde

table A

The general formula is RCHO.

KETONES

A carbonyl compound is described as a ketone if there are only hydrocarbon groups joined to the carbonyl group. The naming system uses the suffix -one, and the carbon chain is named in the same way as an alkane. If locants are used, then one of the end carbon atoms in the chain of the carbonyl group is carbon 1 in the chain. The rules about using the lowest possible numbers, as with alkanes, apply to ketones. Table B shows some examples.



STRUCTURAL FORMULA	NAME	COMMON NAME
CH_3COCH_3	propanone	acetone
$CH_3COCH_2CH_3$	butanone	(methyl ethyl ketone)
$CH_3COCH_2CH_2CH_3$	pentan-2-one	(methyl propyl ketone)
$CH_3CH_2COCH_2CH_3$	pentan-3-one	(diethyl ketone)
$(CH_3)_2CHCOCH_3$	3-methylbutan-2-one	(methyl isopropyl ketone)

table B

The general formula is RCOR′.

For both aldehydes and ketones, the common names in brackets are rarely used.

DISPLAYED AND SKELETAL FORMULAE OF ALDEHYDES AND KETONES

Table C and **table D** show the displayed and skeletal formulae for some aldehydes and ketones.

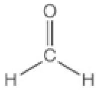
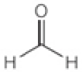
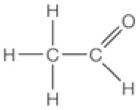
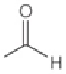
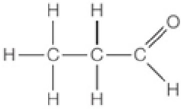
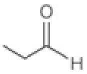
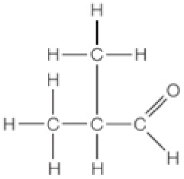
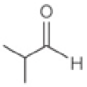
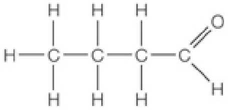
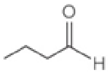
NAME	DISPLAYED FORMULA	SKELETAL FORMULA
methanal		
ethanal		
propanal		
methylpropanal		
butanal		

table C

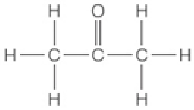
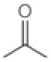
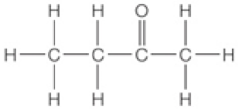
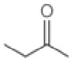
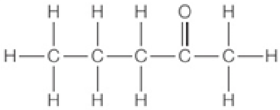
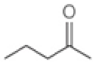
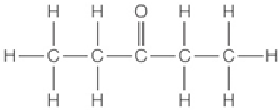
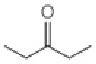
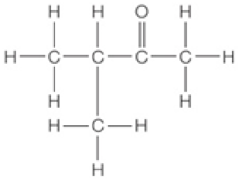
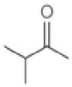
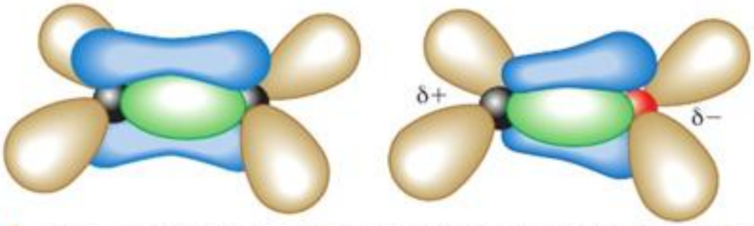
NAME	DISPLAYED FORMULA	SKELETAL FORMULA
propanone		
butanone		
pentan-2-one		
pentan-3-one		
3-methylbutan-2-one		

table D

BONDING

You are familiar with the nature of the C=C double bond in alkenes. It is composed of a combination of sigma and pi bonding. However, the bond is non-polar because there are two identical (carbon) atoms involved. The situation in the carbonyl group is very similar, except that the bond is polar because of the differing electronegativities of carbon and oxygen. Fig A compares the two.



▲ **fig A** The bonding in an alkene is on the left. The bonding in a carbonyl compound is on the right. Green is used to represent sigma bonding and blue is used to represent pi bonding.

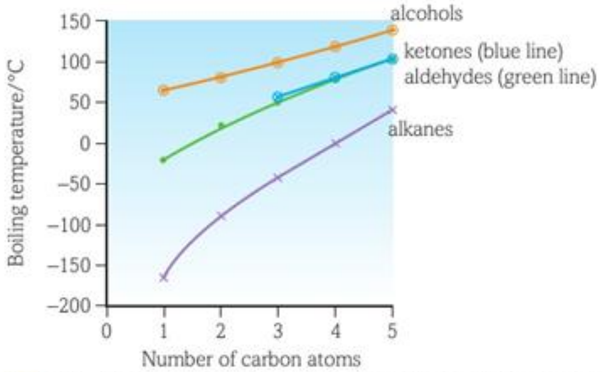
PHYSICAL PROPERTIES

Aldehydes have distinctive smells. Those with short carbon chains have unpleasant smells (butanal smells of rancid butter). Some of those with long carbon chains have very pleasant smells and are used in expensive perfumes (nonanal, with nine carbon atoms per molecule, smells of roses). The smells of the lower ketones, especially propanone, remind most people of solvents. In fact, propanone is widely used as a solvent, including as nail varnish remover.

▲ **fig B** Cinnamon (which contains the alehyde cinnamaldehyde) comes from the dried bark of the tree *Cinnamomum zeylanicum*. It is widely used as a spice in cookery.

BOILING TEMPERATURES

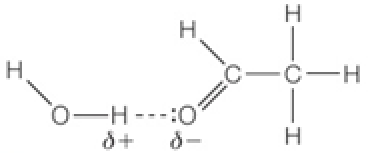
Aldehydes and ketones contain the polar C=O group and so have permanent dipole-dipole interactions, as well as London forces. They do not have hydrogen bonding because all of their hydrogen atoms are joined to carbon atoms. As with other homologous series, for example, alkanes and alcohols, boiling temperatures increase with increasing molar mass as the extent of London forces increases. At room temperature, methanal is a gas. The other carbonyl compounds are liquids. Fig C compares the boiling temperatures of some carbonyl compounds.



▲ **fig C** The boiling temperatures of some alkanes, aldehydes, ketones and alcohols. The effect of the intermolecular forces on the boiling temperatures can be seen clearly, with dipole–dipole attractions, which result from the carbonyl groups of the aldehydes and ketones, causing higher boiling temperatures than the equivalent alkanes but lower than the alcohols with their hydrogen bonding.

SOLUBILITY IN WATER

The lower (shorter chain) aldehydes and ketones are soluble in water because they can form hydrogen bonds (shown as a dashed line) with water molecules. Fig D shows hydrogen bonding between ethanal and water.



▲ **fig D** Hydrogen bonding between water molecules and ethanal molecules is stronger than the intermolecular bonds in the pure aldehyde.

15B 2 Redox reactions of carbonyl compounds

WHICH REACTIONS OCCUR?

You may remember from Topic 10 (Book 1: IAS) that carbonyl compounds (formed by the oxidation of alcohols) differ in their ease of oxidation - aldehydes (but not ketones) are easily oxidised to carboxylic acids. In this section, we will look at these reactions in more detail, and also consider the reduction reactions of carbonyl compounds. Fig A summarises these reactions.

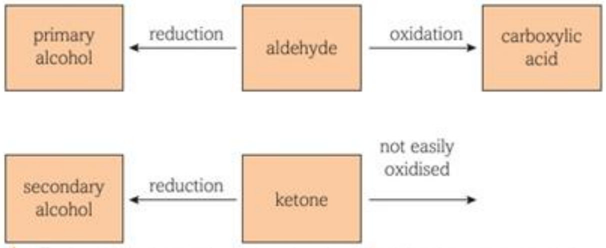


fig A Aldehydes can be reduced and oxidised, but ketones can only be reduced.

REDUCTION REACTIONS

Both aldehydes and ketones can be reduced to alcohols by the same reagent, lithium tetrahydridoaluminate. This reagent is also known as lithium aluminium hydride, and its formula is LiAlH4- The reduction reactions are carried out with both the carbonyl compound and reducing agent dissolved in dry ether. To simplify the equations, the reducing agent is represented by [H], which is the symbol for an atom of hydrogen provided by the reducing agent in an unspecified way. Note that this is a different use of square brackets - it does not indicate a molar concentration (as in kinetics). Here are some examples of equations.

Reduction of propanal to propan-1-ol:

$$CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$$

Reduction of butanone to butan-2-ol:

$$CH_3COCH_2CH_3 + 2[H] \rightarrow CH_3CH(OH)CH_2CH_3$$

OXIDATION REACTIONS

Ketones are very difficult to oxidise, and, as far as this book is concerned, ketones cannot be oxidised. Table A shows the reagents that can oxidise aldehydes to carboxylic acids.

Oxidation of propanal to propanoic acid:

$$CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

Oxidation of butanal to butanoic acid:

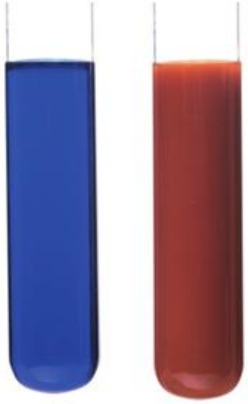
$$CH_3CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2COOH$$

REAGENT	COLOUR CHANGE	NOTES
Acidified potassium dichromate(VI)	orange solution → green solution	The colour change is due to the reduction of chromium from +6 to +3.
Fehling's solution	deep blue solution → red precipitate (see **fig B**)	In both of these solutions, the colour change is due to the conversion of a copper(II) complex to copper(I) oxide. It is not necessary to understand the difference between the chemical compositions of these two reagents.
Benedict's solution	deep blue solution → red precipitate	
Tollens' reagent	colourless solution → silver mirror (see **fig C**)	The colour change is due to the conversion of a silver(I) complex to metallic silver, which often sticks to the inside of the tube. The reagent is also described as ammoniacal silver nitrate.

table A

DISTINGUISHING BETWEEN ALDEHYDES AND KETONES

The oxidation reactions using Fehling's solution, Benedict's solution and Tollens' reagent are often used to distinguish between aldehydes and ketones. A positive result, as described in table A, indicates the presence of an aldehyde. A negative result indicates the absence of an aldehyde. If it is also known that the substance being tested is a carbonyl compound, then the negative result can be taken as confirmation of the presence of a ketone.



▲ **fig B** Colour change of Fehling's solution from a blue solution to a red precipitate in the test for an aldehyde.

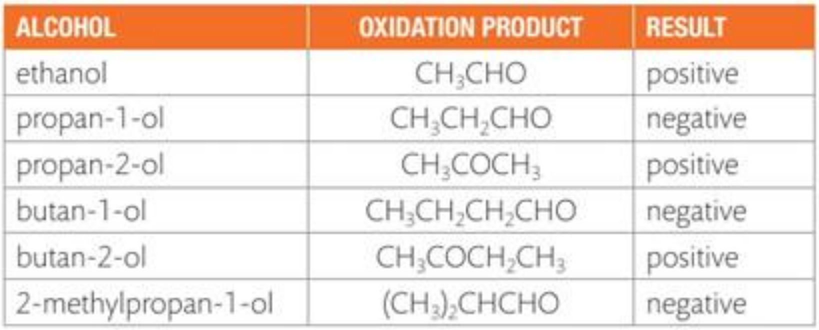
▲ **fig C** Colour change of Tollens' reagent from a colourless solution to a silver mirror in the test for an aldehyde.

REACTIONS WITH IODINE

Another redox reaction of some carbonyl compounds is rather different - it used to be known as the iodoform reaction, but is now described as the triiodomethane reaction. This is because the product is CHI3, a yellow insoluble solid.

If a carbonyl compound is added to an alkaline solution of iodine and the mixture warmed and then cooled, a pale yellow precipitate sometimes forms. This result is a positive test for carbonyl compounds containing the CH,CO group. This group is found in only one aldehyde (ethanal) and in all methyl ketones (those with the carbonyl group as the second carbon in the chain). This means that the reaction occurs with propanone, butanone and pentan-2-one, but not pentan-3-one.

Because oxidising conditions are used in the reaction, some alcohols will also give positive results. Table B shows the results for some common alcohols



ALCOHOL	OXIDATION PRODUCT	RESULT
ethanol	CH_3CHO	positive
propan-1-ol	CH_3CH_2CHO	negative
propan-2-ol	CH_3COCH_3	positive
butan-1-ol	$CH_3CH_2CH_2CHO$	negative
butan-2-ol	$CH_3COCH_2CH_3$	positive
2-methylpropan-1-ol	$(CH_3)_2CHCHO$	negative

table B

15 B 3Nucleophilic addition reactions

REACTION WITH HYDROGEN CYANIDE

Both aldehydes and ketones react with hydrogen cyanide. The reaction is carried out in an aqueous alkaline solution containing potassium cyanide (KCN). The equations and mechanisms are the same for both aldehydes and ketones. Here are some examples of equations.

Addition to propanal:

$CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$

Addition to butanone:

$CH_3COCH_2CH_3 + HCN \rightarrow CH_3C(CN)(OH)CH_2CH_3$

These addition reactions involve a hydrogen atom attaching to the oxygen atom of the carbonyl group and a cyanide group attaching to the carbon atom of the carbonyl group.

These products contain a carbon atom joined to the functional groups OH and CN. They are named differently from other organic compounds we have met so far. According to IUPAC rules, the OH group should be shown as a prefix and the CN group should be shown as a suffix. When this happens, the OH group is shown as hydroxy- and not as -ol, and the CN group is shown as the ending -nitrile. In general, these products are described as hydroxynitriles. Applying these naming rules:

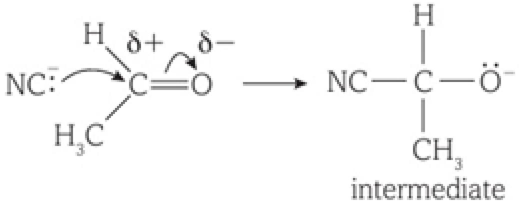
Applying these naming rules:

$CH_3CH_2CH(OH)CN$ is 2-hydroxybutanenitrile

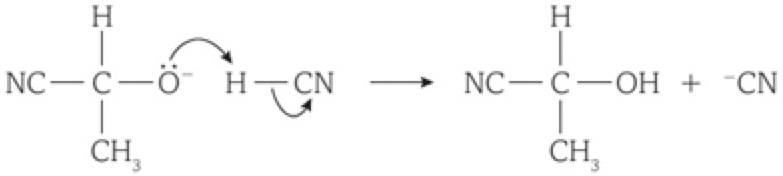
$CH_3C(CN)(OH)CH_2CH_3$ is 2-hydroxy-2-methylbutanenitrile

THE NUCLEOPHILIC ADDITION MECHANISM

Nucleophilic addition is a two-step mechanism, illustrated using ethanal as an example. Step 1 involves the nucleophilic attack by a cyanide ion on the carbon atom of the carbonyl compound.



Step 2 involves the reaction between the intermediate and a hydrogen cyanide molecule.



USING OPTICAL ACTIVITY AS EVIDENCE

A consideration of optical activity can be used as evidence for this mechanism. The arrangement of the two atoms or groups joined to C=O is planar, which means that in Step 1 there is an equal chance of the cyanide ion attacking from each side of the plane. So, although the product of this reaction contains an asymmetric carbon atom (a chiral centre), there are equal amounts of both dextrorotatory and laevorotatory enantiomers formed, giving a product mixture with no optical activity.

Using ethanal as the example, the product is 2-hydroxypropanenitrile. Fig A shows the formation of a racemic mixture containing equal numbers of both enantiomers.

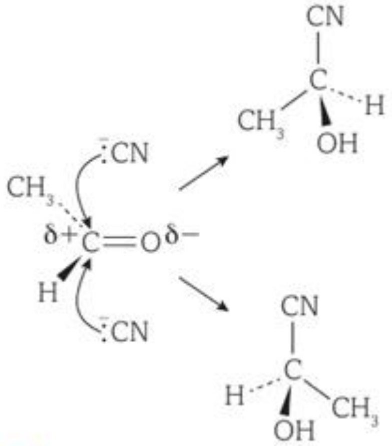


fig A Attack by the cyanide ion from the top leads to the product shown higher up, while attack from the bottom leads to the product shown lower down. Each ethanal molecule is attacked by only one of these cyanide ions.

The cyanide ion can attack from above or below, producing equal amounts of both enantiomers.

MELTING TEMPERATURES OF DERIVATIVES

These reactions with 2,4-dinitrophenylhydrazine give a visual indication of a positive result for the presence of a carbonyl compound. They can also be used to identify individual carbonyl compounds. This is because the compounds formed, known as **derivatives** (because they are derived from particular carbonyl compounds), can be filtered, purified and dried, and their melting temperatures measured. These derivatives have the ending -one, so the derivative of butanal is butanal 2,4-dinitrophenylhydrazone.

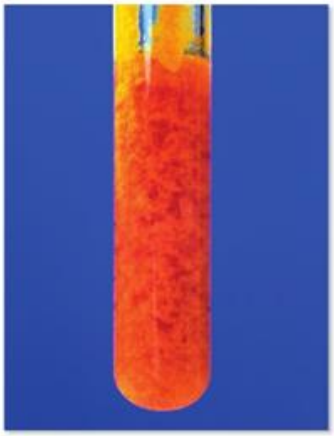


fig C This is the bright orange precipitate formed when a carbonyl compound reacts with 2, 4-dinitrophenylhydrazine.

CARBONYL COMPOUND	BOILING TEMPERATURE/°C	MELTING TEMPERATURE OF 2,4-DINITROPHENYLHYDRAZONE DERIVATIVE/°C
pentanal	102	104
pentan-2-one	102	144
pentan-3-one	102	156

table A

You can see that the original carbonyl compound can now be identified by matching the experimental melting temperature of its derivative to a value in the table.

SUBJECT VOCABULARY

nucleophilic addition a type of mechanism in which a molecule containing two atoms or groups is added across a polar double bond (usually C=O) and the attacking species in the first step is a nucleophile

derivatives compounds formed from other compounds, especially when the properties of the derivatives can be used to identify the original compound

15C 1 Carboxylic acids and their physical properties

NOMENCLATURE

Carboxylic compounds, formed from primary alcohol oxidation, consist of a carbonyl group and a hydroxyl group on the same carbon atom. They have unique properties not found in carbonyl compounds or alcohols. The suffix -oic acid is used, with the carbon chain named similarly to alkanes.

STRUCTURAL FORMULA	NAME	COMMON NAME
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	(propionic acid)
$CH_3CH_2CH_2COOH$	butanoic acid	(butyric acid)
$(CH_3)_2CHCOOH$	methylpropanoic acid	(isobutyric acid)
HOOCCOOH	ethanedioic acid	oxalic acid
C_6H_5COOH	benzenecarboxylic acid	benzoic acid

table A

The general formula is RCOOH; the common names in brackets in **table A** are rarely used.

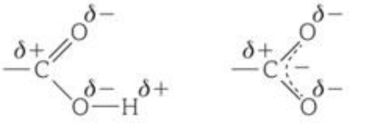
DISPLAYED AND SKELETAL FORMULAE

Table B shows the displayed and skeletal formulae of some carboxylic acids.

BONDING

You are familiar with the nature of the C=O double bond in carbonyl compounds, and of the single bonds in alcohols. The bonding in the carboxylic acid group is a combination of the two. There are now three polar bonds present.

Many reactions of carboxylic acids involve the loss of the hydrogen atom as H+. This produces the carboxylate ion (COO-) in which the two carbon-oxygen bonds are identical. Fig A compares the two.



carboxylic acid carboxylate ion

▲ **fig A** The structures of a carboxylic acid and its carboxylate ion.

Note that the charge and double bond character are evenly distributed across both oxygen atoms in the carboxylate ion.

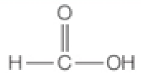
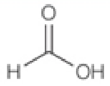
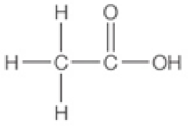
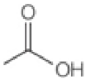
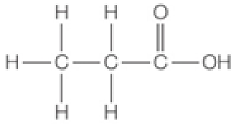
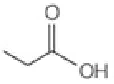
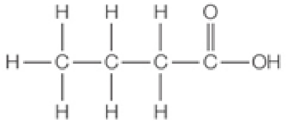
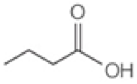
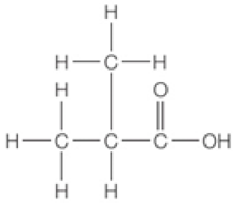
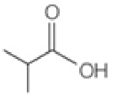
NAME	DISPLAYED FORMULA	SKELETAL FORMULA
methanoic acid		
ethanoic acid		
propanoic acid		
butanoic acid		
methylpropanoic acid		

table B

PHYSICAL PROPERTIES

Carboxylic acids have distinctive smells and sour tastes. The smells of some of them are considered unpleasant. For example, butanoic acid is responsible for the smell of stale sweat, and hexanoic acid for the characteristic smell of goats. Citric acid gives lemons their very sour taste. The Latin word for sour is acidus, and acetum means vinegar, the sour taste of which comes from the acetic acid it contains.

BOILING TEMPERATURES

The presence of three polar bonds, including a polar O-H bond, in the carboxylic acid group means that they have strong intermolecular forces (hydrogen bonding). This means that they have high boiling temperatures compared with other organic compounds with a similar molar mass. As the carbon chain lengthens, the London forces between the non-polar hydrocarbon chains increase. Therefore, boiling temperature increases with increasing molar mass, as shown in table C.

NAME	FORMULA	MOLAR MASS/ g mol^{-1}	BOILING TEMPERATURE /°C
methanoic acid	HCOOH	46	101
ethanoic acid	CH_3COOH	60	118
propanoic acid	CH_3CH_2COOH	74	141
butanoic acid	$CH_3CH_2CH_2COOH$	88	164

table C

SOLUBILITY IN WATER

The shorter-chain carboxylic acids are soluble in water because they can form hydrogen bonds with water molecules. Fig D shows hydrogen bonding between ethanoic acid and water.

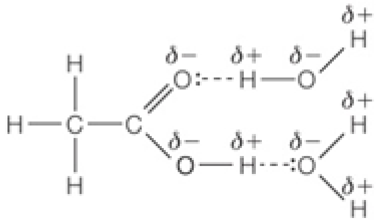


fig D Hydrogen bonding between ethanoic acid and water.

15C 2 Preparations and reactions of carboxylic acids

PREPARATION BY OXIDATION

Although carboxylic acids are formed in many chemical reactions, two main methods are used to prepare them in the laboratory.

Oxidation uses either a primary alcohol or an aldehyde as the starting material. The usual oxidising agent is acidified potassium dichromate(VI), and the method is to heat the mixture under reflux. If a primary alcohol is used, it first oxidises to an aldehyde, then to a carboxylic acid, but both oxidations occur inside the apparatus used. When the oxidation is complete, the reaction mixture is fractionally distilled to obtain a pure sample of the carboxylic acid.

EXAMPLES

Propanoic acid can be prepared from either propan-1-ol or propanal. The equations use [O] to represent the oxygen supplied by acidified potassium dichromate(VI).

From propan-1-ol:

From propan-1-ol:

$$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$$

From propanal:

$$CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

PREPARATION BY HYDROLYSIS

Nitriles are organic compounds containing the CN group. They can be hydrolysed by heating under reflux with either a dilute acid or aqueous alkali. The same apparatus is used for preparation and purification as for oxidation.

In both cases, the C≡N triple bond breaks. The carbon atom remains part of the organic product and the nitrogen atom becomes either ammonia or the ammonium ion.

ACIDIC HYDROLYSIS

Propanoic acid can be prepared from propanenitrile. The equation for the reaction is:

$$CH_3CH_2CN + H^+ + 2H_2O \rightarrow CH_3CH_2COOH + NH_4^+$$

ALKALINE HYDROLYSIS

Butanoic acid can be prepared from butanenitrile. The equation for the reaction is:

$$CH_3CH_2CH_2CN + OH^- + H_2O \rightarrow CH_3CH_2CH_2COO^- + NH_3$$

The product is actually the butanoate ion, but this is easily converted to butanoic acid by adding dilute acid:

$$CH_3CH_2CH_2COO^- + H^+ \rightarrow CH_3CH_2CH_2COOH$$

INTRODUCTION TO REACTIONS

There are four main reactions to consider. These are summarised in **fig A**.

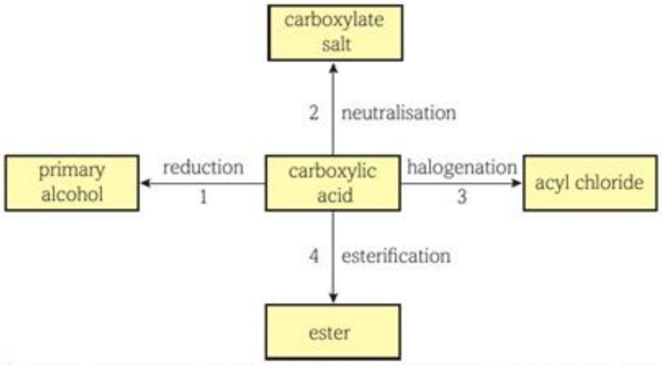


fig A These are the four main reactions of carboxylic acids to form other organic compounds.

1 REDUCTION

You will remember that carboxylic acids are products of oxidation. They can be reduced in the same way as aldehydes and ketones. Carboxylic acids can be reduced to primary alcohols, but not to aldehydes. This is because aldehydes are more easily reduced than carboxylic acids, and so any aldehyde produced during the reduction will be immediately reduced to a primary alcohol. The reducing agent is lithium tetrahydridoaluminate, and is used in a solvent of dry ether. As an example, an equation using butanoic acid is:

$$CH_3CH_2CH_2COOH + 4[H] \rightarrow CH_3CH_2CH_2CH_2OH + H_2O$$

The product is butan-1-ol.

2 NEUTRALISATIONS

Although carboxylic acids are weak acids, they can be completely neutralised by mixing with aqueous alkali. The products are carboxylate salts, which have a wide range of uses. The commonest, sodium ethanoate, is used in hand warmers and to make the additive that gives the flavour to salt and vinegar potato crisps. An equation for the reaction to make sodium ethanoate occurs between ethanoic acid and sodium hydroxide:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

3 HALOGENATION

In this reaction, the OH group is replaced by a halogen atom, usually chlorine, so the functional group becomes COCl. These products are known as acyl chlorides. They are highly reactive compounds with many uses in organic synthesis, as we will see later on. The reagent is phosphorus(V) chloride (old name 'phosphorus pentachloride'). It must be used in anhydrous conditions because both the reagent and the acyl chloride product react with water.

The reaction is vigorous (very active), so no heating is required. An equation for the reaction, using propanoic acid as the example, is:

$$CH_3CH_2COOH + PCl_5 \rightarrow CH_3CH_2COCl + POCl_3 + HCl$$

Acyl chlorides are named using the suffix -oyl chloride, so this product is propanoyl chloride. Their general formula is RCOCl.

The phosphorus-containing product is phosphorus trichloride oxide (also known as phosphorus oxychloride). It is a liquid that mixes with the acyl chloride, which has therefore to be separated by fractional distillation. The hydrogen chloride gas produced escapes, appearing as misty fumes.

4 ESTERIFICATION

In this reaction, a carboxylic acid is mixed with an alcohol and a small amount of an acid catalyst, often concentrated sulfuric acid. Even with a catalyst, the reactions are slow and reversible.

Esters are used in industry for many purposes, including as solvents and in making polymers (polyesters). They also occur very commonly in nature - they are responsible for the characteristic smells of fruits, and most animal fats and vegetable oils are esters.

An equation for the reaction between methanoic acid and ethanol is:

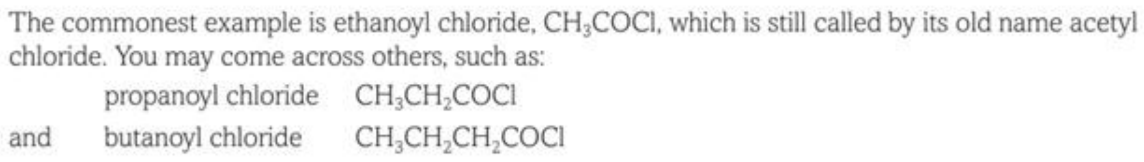
$$HCOOH + CH_3CH_2OH \rightleftharpoons HCOOCH_2CH_3 + H_2O$$

The names of esters always contain two words - the first is the alkyl group from the alcohol and the second is the carboxylate from the carboxylic acid. So, this product is ethyl methanoate.

15D 1 Carboxylic acids derivatives: Acyl chlorides

WHAT ARE ACYL CHLORIDES?

These used to be known as acid chlorides, and have the general formula RCOCl. They are derivatives of carboxylic acids, and can be imagined as the result of replacing the OH group in COOH with Cl. Although they contain a carbonyl group (like carboxylic acids, aldehydes and ketones), they are not classed as carbonyl compounds. As with carboxylic acids, having two functional groups sharing the same carbon atom means that the properties are different from both carbonyl compounds and halogenoalkanes.



The commonest example is ethanoyl chloride, CH_3COCl, which is still called by its old name acetyl chloride. You may come across others, such as:

	propanoyl chloride	CH_3CH_2COCl
and	butanoyl chloride	$CH_3CH_2CH_2COCl$

DISPLAYED AND SKELETAL FORMULAE

Table A shows the displayed and skeletal formulae of some acyl chlorides.

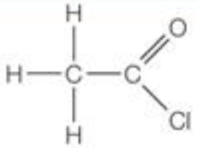
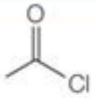
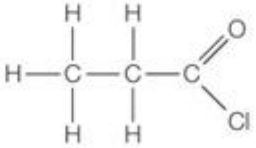
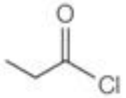
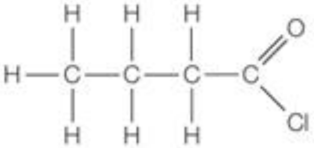
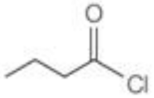
NAME	DISPLAYED FORMULA	SKELETAL FORMULA
ethanoyl chloride		
propanoyl chloride		
butanoyl chloride		

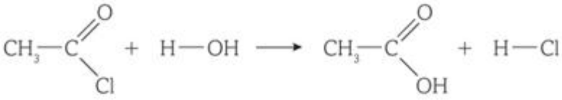
table A

REACTIONS OF ACYL CHLORIDES

The carbon atom in RCOCl is joined to two electronegative atoms, and so is electron-deficient (δ+). You can therefore predict that it will be readily attacked by nucleophiles, such as molecules containing O or N atoms. You need to know about four reactions of acyl chlorides, although no mechanisms are needed for any of them.

REACTION WITH WATER

Acyl chlorides react vigorously (very actively) with cold water, forming a carboxylic acid and releasing hydrogen chloride gas, which appears as misty fumes (fig A). The equation for the reaction of ethanoyl chloride with water is as follows:

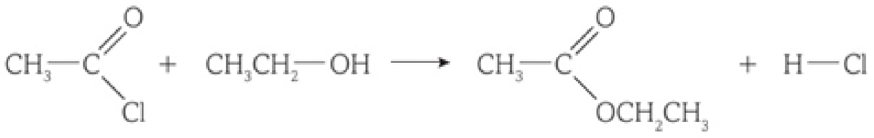


$$CH_3COCl + H{-}OH \longrightarrow CH_3COOH + H{-}Cl$$

fig A Adding ethanoyl chloride to water produces fumes of hydrogen chloride.

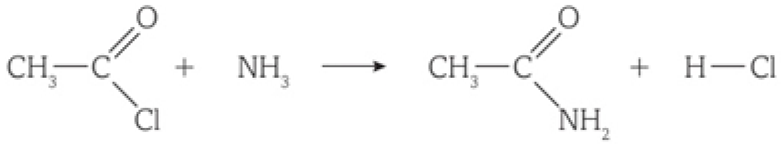
REACTION WITH ALCOHOLS

Acyl chlorides react readily with ethanol to form an ester and hydrogen chloride gas. The equation for the reaction of ethanoyl chloride with ethanol is as follows:



REACTION WITH CONCENTRATED AMMONIA SOLUTION

Similar to alcohols, acyl chlorides react readily with concentrated ammonia solution. You can now predict the reaction that occurs: the H of the second reactant combines with Cl to form HCl, and the other part of the reactant becomes joined to the carbonyl group. The NH2 group joined to the carbonyl group produces a different functional group - amide (not to be confused with amine). The equation for the reaction of ethanoyl chloride with ammonia is as follows:



Unlike with water and alcohols, a further reaction occurs. The reactant is a base and the product is an acidic gas, so these react together to form ammonium chloride:

$NH_3 + HCl \rightarrow NH_4Cl$

You could write a single equation that combines both of these reactions:

$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

REACTION WITH AMINES

This reaction is similar to the previous one. A primary amine can be shown as RNH_2, so you can again predict the reaction that occurs: the H of the second reactant combines with Cl to form HCl, and the other part of the reactant (RNH) becomes joined to the carbonyl group. The equation for the reaction of ethanoyl chloride with the simplest primary amine, methylamine, is as follows:

The product of this reaction is a substituted amide, often called an N-substituted amide. The capital N emphasises that there is an alkyl group attached to N, rather than the usual situation in which it is attached to another C atom. You can see from the product name (N-methylethanamide) that N- is used as a locant, in the same way as in names such as 2-methylbutane - it shows where the methyl group is attached.

Secondary amines (represented as R2NH) react in the same way, although the product will contain two substituted alkyl groups. A sample equation is:

$CH_3COCl + (CH_3)_2NH \rightarrow CH_3CON(CH_3)_2 + HCl$

The organic product is N,N-dimethylethanamide.

You might be able to predict why this type of reaction does not occur with a tertiary amine (R_3N). With three alkyl groups, there is now no H atom to react with Cl to form hydrogen chloride.

15D 2 Carboxylic acids derivatives: Esters

INTRODUCTION

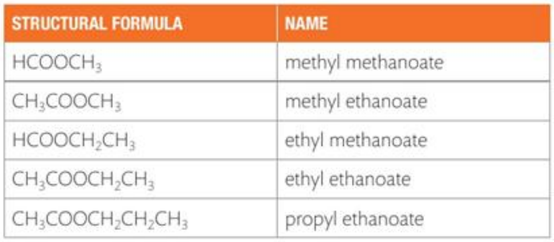
In previous sections, you have come across esters as the products of reactions of other organic compounds. We will now take a closer look at esters, including their reactions.

NAMING ESTERS

This is straightforward, but you need to remember these points:

- As for carboxylic acids and acyl chlorides (but not amides), an ester name contains two words.
- The first word comes from the alkyl group joined to O.
- The second word comes from the alkyl group joined to C.

Table A shows some examples.



STRUCTURAL FORMULA	NAME
$HCOOCH_3$	methyl methanoate
CH_3COOCH_3	methyl ethanoate
$HCOOCH_2CH_3$	ethyl methanoate
$CH_3COOCH_2CH_3$	ethyl ethanoate
$CH_3COOCH_2CH_2CH_3$	propyl ethanoate

table A

DISPLAYED AND SKELETAL FORMULAE

Table B shows the displayed and skeletal formulae of some esters.

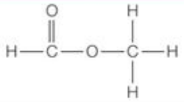
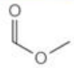
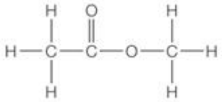
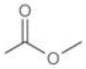
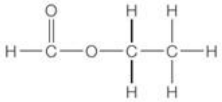
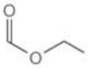
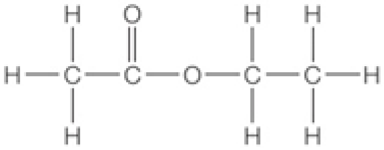
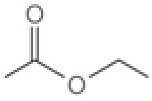
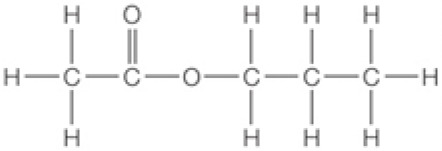
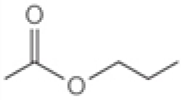
NAME	DISPLAYED FORMULA	SKELETAL FORMULA
methyl methanoate		
methyl ethanoate		
ethyl methanoate		
ethyl ethanoate		
propyl ethanoate		

table B

PHYSICAL PROPERTIES

Esters are colourless liquids with relatively low melting and boiling temperatures, and are insoluble in water. All of the hydrogen atoms in their molecules are attached to carbon atoms, so hydrogen bonding is not possible.

The generally pleasant smells of esters are largely responsible for the familiar odours of flowers and fruits.

HYDROLYSIS OF ESTERS

The only reactions of esters that you need to know about are two slightly different types of hydrolysis. The term 'hydrolysis' means
breaking down (lysis) using water (hydro). It can be considered as the reverse of esterification. You may remember equations such as this from a previous section:

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

This shows the formation of ethyl ethanoate from the corresponding carboxylic acid and alcohol. The reversible arrow indicates that a mixture of ethyl ethanoate and water reacts together to form ethanoic acid and ethanol. This reverse reaction could be described as the hydrolysis of ethyl ethanoate.

HYDROLYSIS IN ACIDIC SOLUTION

We partly covered this type of hydrolysis in the previous paragraph. For a given ester, warming it with water will cause hydrolysis. As with esterification, the reaction is slow. A catalyst such as sulfuric acid will speed up hydrolysis, but will not affect the position of equilibrium, so the reaction will not go to completion:

$$CH_3COOCH_2CH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH$$

HYDROLYSIS IN ALKALINE SOLUTION

The disadvantage of using an alkali such as aqueous sodium hydroxide instead of sulfuric acid is that the reaction produces a carboxylate salt instead of a carboxylic acid. However, the advantage easily outweighs this disadvantage - the reaction goes to completion instead of reaching an equilibrium. The equation for methyl propanoate is:

$$CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COO^- + Na^+ + CH_3OH$$

Converting the carboxylate salt into a carboxylic acid only needs a dilute acid to be added:

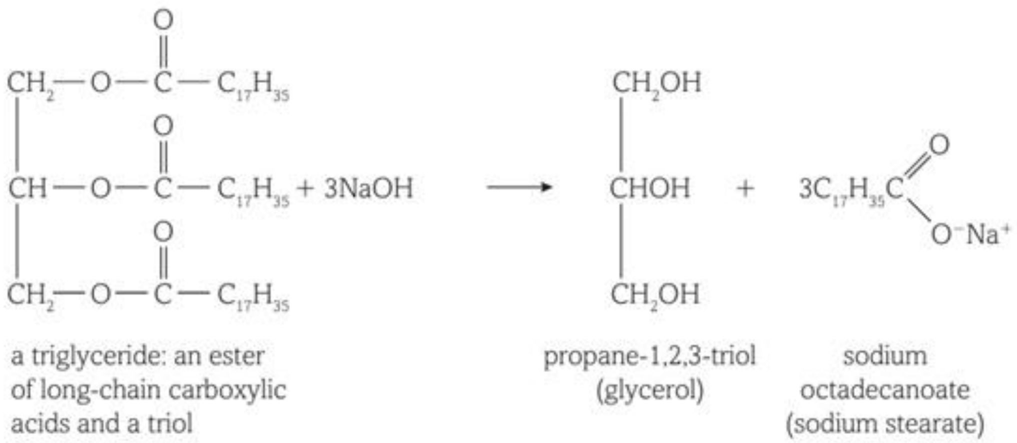
$$CH_3CH_2COO^- + H^+ \rightarrow CH_3CH_2COOH$$

The final organic products are methanol and propanoic acid.

SAPONIFICATION

The Latin word for soap is sapo, so saponification means 'soap-making'. This is a particular example of the alkaline hydrolysis of esters. Soaps and detergents have similar uses, but the main difference is that detergents use organic compounds obtained from crude oil, while soaps use organic compounds obtained from vegetable (and, originally, animal) sources.

Vegetable oils contain large quantities of triglycerides. These are triesters, each of which consists of a large ester molecule that can be hydrolysed to one alcohol and three carboxylic acid molecules. The hydrolysis of a typical triglyceride is shown in fig B.



▲ **fig B** The hydrolysis of a typical triglyceride is an example of saponification.

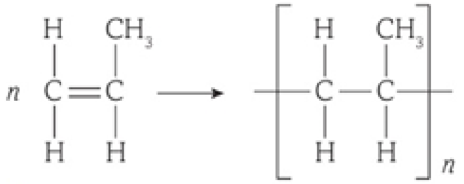
SUBJECT VOCABULARY

hydrolysis the breaking of a compound by water into two compounds

15D 2 Carboxylic acids derivatives: Polyesters

ADDITION POLYMERISATION

Examples of addition polymerisation were covered in Topic 5 (Book 1: IAS), so may be useful for reminding you of this type of polymerisation. The monomer propene can combine with many thousands of other propene molecules to form a very long chain. This process can be represented as:



▲ **fig A** This equation represents the polymerisation of propene.

One thing to notice is that all of the atoms in the monomer molecules end up in the structure of the polymer.

CONDENSATION POLYMERISATION

There are two main differences between addition polymerisation and condensation polymerisation. In condensation polymerisation:

- each time two monomer molecules join together, another small molecule is formed
- usually two different monomers react together.

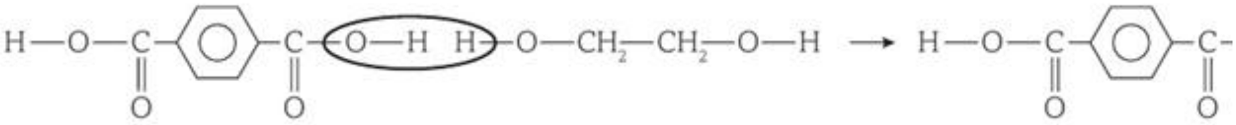
POLYESTERS

The example we will use to introduce condensation polymerisation is the formation of polyesters. You will remember that esters are the products of the reaction between alcohols and carboxylic acids. However, once one molecule of an alcohol has reacted with one molecule of a carboxylic acid, the reaction is complete. The only organic product is a slightly larger ester molecule.

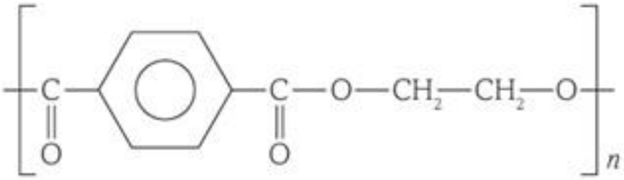
For a reaction to produce a polymer, we need two monomers, each with two reactive groups (one at each end). The alcohol usually involved in this type of reaction, more accurately called a 'diol', has two hydroxyl groups, one at each end:

$H-O-CH_2-CH_2-O-H$

One of the most common carboxylic acids used (more accurately a dicarboxylic acid) has the structure below. The common name for this compound is terephthalic acid.



This larger molecule that has formed still has reactive groups at both ends. This means it can continue reacting with other molecules in the same way as above, until a very long polymer chain has formed. The structure of the polymer is:



Because of the original name of the acid (terephthalic acid), the polymer was originally known as Terylene.

SUBJECT VOCABULARY

condensation polymerisation the formation of a polymer, usually by the reaction of two different monomers, when another small molecule is also formed

15E 1 Simple chromatography

CHROMATOGRAPHY

You may know about paper chromatography from your early experiences of chemistry. This is a suitable place to remind you of this technique and to explain some of the principles that relate to most types of chromatography.

However, the technique can also be used with colourless substances because these can be detected in other ways without considering their colours. Chromatography is used:

- to separate a mixture into its individual components
- to identify the components of a mixture by considering how far they have travelled up the paper.

APPARATUS

All forms of paper chromatography need the following:

- A container (usually glass) with a lid. The lid is there to prevent evaporation of the solvent. The container could be a beaker or a rectangular tank.
- Paper. In introductory experiments you may have used filter paper or kitchen towel, but specially formulated chromatography paper gives better results. There also needs to be a method of supporting the paper in the container.
- A solvent. In some cases, water works well, but often the solvent is a mixture of organic compounds, and is chosen to fit the characteristics of the components of the mixture.

Paper chromatography involves spotted mixtures onto paper, with known substances often at the same level. A solvent is added, paper is inserted, and the apparatus is left until the solvent front reaches the top. The paper is then dried, creating a chromatogram.

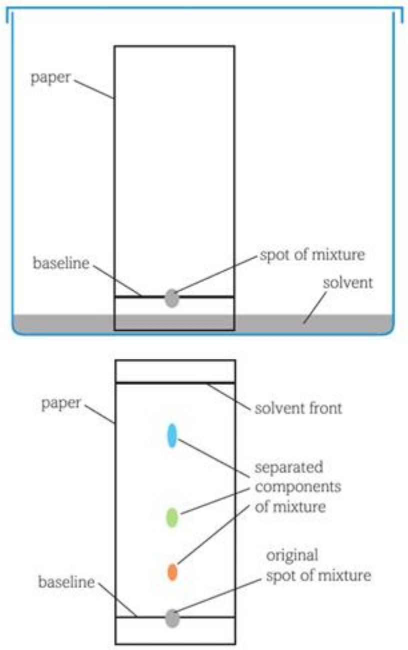
HOW DOES CHROMATOGRAPHY WORK?

All types of chromatography depend on the use of a stationary phase and a mobile phase. Each component in the mixture is attracted to both phases, but more strongly to one than the other.

- A component that is strongly attracted to the stationary phase but weakly attracted to the mobile phase will not travel very far up the paper.

- A component that is weakly attracted to the stationary phase but strongly attracted to the mobile phase will travel a long way up the paper.

Paper chromatography involves a stationary phase of water trapped in paper fibers and a mobile phase of solvent. Colours are used to illustrate substances, but most organic compounds are colorless.



▲ **fig A** The chromatogram here is shown in a rather idealised way – in reality the spots are often elongated and their centres are difficult to identify.

THIN-LAYER CHROMATOGRAPHY

The apparatus and method used in thin-layer chromatography (TLC) are very similar to those of paper chromatography. The only difference is that instead of paper, a sheet of glass or plastic coated in a thin layer of a solid such as silica or alumina is used (fig B).

fig B This is a TLC plate after a chromatography experiment.

CALCULATING R1 VALUES

The chromatogram is analysed and the distance travelled by the solvent (from the baseline to the solvent front) is measured. For each component in the mixture, the distance it has travelled (starting from the baseline) is measured.

The R_1 value is calculated using the expression:

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

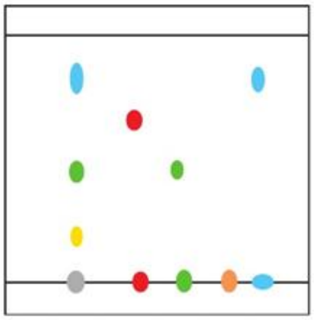


fig C Chromatogram.

COLUMN CHROMATOGRAPHY

Column chromatography uses the same principles as thin-layer chromatography. The stationary phase is alumina or silica packed into a tube (a burette will be suitable) and soaked in a solvent. The mixture is placed on top of the stationary phase and more solvent (the mobile phase) added on top. When the tap is opened, the solvent drips through the tip and the components of the mixture begin to move down the tube and separate.

SUBJECT VOCABULARY

stationary phase in chromatography the liquid or solid that does not move

mobile phase in chromatography the liquid that moves through the stationary phase and transports the components

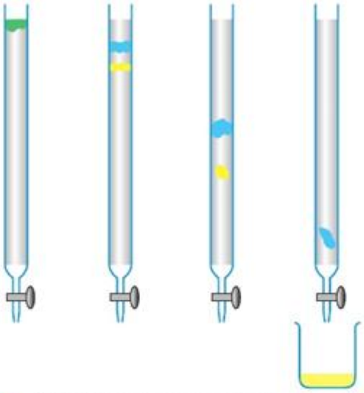


fig D Separation of a mixture by column chromatography.

15E 2 Determining structures using mass spectra

MASS SPECTROMETRY SO FAR

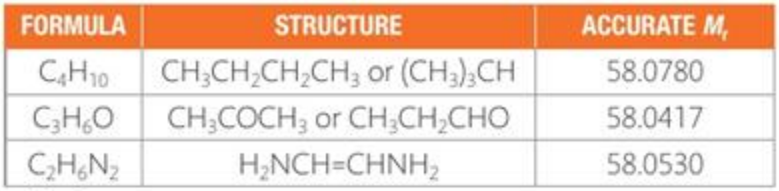
In Topic 10 (Book 1: IAS) you learned about two aspects of mass spectrometry. They were:

- determining the relative atomic masses of elements from isotopic abundances
- using fragmentation patterns to determine the structures of organic compounds.

In this section we will learn about another use - determining the molecular formula (although not always the structure or identity) of an organic compound from a precise relative molecular mass obtained from **high resolution mass spectrometry (HRMS).**

HIGH RESOLUTION MASS SPECTROMETRY

Without going into technical detail, there are mass spectrometers that can provide a value for a relative molecular mass to four or more decimal places. Values with this degree of precision sometimes enable a compound to be positively identified from the relative molecular mass alone, without the need for any other information. Consider compounds with M_r, = 58 (or 58.0). There are several possible structures, including those in table A:



FORMULA	STRUCTURE	ACCURATE M_r
C_4H_{10}	$CH_3CH_2CH_2CH_3$ or $(CH_3)_3CH$	58.0780
C_3H_6O	CH_3COCH_3 or CH_3CH_2CHO	58.0417
$C_2H_6N_2$	$H_2NCH{=}CHNH_2$	58.0530

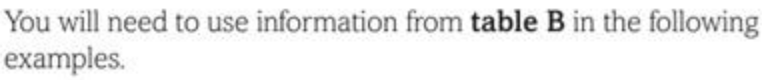
table A

CALCULATING THE ACCURATE RELATIVE MOLECULAR MASS

We can also obtain accurate M_r, values by doing some simple calculations. You know that relative atomic masses are relative to the average mass of a carbon atom (^{12}C) taken as exactly 12, which for our purposes means 12.0000. Table B shows the accurate atomic masses of some common elements:

ELEMENT	SYMBOL	ACCURATE ATOMIC MASS
hydrogen	H	1.0078
carbon	C	12.0000
nitrogen	N	14.0031
oxygen	O	15.9949

table B



You will need to use information from **table B** in the following examples.

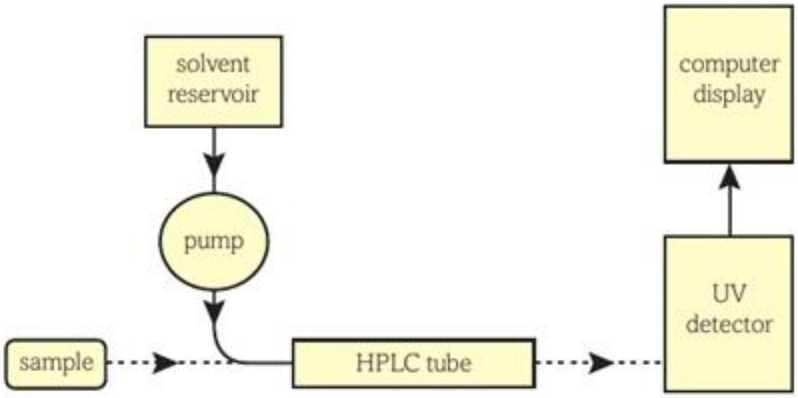
15E 3 Chromatography: HPLC and GC

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

High performance liquid chromatography (HPLC) is a refinement of column chromatography, described in Section 15E.1. The main differences are:

- The solvent is forced through a metal tube under high pressure, rather than being allowed to pass through by gravity.
- The particle size of the stationary phase is much smaller, which leads to better separation of the components.
- The sample is injected into the column.
- The components are detected after passing through the column, usually by their absorption of ultraviolet radiation.
- The whole process is automated, and the results are quickly available on a computer display.

Fig A shows a typical setup.



▲ **fig A** Apparatus for HPLC.

As each component reaches the detector, a signal is displayed on the computer screen. Just as retention factor (R) values can be obtained from paper and thin-layer chromatography, in HPLC values of **retention** time are obtained.

However, retention times depend on several variables, including:

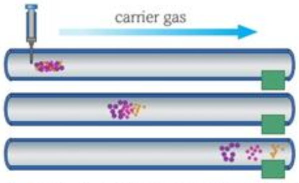
- the nature of the solvent
- the pressure used
- the temperature inside the column.

GAS CHROMATOGRAPHY

Gas chromatography (GC) is another refinement of column chromatography. The main differences are:

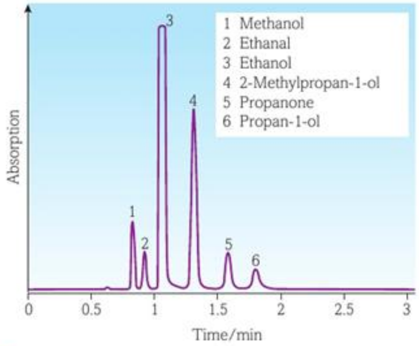
- The metal tube can be several metres long and is coiled to save space.
- The stationary phase is a solid or liquid coated on the inside of the tube.
- The mobile phase is an inert carrier gas (often nitrogen or helium).
- The sample is injected into the column, as in HPLC.
- The components passing through the column are detected.
- The whole process is automated, and the results are quickly available on a computer display (fig B).

After the sample is injected, the components vaporise and move through the coiled tube with the carrier gas. They move at different speeds, depending on how strongly they are attracted to the stationary phase. Those with weaker attractions move more quickly and have shorter retention times. **Fig D** shows the separation occurring in the coiled tube.

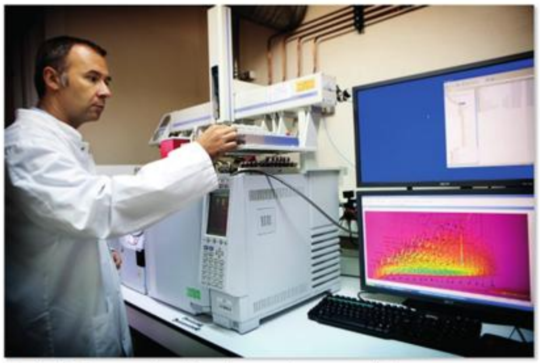


▲ **fig D** A gas chromatograph separating three components.

The relative concentrations of the different components are often displayed on a graph like that in **fig E**.

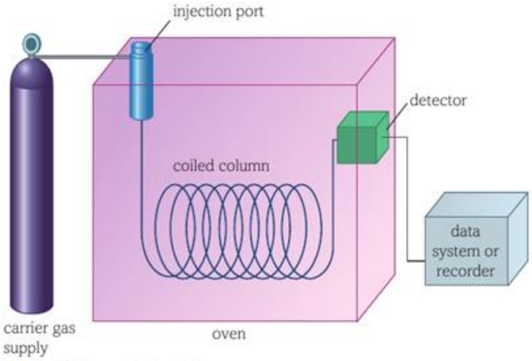


▲ **fig E** The areas under the peaks represent the relative concentrations of the components.



▲ **fig B** The complete GC equipment takes up very little room.

Fig C shows a typical setup.



▲ **fig C** Apparatus for GC.

SUBJECT VOCABULARY

retention time (of a component) in HPLC and GC, the time taken from injection to detection

15E 4 Chromatography and mass spectrometry

LIMITATIONS OF HPLC AND GC

Section 15E.3 outlines two types of chromatography for separating small mixture components, but struggles with positively identifying them due to variable control and similar retention times. Components are often identified using a database, but without reference, these techniques are ineffective..

Here are two areas in which the results of these chromatography methods have to be exactly correct:

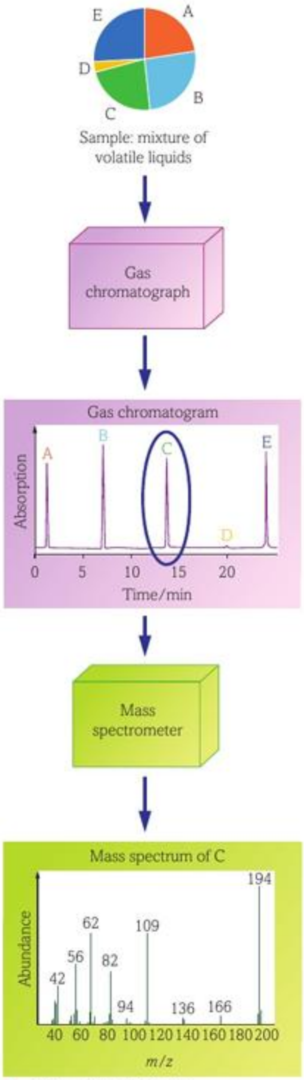
- in providing forensic evidence (for use in a court of law)
- in detecting banned drugs in sportsmen and sportswomen and racehorses.

▲ **fig A** GC-MS is widely used for forensic purposes.

HPLC and GC are used in environmental pollutants analysis, explosive detection, and space probes. They are often combined with mass spectrometry (MS) to provide information about compound structures, often abbreviated as HPLC-MS and GC-MS.

GC-MS

As the two combined techniques are very similar, we will focus only on GC-MS. Fig B shows the stages in a typical setup.
Imagine a sample containing a mixture of five different substances, A-E.



▲ **fig B** Stages in GC-MS.

Stage 1: The mixture is injected into a gas chromatograph.

Stage 2: Each component has a different retention time, so emerges at a different time.

Stage 3: One at a time, each component enters the mass spectrometer.

Stage 4: Component C has its mass spectrum displayed.

Stage 5: The m/z values and relative abundances of components are compared with a database of known substances.

Stage 6: When a match is found, component C has been positivel identified.
Very small traces of substances, for example in a human hair or a paint fleck, can be accurately identified by this method.

PROBLEMS WITH DRUG TESTING

GC-MS is used to detect small amounts of banned drugs, but sometimes problems arise. Anabolic steroids, like nandrolone, have legitimate uses in medicine, but are prohibited by sporting authorities due to their muscle-promoting effects. Nandrolone is converted into 19-norandrosterone, excreted in urine, and the International Olympic Committee sets a limit of 2 nanograms per cm3 of urine.
The skeletal formulae of these two related compounds are:

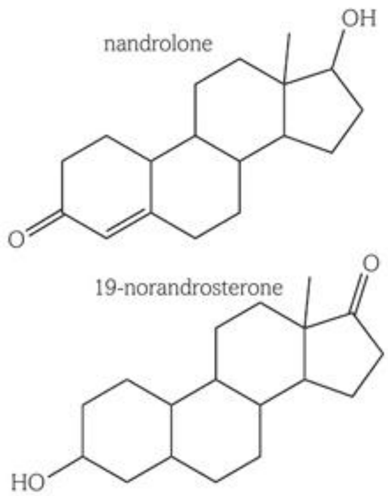


fig C Skeletal formulae of nandrolone and 19-norandrosterone.

fig D A urine sample from an athlete about to be tested for illegal drugs.

15E 2 Principles of NMR spectroscopy

WHAT IS NMR?

This section and the following sections in Topic 15 are about a third major technique, **nuclear magnetic resonance spectroscopy (NMR).** This is important for determining the structures of organic compounds. Every major hospital has a department with an NMR scanner, although they are normally described as MRI (magnetic resonance imaging) scanners.

A SIMPLIFIED EXPLANATION

NMR is much more difficult to fully understand than MS or IR spectroscopy. Fortunately, our emphasis will be on interpreting the spectra produced, and not on fully understanding how it works. Even so, it will help if you read a bit of the theory behind it. Table A shows some of the key points.

KEY ASPECTS OF NMR

You need to know about several aspects of NMR.

NMR SPECTRUM

The output of a mass spectrometer or of an infrared spectrometer produces a spectrum (a kind of graph). Similarly, each compound tested using NMR produces a characteristic spectrum. The vertical axis is sometimes labelled 'absorption' (for 'absorption of radio frequency energy') and has no units, although the label is often omitted. The horizontal axis is labelled **chemical shift** (or sometimes with the 8 symbol - the same symbol as used for partial charges) and has the units 'ppm' (parts per million).

fig A A hospital patient about to have an MRI scan. MRI is a development of NMR spectroscopy.

POINT	COMMENT
Nucleons (protons and neutrons) have spin.	You know that electrons in atoms that pair up in orbitals have opposite spins. Well, protons and neutrons in the nucleus also have opposite spins.
Nuclei have either an even or an odd number of nucleons.	In nuclei with an even number of nucleons, these spins cancel out. In nuclei with an odd number of nucleons, these spins cancel out, except for the odd one, which leaves the nucleus with residual spin.
Residual spin causes a tiny magnetic field.	Such nuclei can be imagined as tiny magnets.
These nuclei are affected by an external magnetic field.	Nuclei can be imagined as either lining up or opposing the external magnetic field.
There is a difference in energy between these two different states of a nucleus.	As the spins of nuclei 'flip' between lining up and opposing the external magnetic field, the nuclei can absorb electromagnetic radiation.
The nuclei of two adjacent (neighbouring) atoms in a molecule influence each other, and electrons also have an effect.	This means that electromagnetic radiation is absorbed differently by different atoms in a molecule, and these are detected as different 'signals' at different frequencies.

table A

WHICH ATOMS ARE DETECTED BY NMR?

NMR spectrums can detect atoms with odd nucleon numbers, including carbon atoms. However, 1.1% of naturally occurring carbon atoms are ^{13}C isotopes with odd neutrons, allowing detection of carbon atoms in molecules.

This process is known as carbon-13 or **^{13}C NMR**. Hydrogen atoms are also detected - at least the 'H isotopes that make up 99.985% of all hydrogen atoms. In the context of NMR, 'H hydrogen atoms are often referred to as protons, so an alternative name for the process is **proton NMR.**

SUITABLE SOLVENTS

The organic compound being analyzed must dissolve in a solvent, which typically contains carbon and hydrogen atoms, which can interfere with the compound's signals. The common solvent is $CDCl_3$, which produces no hydrogen-related signals but can interfere with carbon atom signals.

TMS

Carbon and hydrogen atoms in different chemical environments will produce different signals. Therefore, there needs to be a reference standard that will give a prominent signal. The compound used for this purpose is tetramethylsilane (usually abbreviated to TMS). Its structure is shown below:

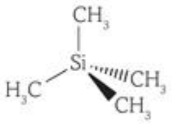
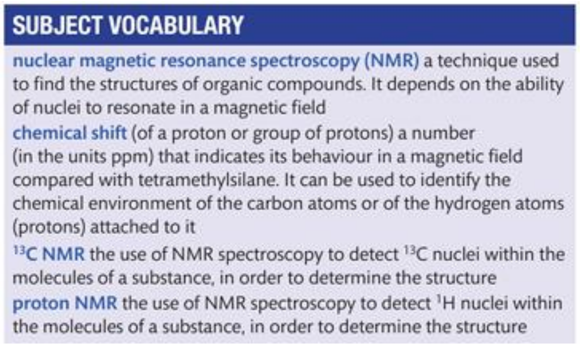


fig B The largest part of NMR equipment is often the large vacuum flask containing liquid helium, needed to cool the magnets to below 4 K.

CHEMICAL SHIFT

Each 13C and 'H atom in a compound produces a signal at a characteristic chemical shift (8 value), depending on the other atoms it is joined to. The reference standard, TMS, is given a chemical shift of zero (8= 0.0 ppm), and all other atoms have values related to this. Chemical shift can be thought of as the resonant frequency of an atom. In Sections 15E.6 and 15E.7 you will learn to use a data booklet containing values (or more often, ranges) of chemical shifts to identify specific atoms in molecules. Here are two examples:

carbon in a ketone group	—C—**C**O—C—	δ = 210 ppm
carbon in an alcohol	—**C**—OH	δ = 60 ppm



SUBJECT VOCABULARY

nuclear magnetic resonance spectroscopy (NMR) a technique used to find the structures of organic compounds. It depends on the ability of nuclei to resonate in a magnetic field

chemical shift (of a proton or group of protons) a number (in the units ppm) that indicates its behaviour in a magnetic field compared with tetramethylsilane. It can be used to identify the chemical environment of the carbon atoms or of the hydrogen atoms (protons) attached to it

^{13}C NMR the use of NMR spectroscopy to detect ^{13}C nuclei within the molecules of a substance, in order to determine the structure

proton NMR the use of NMR spectroscopy to detect ^{1}H nuclei within the molecules of a substance, in order to determine the structure

15E 6 ^{13}C NMR spectroscopy

WHAT IS SHOWN BY A 13C NMR SPECTRUM?

The actual spectrum of a compound is usually shown as a horizontal line just above the horizontal scale, but with vertical lines showing the signals produced by the 13C carbon atoms in the molecule. These vertical lines are usually referred to as signals or peaks.

- The number of vertical lines tells you the number of different chemical environments of carbon atoms in the molecule, but not necessarily the total number of carbon atoms.

- The positions of the vertical lines on the horizontal scale tell you the chemical shifts of each carbon atom and, with reference to a list of chemical shifts, allow you to deduce the chemical environments.

The two isomers of propanol can be used to illustrate these points.

Propan-1-ol has the structure CH_3—CH_2—CH_2—OH. Each molecule contains three carbon atoms, all in different chemical environments. You might think that the two carbon atoms in the CH_2 groups are in the same chemical environment, but they are not. The second one is joined to CH_3 and CH_2, but the third one is joined to CH_2 and OH, which means they are in different chemical environments. There should therefore be three peaks in the spectrum.

Propan-2-ol has the structure CH_3—CH(OH)—CH_3. Each molecule contains three carbon atoms, but those in the two CH_3 groups are in the same chemical environment. This is because each CH_3 group is joined to CH(OH). This means that there should be two peaks in the spectrum. **Fig A** shows the ^{13}C spectra of these isomers.

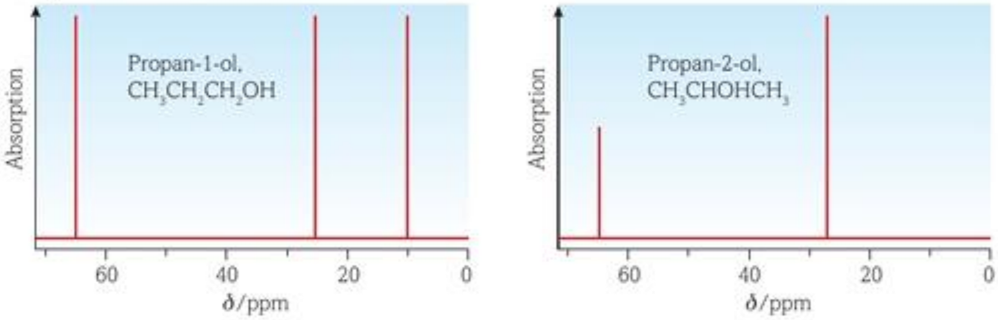


fig A ^{13}C NMR spectra of propan-1-ol and propan-2-ol.

The spectra confirm the number of peaks expected, but show two other features.

- The less important feature is that in propan-1-ol the three peaks are of equal height, but in propan-2-ol the two peaks have different heights.

- The more important one is that the peaks have different chemical shifts.

INTERPRETING CHEMICAL SHIFTS

To interpret chemical shifts you need a table of values and corresponding carbon atoms or a chart. The chart in fig B will be provided in an examination, and you need to become familiar with using it.

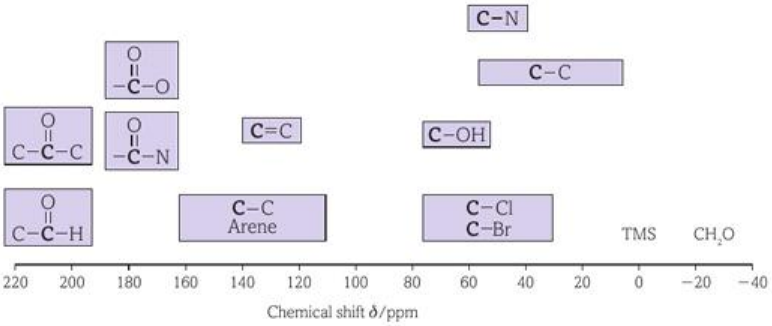


fig B ^{13}C NMR chemical shift ranges.

The chart analyzes two spectra for propanol. The first spectra shows peaks at 65, 25 and 10 ppm, corresponding to C-C and C-OH, respectively. The second spectra shows peaks at 65 and 27 ppm, corresponding to C-C and CH3 groups, respectively. The peak at 27 ppm is larger than the 65 ppm peak, as it is caused by two carbon atoms. The interpretation of these spectra is shown in Fig C.

Fig C shows the interpretation of these two spectra.

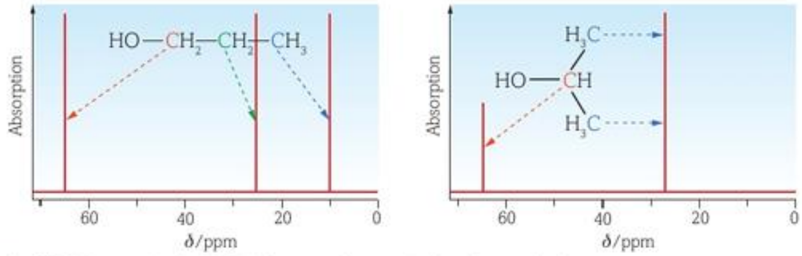


fig C Interpreting the ^{13}C NMR spectra of propan-1-ol and propan-2-ol.

PRACTICE MAKES PERFECT!

The way to check how well you understand how to use ^{13}C NMR spectra is to try lots of examples. In this section we will continue with some examples of varying types.

15E 7 ^{1}H NMR spectroscopy

LOW RESOLUTION 'H NMR SPECTROSCOPY

^{1}H NMR spectroscopy comes in two forms - low resolution and high resolution. The low resolution form is no longer used, but if we start with this, it will help you to understand the high resolution form more easily.

WHAT DOES A LOW RESOLUTION 'H NMR SPECTRUM SHOW?

The actual spectrum of a compound is usually shown as a horizontal line just above the horizontal scale, but with peaks produced by the ^{1}H hydrogen atoms in the molecule. The horizontal scale often starts from δ= 12.0 ppm on the left to 0.0 ppm on the right. Quite often, only the part of the scale where the peaks appear is shown.

- The number of peaks tells you the number of different chemical environments of the hydrogen atoms in the molecule but not the total number of hydrogen atoms.

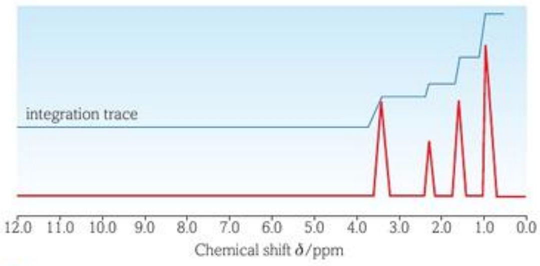


fig A The low resolution ^{1}H NMR spectrum of propan-1-ol.

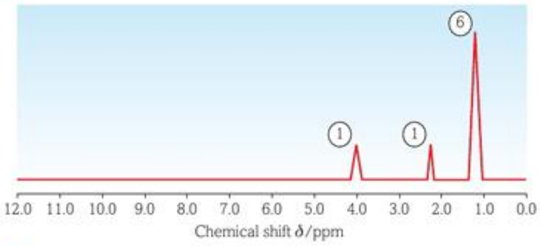


fig B The low resolution ^{1}H NMR spectrum of propan-2-ol.

- The positions of the peaks on the horizontal scale tell you the chemical shifts of each hydrogen atom, and, with reference to a list or chart of chemical shifts, these allow you to deduce the types of chemical environment.
- The areas under the peaks represent the relative numbers of hydrogen atoms in each environment.
- Sometimes a number is added at the side of each peak to show the relative area under the peak.

Another way to represent the relative areas is by an **integration trace**.

INTERPRETING CHEMICAL SHIFTS

To interpret chemical shifts you need a table of reference values with corresponding hydrogen atoms or a chart. Fig C shows a simplified version of the chart that will be provided in an examination, and you need to become familiar with using it.

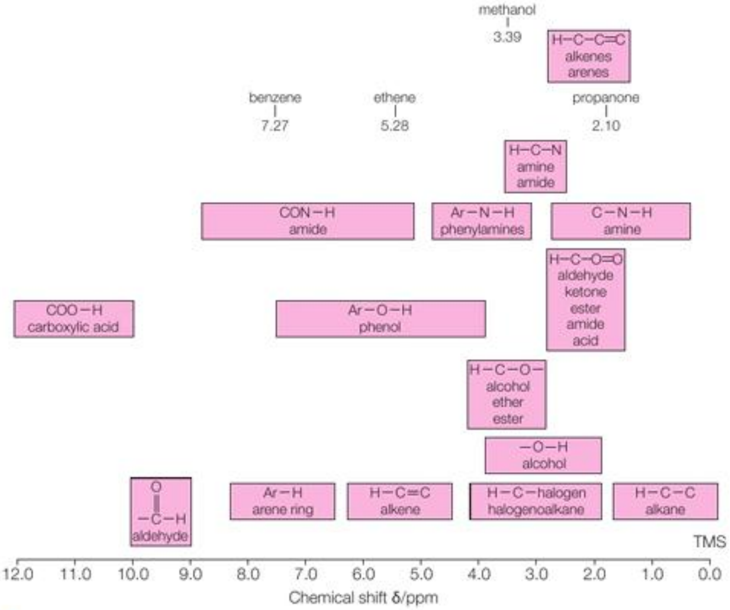


fig C ^{1}H NMR chemical shift ranges.

For two of the chemical shift ranges in this chart, the compounds included show trends in chemical shift values, as shown here in **table A**.

TYPE OF COMPOUND	TREND
halogenoalkane	$R_2CHF > R_2CHCl > R_2CHBr > R_2CHI$
alkane	$R_3CH > R_2CH_2 > RCH_3$

table A

BUTANAL AND BUTANONE

We will use the chart to interpret the low resolution ^{1}H NMR spectra of these isomers with the molecular formula C_4H_8O. **Fig D** shows the spectrum for butanal.

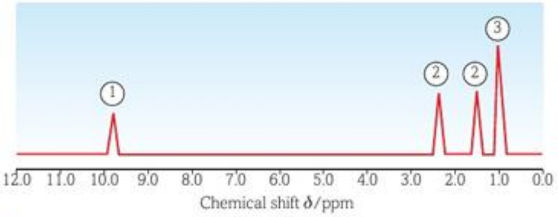


fig D The low resolution ^{1}H NMR spectrum of butanal.

Now for the spectrum of butanone, shown in **Fig E**.

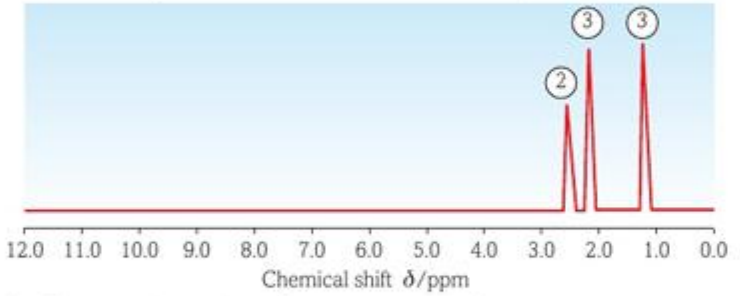


fig E The low resolution ^{1}H NMR spectrum of butanone.

The peak at $\delta = 2.5$ ppm is within the range for H—C—C=O, so must be due to the two H atoms in the CH_2 group joined to the CO group.

The peak at $\delta = 2.1$ ppm is within the range for H—C—C=O, so must be due to the three H atoms in the CH_3 group joined to the CO group.

The peak at $\delta = 1.1$ ppm is within the range for H—C—C (alkane), so must be due to the three H atoms in the CH_3 group not directly joined to the CO group.

SUBJECT VOCABULARY

peak a peak in a ^{1}H NMR spectrum shows the presence of hydrogen atoms (protons) in a specific chemical environment

integration trace this shows the relative numbers of equivalent protons (i.e. in the same chemical environment)

15E 8 Splitting pattens in ^{1}H NME spectra

HIGH RESOLUTION 'H NMR SPECTROSCOPY

In Section 15E.7 we introduced NMR by starting with the low resolution form, although only the high resolution form is actually used now. Both forms have two features in common:

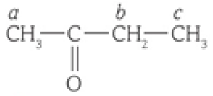
- Peaks at different chemical shift values help to identify the different chemical environments of the hydrogen atoms. If the environments are identical, then the protons are often described as being equivalent (i.e. they are **equivalent protons**).
- The relative peak areas (i.e. the ratio of peak areas) help to decide the numbers of hydrogen atoms responsible.

A high resolution ^{1}H NMR spectrum has one extra feature not seen in a low resolution spectrum - the peaks may have a **splitting pattern**. This means that the peak is split into a group of smaller peaks (sub-peaks) grouped very closely together. When considering these split peaks:

- you can take the chemical shift to be at the centre of the group of sub-peaks
- the relative peak areas are shown in the same way as in a low resolution spectrum - by an integration trace or by showing numbers next to the peaks
- remember that the numbers indicate the ratios of the numbers of protons - they may happen to be the actual numbers of protons, but this is not always the case.

WHAT CAUSES THE SPLITTING OF PEAKS?

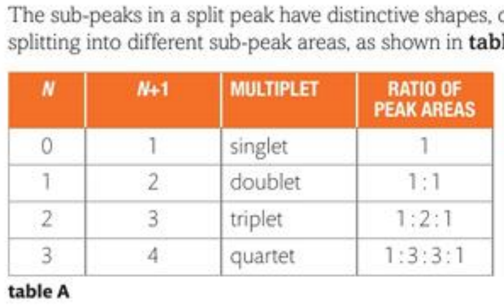
Although the most important thing is for you to be able to interpret the splitting patterns, it will help if you understand how the splitting is caused. The fundamental point to be aware of is that hydrogen atoms (we will call them protons from now on) joined to a carbon atom have an influence on the protons on adjacent or neighbouring carbon atoms. Consider a molecule of butanone, in which the protons are labelled with letters:



$\overset{a}{CH_3}—\underset{\underset{O}{\|}}{C}—\overset{b}{CH_2}—\overset{c}{CH_3}$

fig A The three different chemical environments for the protons in butanone.

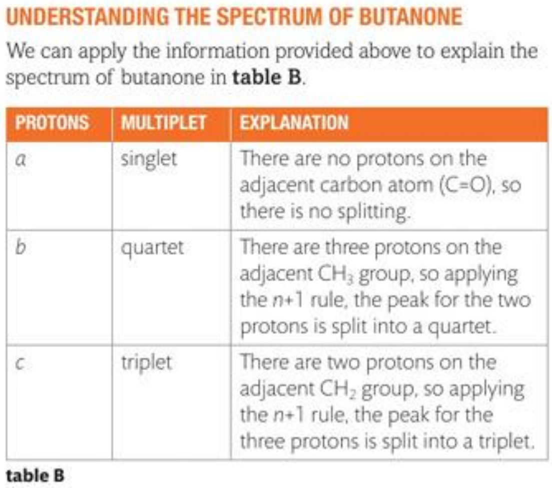
Protons a and b are influenced by protons c and a, causing spin-spin coupling, or splitting of peaks. The n+1 rule states that if a carbon atom has n protons, adjacent peaks are split into n+1 sub-peaks, known as multiplets or multiplets. The number of sub-peaks varies, with distinct shapes due to the splitting into different areas.



The sub-peaks in a split peak have distinctive shapes, owing to splitting into different sub-peak areas, as shown in **table A**.

N	*N*+1	MULTIPLET	RATIO OF PEAK AREAS
0	1	singlet	1
1	2	doublet	1 : 1
2	3	triplet	1 : 2 : 1
3	4	quartet	1 : 3 : 3 : 1

table A

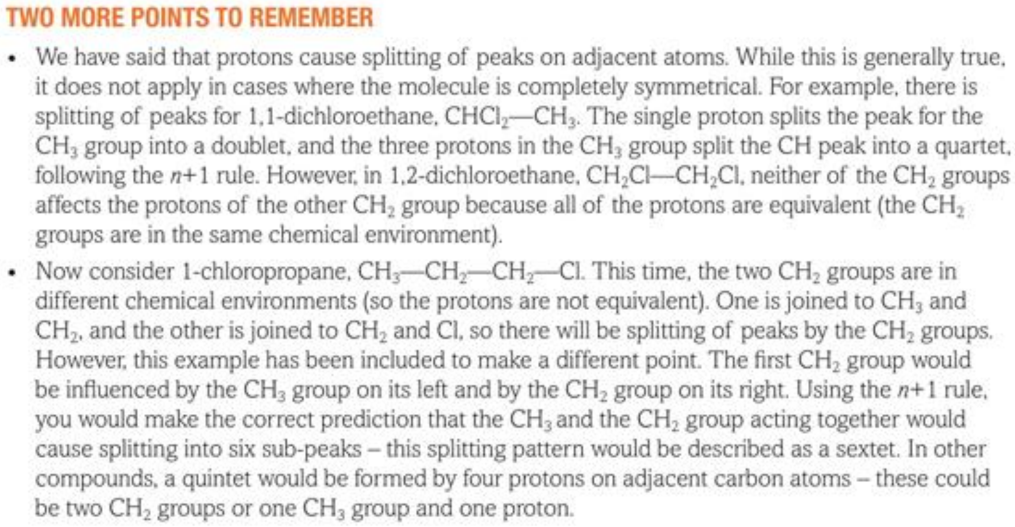


UNDERSTANDING THE SPECTRUM OF BUTANONE

We can apply the information provided above to explain the spectrum of butanone in **table B**.

PROTONS	MULTIPLET	EXPLANATION
a	singlet	There are no protons on the adjacent carbon atom (C=O), so there is no splitting.
b	quartet	There are three protons on the adjacent CH_3 group, so applying the n+1 rule, the peak for the two protons is split into a quartet.
c	triplet	There are two protons on the adjacent CH_2 group, so applying the n+1 rule, the peak for the three protons is split into a triplet.

table B



TWO MORE POINTS TO REMEMBER

- We have said that protons cause splitting of peaks on adjacent atoms. While this is generally true, it does not apply in cases where the molecule is completely symmetrical. For example, there is splitting of peaks for 1,1-dichloroethane, $CHCl_2—CH_3$. The single proton splits the peak for the CH_3 group into a doublet, and the three protons in the CH_3 group split the CH peak into a quartet, following the n+1 rule. However, in 1,2-dichloroethane, $CH_2Cl—CH_2Cl$, neither of the CH_2 groups affects the protons of the other CH_2 group because all of the protons are equivalent (the CH_2 groups are in the same chemical environment).
- Now consider 1-chloropropane, $CH_3—CH_2—CH_2—Cl$. This time, the two CH_2 groups are in different chemical environments (so the protons are not equivalent). One is joined to CH_3 and CH_2, and the other is joined to CH_2 and Cl, so there will be splitting of peaks by the CH_2 groups. However, this example has been included to make a different point. The first CH_2 group would be influenced by the CH_3 group on its left and by the CH_2 group on its right. Using the n+1 rule, you would make the correct prediction that the CH_3 and the CH_2 group acting together would cause splitting into six sub-peaks – this splitting pattern would be described as a sextet. In other compounds, a quintet would be formed by four protons on adjacent carbon atoms – these could be two CH_2 groups or one CH_3 group and one proton.