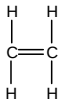
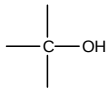
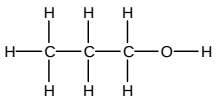
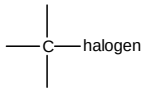
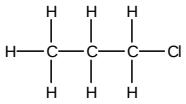
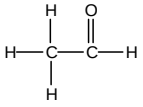
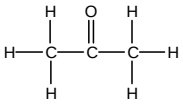
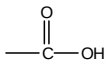
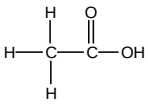
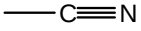
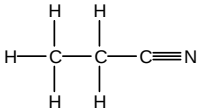
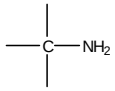
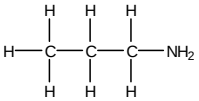
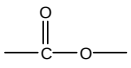
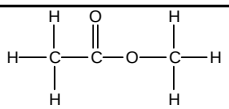
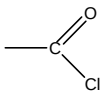
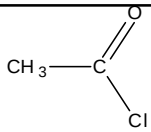
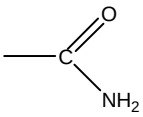
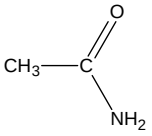
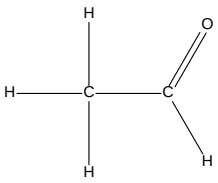
15. Carbonyls, Carboxylic Acids and chirality

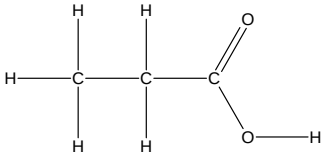
homologous series	functional group	prefix / suffix (* = usual use)	example
alkenes		*suffix* -**ene**	 ethene
alcohols		*suffix** -**ol** *prefix* **hydroxy-**	 propan-1-ol
halogenoalkane		*prefix* **chloro-** **bromo-** **iodo-**	 1-chloropropane
aldehydes		*suffix* -**al** *prefix* **formyl-**	 ethanal
ketones		*suffix** -o**ne** *prefix* **oxo-**	 propanone
carboxylic acids		*suffix* -**oic acid**	 ethanoic acid
nitriles		*suffix* -**nitrile** *prefix* **cyano-**	 propanenitrile
amines		*suffix** -**amine** *prefix* **amino-**	 propylamine Or propan-1-amine
esters		*-yl –oate*	 methyl ethanoate
acyl chloride		*-oyl chloride*	 ethanoyl chloride
amide		*-amide*	 ethanamide

Aldehydes
An aldehyde's name ends in **–al**
It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain



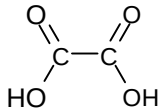
ethan**al**

Carboxylic acids
These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end



propan**oic acid**

If there are carboxylic acid groups on both ends of the chain then it is called a - dioic acid



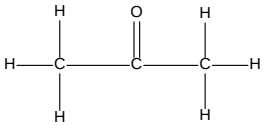
Ethan**edioic acid**

Note the **e** in this name

Ketones

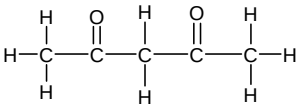
Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



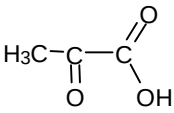
propan**one**

If two ketone groups then **di** is put before **–one** and an an **e** is added to the stem



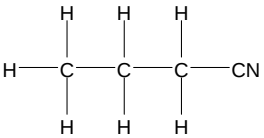
pentan**e**-2,4-dione

The prefix oxo- should be used for compounds that contain a ketone group in addition to a carboxylic acid or aldehyde

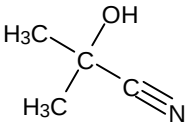


2-oxopropanoic acid

Nitriles
These end in **–nitrile**, but the C of the CN group counts as the first carbon of the chain. Note the stem of the name is different : but**ane**nitrile and not butannitrile.



butanenitrile

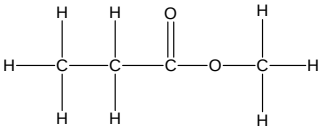


2-hydroxy-2-methylpropanenitrile

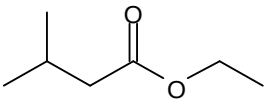
Carboxylic acid derivatives

Esters
Esters have two parts to their names

The bit ending in **–yl** comes from the alcohol that has formed it and is next to the single bonded oxygen.
The bit ending in **–anoate** comes from the carboxylic acid. (This is the chain including the C=O bond)



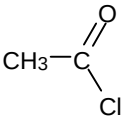
methyl propanoate



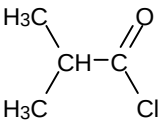
ethyl 3-methylbutanoate

Acyl Chlorides

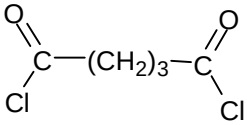
add **–oyl chloride** to the stem name



ethanoyl chloride



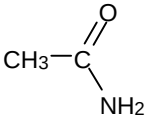
2-methylpropanoyl chloride



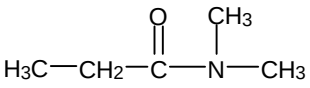
Pentan**e**dioyl dichloride

Amides

Add **–amide** to the stem name

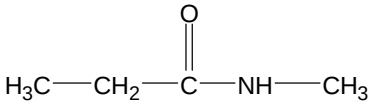


ethanamide

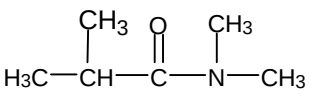


N,*N*-dimethylpropanamide

Secondary and tertiary amides are named differently to show the two (or three) carbon chains. The smaller alkyl group is preceded by an –N which plays the same role as a number in positioning a side alkyl chain



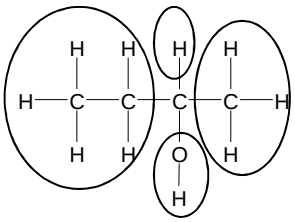
N-methylpropanamide



N,*N*,2-trimethylpropanamide

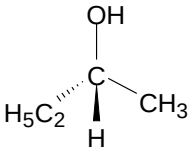
15A Chirality

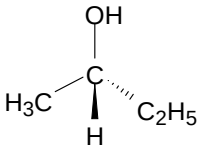
Optical isomerism occurs in carbon compounds with 4 different groups of atoms attached to a carbon (called an **asymmetric carbon**).



A carbon atom that has four different groups attached is called a **chiral** (asymmetric) carbon atom

These four groups are arranged tetrahedrally around the carbon.





This causes two different isomers that are not superimposable to be formed. They are mirror images

A mixture containing a 50/50 mixture of the two isomers (enantiomers) is described as being a **racemate** or **racemic mixture**.

Many naturally occurring molecules contain chiral C atoms, but are usually found in nature as a pure enantiomer

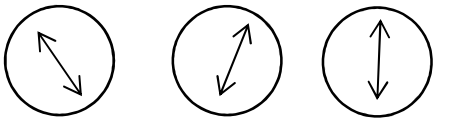
Two compounds that are optical isomers of each other are called **enantiomers**.

Optical isomers have similar physical and chemical properties, but they rotate plane polarised light in different directions.

Different systems of nomenclature are is existence for optical isomers. D/L or +/- are commonly used, but both have been superseded by the more useful and informative R/S system (this is not on the syllabus – for information only).

One enantiomer rotates it in one direction and the other enantiomer rotates it by **the same amount in the opposite direction**.

One optical isomer will rotate light clockwise (+)(called dextrorotatory). The other will rotate it anticlockwise(-)(called laevorotatory).



-ve enantiomer Anticlockwise rotation

+ve enantiomer clockwise rotation

Racemate no rotation

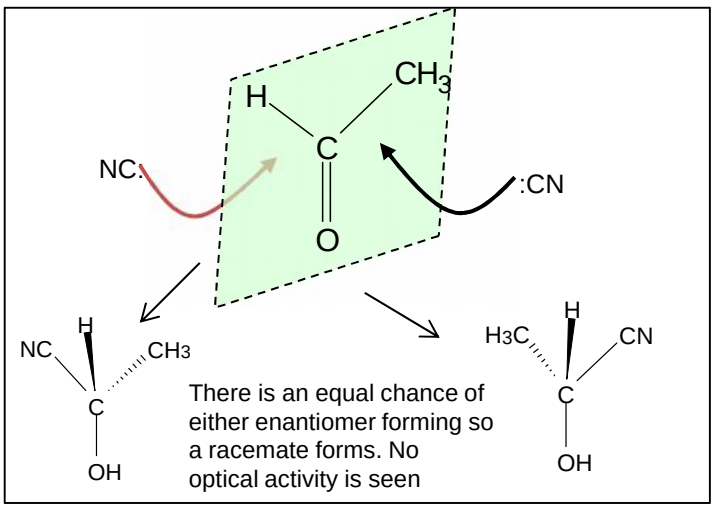
A racemic mixture (a mixture of equal amounts of the two optical isomers) **will not rotate** plane-polarised light.

Chemical Reactions and Optical Isomers

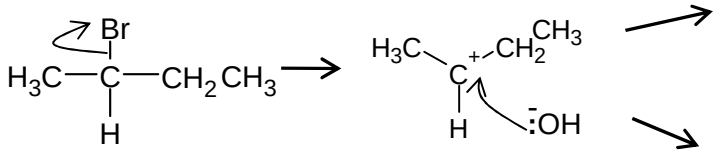
Formation of a racemate

A racemate will be formed in a reaction mechanism when a trigonal planar reactant or intermediate is approached from both sides by an attacking species

Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate

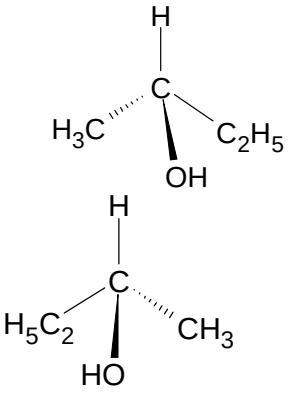


Formation of a racemate with SN_1 mechanism



The Br first breaks away from the haloalkane to form a planar carbocation intermediate

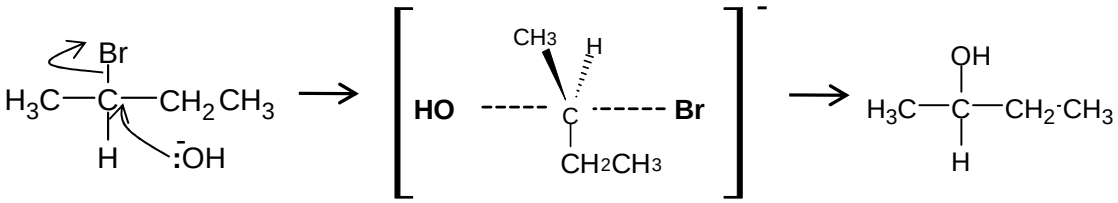
The OH^- ion can then attack from either side resulting in different enantiomers and a **racemate forms**



Because a racemate forms there will be no optical activity in the products

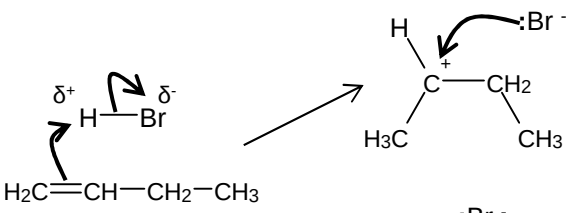
Comparison with SN_2 mechanism

In the SN_2 mechanism no intermediates are formed and the reaction occurs via a transition state.

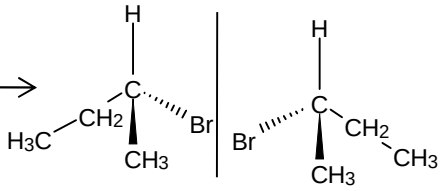


If the reactant was chiral then during the reaction the **opposite enantiomer would form**.
The product will rotate light in the opposite direction to the reactant

A racemate can also be formed in the AS reaction of the electrophilic addition of HBr to an unsymmetrical alkene

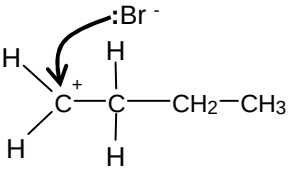


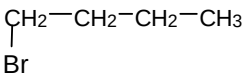
The bromide can attack this planar carbocation from both sides leading to a racemate



Major product s 90%

If the alkene is unsymmetrical, addition of hydrogen bromide can lead to isomeric products.



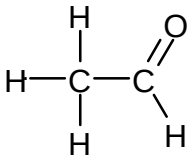


Minor product 10%

Compounds with C=O group

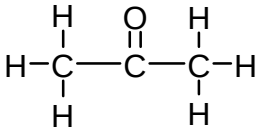
15B Carbonyls: Aldehydes and Ketones

Carbonyls are compounds with a C=O bond. They can be either aldehydes or ketones



If the C=O is on the end of the chain with an H attached it is an aldehyde.
The name will end in **–al**

CH_3CHO ethan**al**

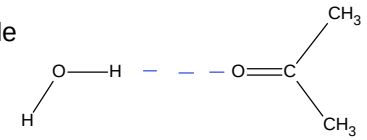


If the C=O is in the middle of the chain it is a ketone
The name will end in **-one**

CH_3COCH_3 propan**one**

Solubility in water

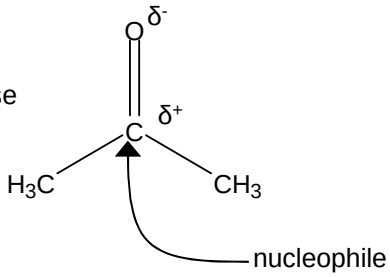
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



Pure carbonyls cannot hydrogen bond, but bond instead by permanent dipole bonding.

Reactions of carbonyls

The C=O bond is polarised because O is more electronegative than carbon. The positive carbon atom attracts nucleophiles.



In comparison to the C=C bond in alkenes, the C=O is stronger and does not undergo addition reactions easily.

This is in contrast to the electrophiles that are attracted to the C=C .

Oxidation Reactions

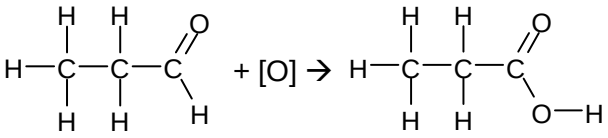
Potassium dichromate $K_2Cr_2O_7$ is an oxidising agent that causes alcohols and aldehydes to oxidise.

Primary alcohol → aldehydes → carboxylic acid
Secondary alcohol → ketones
Tertiary alcohols do not oxidise

Key point: Aldehydes can be oxidised to carboxylic acids, but ketones cannot be oxidised.

Oxidation of Aldehydes

Reaction: aldehyde → carboxylic acid
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: heat under reflux



$RCHO + [O] \rightarrow RCO_2H$

Full Equation for oxidation

$3CH_3CHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3\,CH_3CO_2H + 4H_2O + 2Cr^{3+}$

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

Aldehydes can also be oxidised using Fehling's solution or Tollen's reagent. These are used as tests for the presence of aldehyde groups

Tollen's reagent

Reagent: Tollen's reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[Ag(NH_3)_2]^+$.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.

$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$

Fehling's solution

Reagent: Fehling's solution containing blue Cu^{2+} ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide . .

Observation: Aldehydes : Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O. **Ketones do not react.**

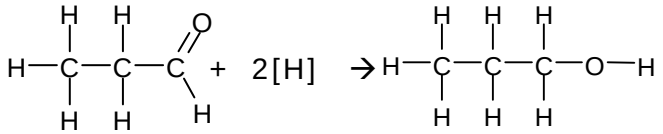
$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$

Reduction of carbonyls

Reagents: $LiAlH_4$ in dry ether
Conditions: Room temperature and pressure
Type of reaction: Reduction
Role of reagent: Reducing agent

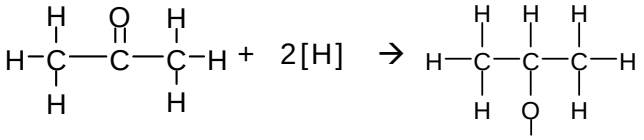
Reducing agents such as $NaBH_4$ (sodium tetrahydridoborate) or $LiAlH_4$ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

Aldehydes will be reduced to primary alcohols



propanal → Propan-1-ol

Ketones will be reduced to secondary alcohols.

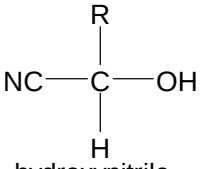


propanone → Propan-2-ol

Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

Reaction: carbonyl → hydroxynitrile
Reagent: HCN in presence of KCN
Conditions: Room temperature and pressure
Mechanism: nucleophilic addition

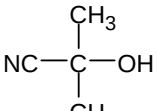
When naming hydroxy nitriles the CN becomes part of the main chain



hydroxynitrile

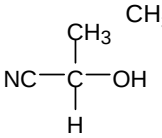
$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$

2-hydroxy-2-methylpropanenitrile



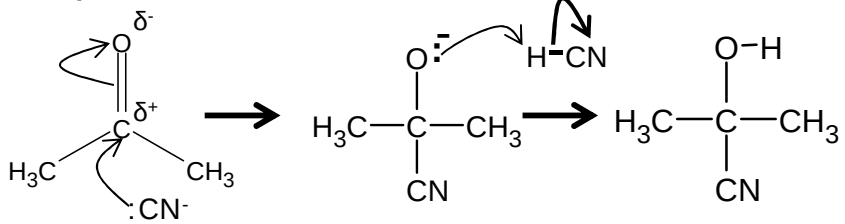
$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

2-hydroxypropanenitrile



The extra KCN increases the concentration of the CN^- ion nucleophile needed for the first step of the mechanism

Nucleophilic Addition Mechanism

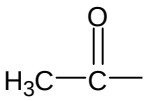


Reaction of carbonyls with iodine in presence of alkali

Reagents: Iodine and sodium hydroxide
Conditions: warm very gently

The product CHI_3 is a yellow crystalline precipitate with an antiseptic smell.

Only carbonyls with a methyl group next to the C=O bond will do this reaction. Ethanal is the only aldehyde that reacts. More commonly is methyl ketones.



This reaction is called the Iodoform test.

$CH_3COCH_3 + \mathbf{3}I_2 + \mathbf{4}NaOH \rightarrow CHI_3 + CH_3COONa + \mathbf{3}NaI + \mathbf{3}H_2O$

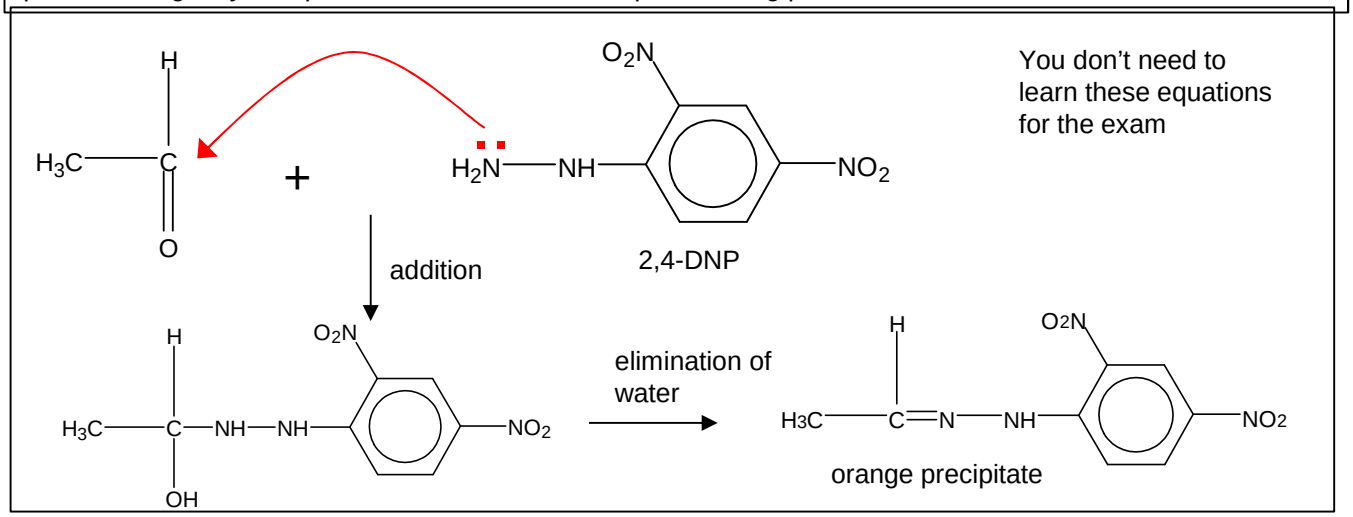
$CH_3COCH_2CH_3 + \mathbf{3}I_2 + \mathbf{4}NaOH \rightarrow CHI_3 + CH_3CH_2COONa + \mathbf{3}NaI + \mathbf{3}H_2O$

Reaction with 2,4-dinitro phenylhydrazine

2,4-DNP reacts with both aldehydes and ketones. The product is an orange precipitate, It can be used as a test for a carbonyl group in a compound.

Use 2,4-DNP to identify if the compound is a carbonyl. Then to differentiate an aldehyde from a ketone use Tollen's reagent.

The melting point of the crystal formed can be used to help identify which carbonyl was used. Take the melting point of orange crystals product from 2,4-DNP. Compare melting point with known values in database



You don't need to learn these equations for the exam

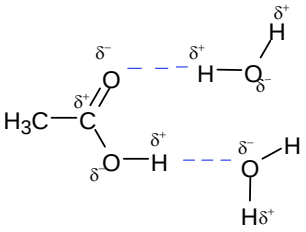
15C Carboxylic Acids

Acidity
The carboxylic acid are only weak acids in water and only slightly dissociate, but they are strong enough to displace carbon dioxide from carbonates.

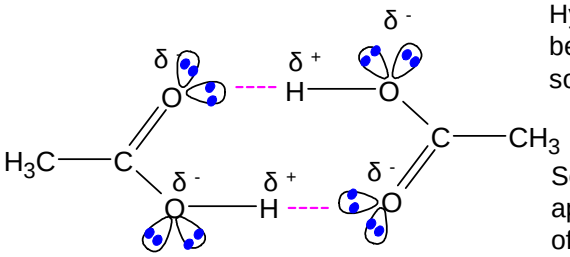
$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$

Solubility in Water

The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.



Hydrogen bonding in solid ethanoic acid

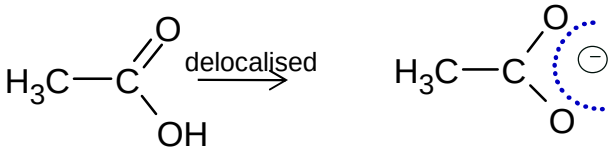


Hydrogen bonding between dimer in solid ethanoic acid

Solid ethanoic appears to have Mr of 120

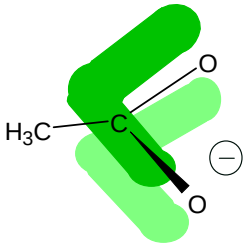
Delocalisation

The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.

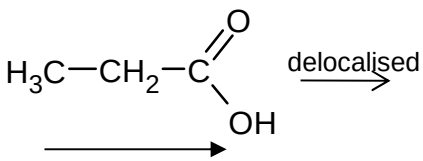


The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.

The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form.



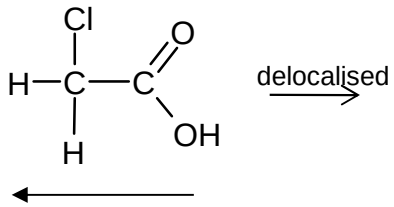
Strength of carboxylic acids



Alkyl groups electron releasing

Increasing chain length pushes electron density on to the COO^- ion, making it more negative and less stable. This make the acid less strong.

Propanoic acid less acidic than ethanoic acid



Chlorine electron withdrawing

Electronegative chlorine atoms withdraw electron density from the COO^- ion, making it less negative and more stable. This make the acid more strong.

chloroethanoic acid more acidic than ethanoic acid

HO_2C- group electron withdrawing

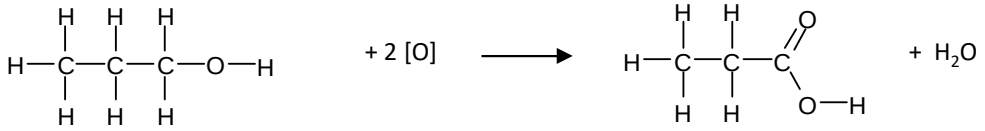
In a dibasic acid the second HO_2C- group withdraws electron density from the COO^- ion, making it less negative and more stable and weakens the O-H bond. This make the acid more strong.

Methods of preparing carboxylic acids

Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)

Observation: the orange dichromate ion ($Cr_2O_7^{2-}$) reduces to the green Cr^{3+} ion

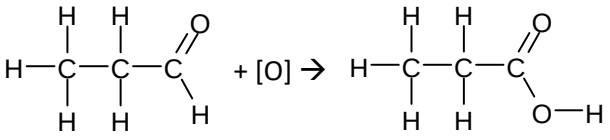


$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$

propan-1-ol **Propanoic acid**

Oxidation of Aldehydes

Reaction: aldehyde → carboxylic acid
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: heat under reflux



RCHO + [O] → RCOOH

Full equation for oxidation

$3CH_3CHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3\ CH_3COOH + 4H_2O + 2Cr^{3+}$

Hydrolysis of Nitriles

Reaction: Nitrile → carboxylic acid
Reagent: dilute hydrochloric/ sulfuric acid.
Conditions: heat under reflux

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

The Reactions of Carboxylic Acids

Reduction of carboxylic acids to alcohols

Lithium tetrahydridoaluminate **(**$LiAlH_4$) is a strong reducing agent

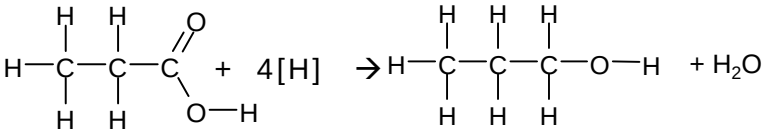
Reagents: $LiAlH_4$ in dry ether

Conditions: Room temperature and pressure

Type of reaction: Reduction

Role of reagent: Reducing agent

Carboxylic acids will be reduced to primary alcohols



Propanoic acid — Propan-1-ol

Salt formation reactions of carboxylic acids

Carboxylic acids can form salts with metals, alkalis and carbonates.

acid + metal (Na) → salt + hydrogen

$2CH_3CO_2H + 2Na \rightarrow 2CH_3CO_2^-Na^+ + H_2$

acid + alkali (NaOH) → salt + water

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$

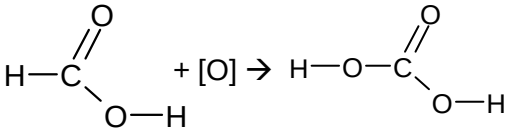
acid + carbonate (Na_2CO_3) → salt + water + CO_2

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

The effervescence caused by production of CO_2 with carboxylic acids with solid Na_2CO_3 or aqueous $NaHCO_3$ can be used as a functional group test for carboxylic acids

Oxidation of methanoic acid

Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group



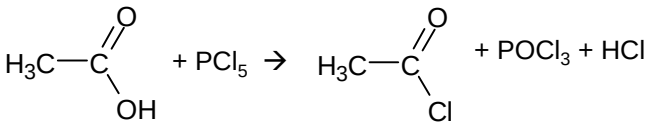
It forms carbonic acid (H_2CO_3) which can decompose to give CO_2

Reaction of carboxylic acid with phosphorous (V) chloride

Reaction: carboxylic acid → acyl chloride
Reagent: PCl_5 phosphorous(V) chloride
Conditions: room temp

This reaction with PCl_5 (phosphorous (V)chloride) is used as a test for carboxylic acids. You would observe misty fumes of HCl produced.

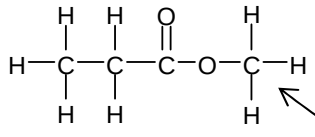
$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$



Esterification

Carboxylic acids react with alcohols, in the presence of a strong acid catalyst, to form esters and water.

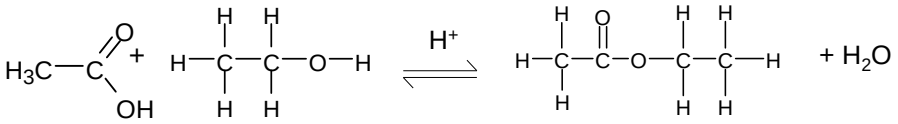
Carboxylic Acid + Alcohol $\overset{H^+}{\rightleftharpoons}$ Ester + water



Esters have two parts to their names, eg **methyl** propanoate.

The bit ending in **–anoate** comes from the carboxylic acid and includes the C in the C=O bond.

The bit ending in **–yl** comes from the alcohol that has formed it and is next to the single bonded oxygen.



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

ethanoic acid ethanol ethyl ethanoate

The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst (H_2SO_4) is needed.

Uses of Esters

Esters are sweet smelling compounds that can be used in **perfumes** and **flavourings.**

Esters can have pleasant smells

For use in perfumes they need to be non toxic, soluble in solvent such as ethanol, volatile (turns into gas easily), and not react with water.

Esters can be used as **solvents** for polar organic substances

Ethyl ethanoate is used as a solvent in glues and printing inks

Although polar, they do not form hydrogen bonds (reason: there is no hydrogen bonded to a highly electronegative atom)
thus, they have much lower b.p. than the hydrogen-bonded carboxylic acids they came from. They are also almost insoluble in water

Hydrolysis of esters

Esters can be hydrolysed and split up by either heating with acid or with sodium hydroxide.

i) with acid
reagents: dilute acid (HCl)
conditions: heat under reflux

This reaction is the reverse reaction of ester formation. When an ester is hydrolysed a carboxylic acid and an alcohol are formed.

$CH_3CH_2CO_2CH_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CH_2CO_2H + CH_3CH_2OH$

ethyl propanoate

This reaction is reversible and does not give a good yield of the products.

ii) with sodium hydroxide
reagents: dilute sodium hydroxide
conditions: heat under reflux

$CH_3CH_2CO_2CH_3 + NaOH \rightarrow CH_3CH_2CO_2^- Na^+ + CH_3OH$

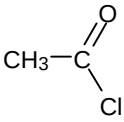
methyl propanoate sodium propanoate methanol

This reaction goes to completion.

The carboxylic acid salt product is the anion of the carboxylic acid.
The anion is resistant to attack by weak nucleophiles such as alcohols, so the reaction is not reversible.

Carboxylic acid derivatives: Acyl Chlorides

Acyl Chlorides



ethanoyl chloride

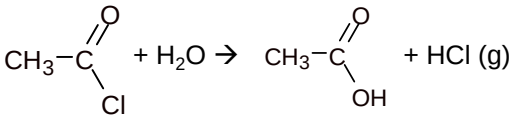
Acyl chlorides are much more reactive than carboxylic acids

The Cl group is classed as a good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides and acid anhydrides much more reactive than carboxylic acids and esters

Reaction with water

Change in functional group**: acyl chloride → carboxylic acid**
Reagent: **water**
Conditions: **room temp.**

$RCOCl\ (l) + H_2O \rightarrow RCO_2H + HCl\ (g)$

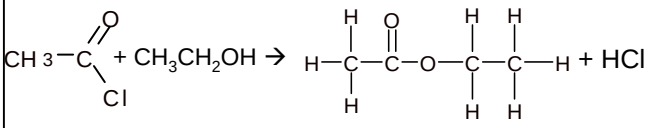


Observation: Steamy white fumes of HCl are given off

Reaction with alcohol

Change in functional group**: acyl chloride → ester**
Reagent: **alcohol**
Conditions: **room temp.**

$RCOCl\ (l) + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + HCl\ (g)$



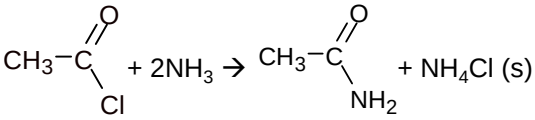
Observation: Steamy white fumes of HCl are given off

This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction

Reaction with ammonia

Change in functional group**: acyl chloride → primary amide**
Reagent: **ammonia**
Conditions: **room temp.**

$RCOCl\ (l) + 2NH_3 \rightarrow RCONH_2 + NH_4Cl\ (s)$

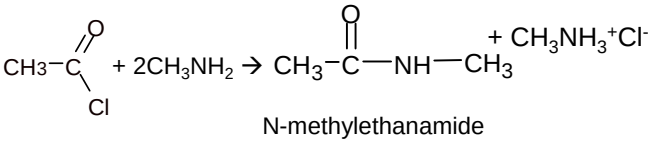


Observation: white smoke of NH_4Cl is given off

Reaction with primary amines

Change in functional group**: acyl chloride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

$RCOCl + 2CH_3NH_2 \rightarrow RCONHCH_3 + CH_3NH_3^+Cl^-$



N-methylethanamide

Polyesters

There are two **types** of **polymerisation**: **addition** and **condensation**

Condensation Polymerisation

The two most common **types** of condensation polymers are **polyesters** and **polyamides** which involve the formation of an **ester** linkage or an **amide** linkage.

In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H_2O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters uses these reactions we met earlier in the course

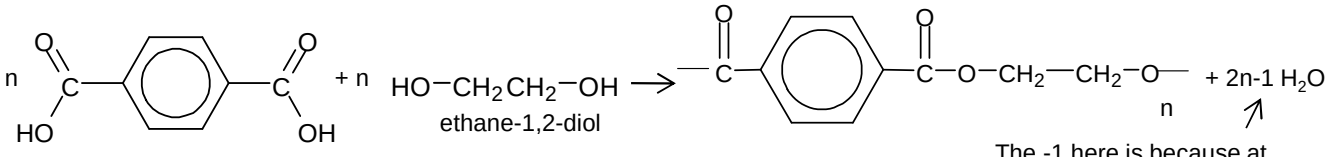
Carboxylic Acid + Alcohol → Ester + Water Acyl chloride + Alcohol → Ester + HCl

If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

dicarboxylic acid + diol → poly(ester) + water diacyl dichloride + diol → poly(ester) + HCl

Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

Terylene- a common polyester

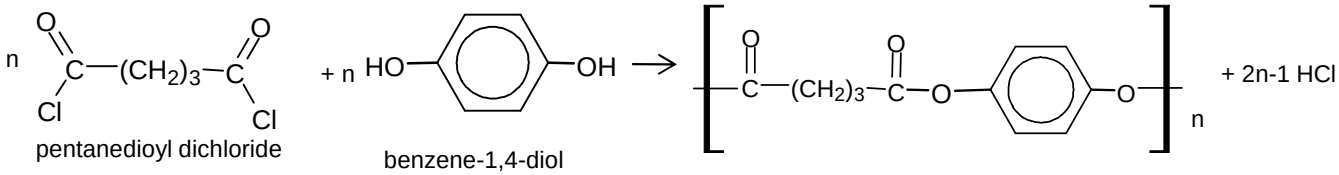


benzene-1,4-dicarboxylic acid

ethane-1,2-diol

The -1 here is because at each end of the chain the H and OH are still present

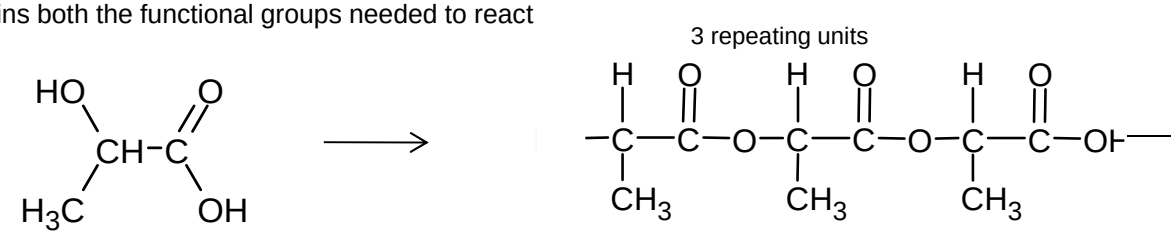
Terylene fabric is used in clothing, tire cords



pentanedioyl dichloride

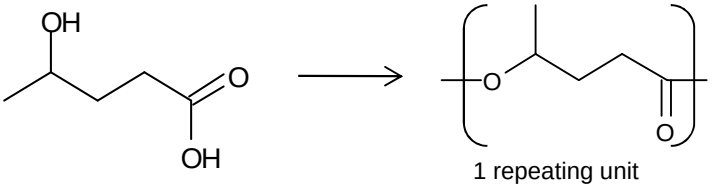
benzene-1,4-diol

It is also possible for polyamides and polyesters to form from **one** monomer, if that monomer contains both the functional groups needed to react

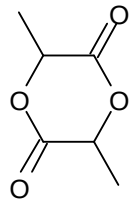


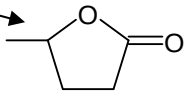
2-hydroxypropanoic acid (lactic acid)

poly(lactic acid)



4-hydroxypentanoic acid





It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer.
You do not need to learn these but may be asked to deduce structures from information given

Chemical reactivity of condensation polymers

polyesters can be broken down by **hydrolysis** and are, therefore, biodegradable

The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids

Polyesters can be hydrolysed by acid and alkali
With HCl a polyester will be hydrolysed and split up in to the original dicarboxylic acid and diol
With NaOH an polyester will be hydrolysed and split up into the diol and dicarboxylic acid salt.

15E. Spectroscopy and chromatography

The effect of different types of radiation on molecules
i **infrared in analysis** – infra red energy causes bonds to vibrate. This can be used to identify the types of bond in a molecule
ii **microwaves for heating-** certain molecules absorb the microwaves causing them to rotate
iii **radio waves in NMR** – can cause the hydrogen nucleus to **change its spin state.** This can give us information about the arrangements of hydrogens in a molecule.
iv **ultraviolet in initiation of reactions** – UV energy can break bonds such as the Cl-Cl bond or C-Cl bond

NMR spectroscopy

NMR spectroscopy involves interaction of materials with the low-energy radiowave region of the electromagnetic spectrum

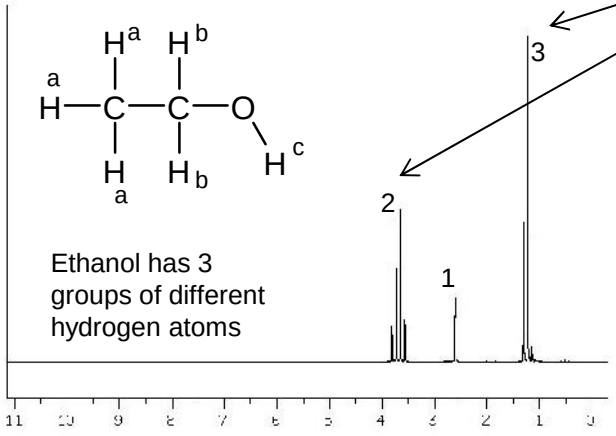
NMR spectroscopy is the same technology as that used in 'magnetic resonance imaging' (MRI) to obtain diagnostic information about internal structures in body scanners e.g. scanning for brain disorders

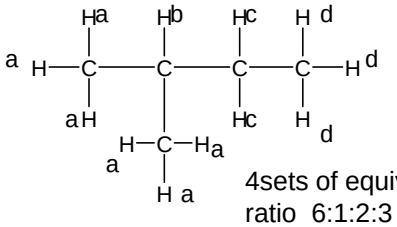
The radio waves used in proton NMR cause the hydrogen nucleus to **change its spin state.**

Equivalent Hydrogen atoms.

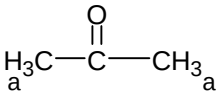
In an H NMR spectrum, there is one signal for each set of equivalent H atoms.

In addition the **intensity (integration value)** of each signal is proportional to the **number of equivalent H atoms** it represents.

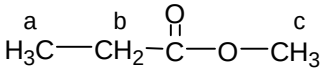




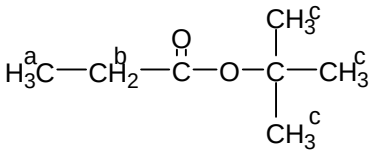
4sets of equivalent H's: ratio 6:1:2:3



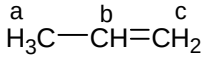
1 signal



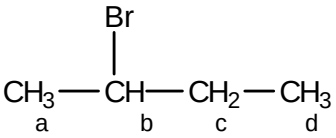
3 sets of equivalent H's: ratio 3:2:3



3 sets of equivalent H's: ratio 3:2:9



3 sets of equivalent H's: ratio 3:1:2



4 sets of equivalent H's: ratio 3:1:2:3

Solvents

Samples are dissolved in solvents without any ^1H atoms, e.g. CCl_4, $CDCl_3$.

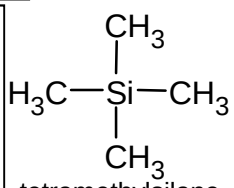
This means that in the H NMR the solvent will not give any peaks

CCl_4 is a non-polar compound that is a good solvent for non-polar organic molecules
$CDCl_3$ is a polar covalent molecule that is a good solvent for polar organic molecules

Calibration and shift

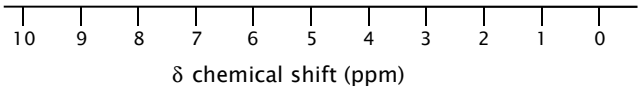
A small amount of TMS (tetramethylsilane) is added to the sample to calibrate the spectrum

TMS is used because:
- it only gives **one signal**
- its signal is **away from all the other H signals**
- gives strong signal so only a small amount needed
- it is non-toxic
- it is inert
- it has a **low boiling point** and so **can be removed from sample easily**



tetramethylsilane

The spectra are recorded on a scale known as the chemical shift (δ), which is how much the field has shifted away from the field for TMS..



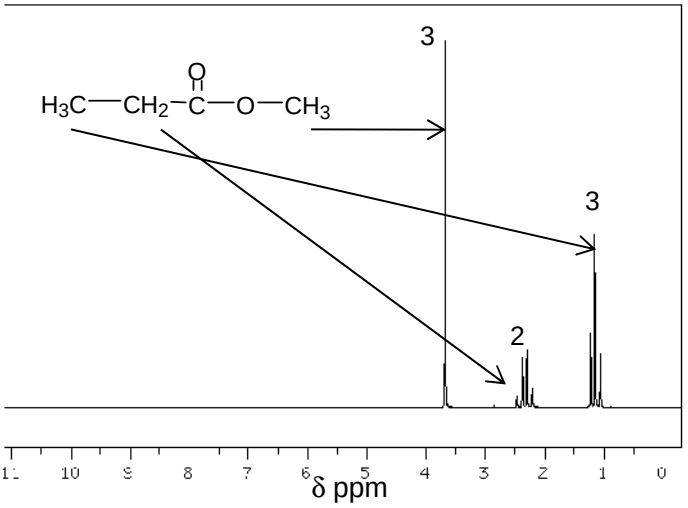
The δ is a measure in parts per million (ppm) is a relative scale of how far the frequency of the proton signal has shifted away from that for TMS.

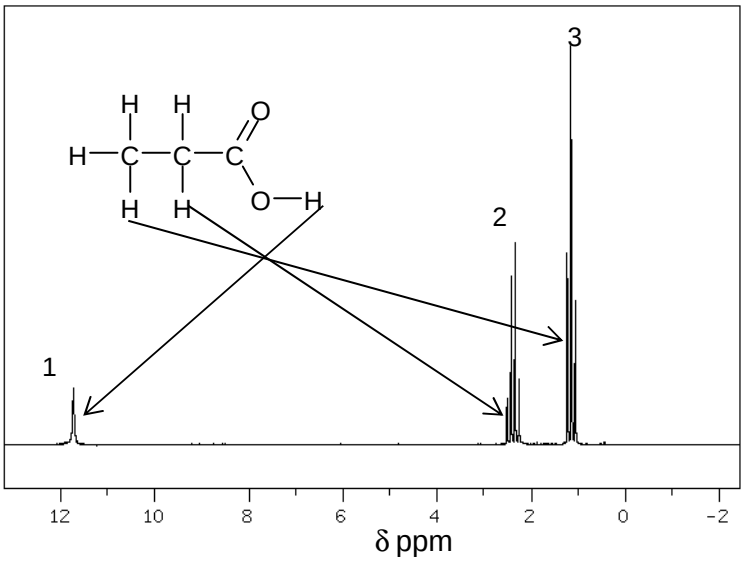
H NMR shift

The δ depends on what other atoms/groups are near the H – more electronegative groups gives a greater shift.

^{1}H n.m.r. chemical shift data

Type of proton	δ/ppm
ROH	0.5–5.0
RCH_3	0.7–1.2
RNH_2	1.0–4.5
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
R–C(=O)–C(H)–	2.1–2.6
R–O–C(H)–	3.1–3.9
RCH_2Cl or Br	3.1–4.2
R–C(=O)–O–C(H)–	3.7–4.1
R(H)C=C(H)	4.5–6.0
R–C(=O)–H	9.0–10.0
R–C(=O)–O–H	10.0–12.0



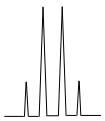
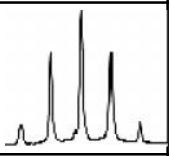


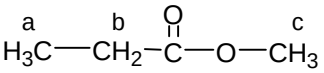
Spin-Spin coupling in H NMR

In high resolution H NMR each signal in the spectrum can be split into further lines due to inequivalent H's on neighbouring C atoms.

Nuclei in identical chemical environments do not show coupling amongst themselves!

Splitting of peak = number of inequivalent H's on neighbouring C atoms + 1

signal	singlet	doublet	triplet	quartet	quintet
appearance					
Split number of peaks	1	2	3	4	5
number of neighbouring inequivalent H atoms	0	1	2	3	4
relative size		1:1	1:2:1	1:3:3:1	1:4:6:4:1

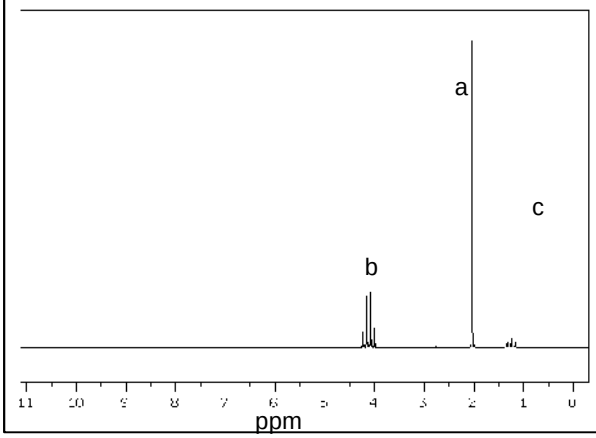


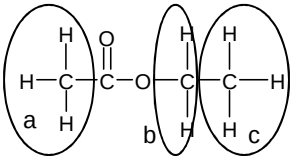
The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

The peak due to group **b** will be a **quartet** as it is next to **a** (a carbon with 3H's)

The peak due to group **c** will be a **singlet** as it is next to a carbon with no H's)

For 6 split peaks use the term hextet or multiplet





The peak due to group **a** will be a **singlet** as it is next to a carbon with 0 H's
Shift 2.1-2.6
Integration trace 3

The peak due to group **b** will be a **quartet** as it is next to a carbon with 3 H's
Shift 3.7 -4.1
Integration trace 2

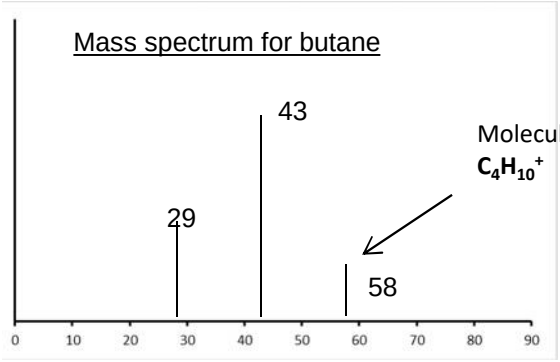
The peak due to group **c** will be a **triplet** as it is next to a carbon with 2 H's
Shift 0.7-1.2
Integration trace 3

Mass spectrometry

Measuring the M_r of an organic molecule

If a molecule is put through a mass spectrometer it will often break up and give a series of peaks caused by the fragments. The peak with the largest m/z, however, will be due to the complete molecule and will be equal to the M_r of the molecule. This peak is called the parent ion or **molecular ion**

Spectra for C_4H_{10}



Fragmentation

When organic molecules are passed through a mass spectrometer, it detects both the whole molecule and fragments of the molecule.

Molecular ion formed: $M \rightarrow [M]^{+\cdot} + e^-$

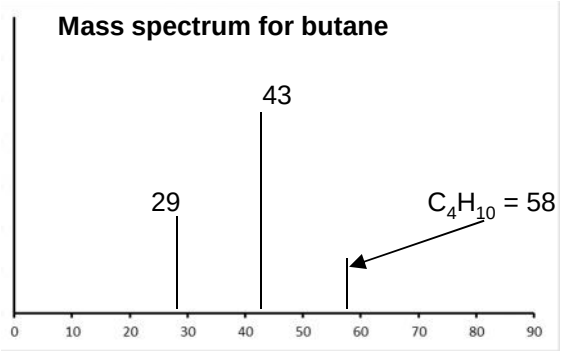
The molecule loses an electron and becomes both an ion and a free radical

Several peaks in the mass spectrum occur due to fragmentation.
The molecular ion fragments due to covalent bonds breaking: $[M]^{+\cdot} \rightarrow X^+ + Y\cdot$

This process produces an ion and a free radical. The ion is responsible for the peak

Relatively stable ions such as carbocations R^+ such as $CH_3CH_2^+$ and acylium ions $[R\text{-}C{=}O]^+$ are common. The more stable the ion, the greater the peak intensity.

The peak with the highest mass/charge ratio will be normally due to the original molecule that hasn't fragmented (called the molecular ion) . As the charge of the ion is +1 the mass/ charge ratio is equal to *M*r.



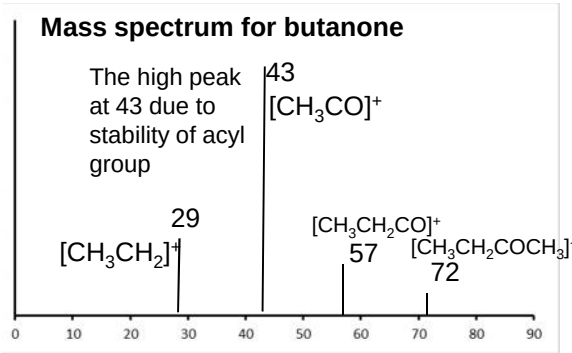
Equation for formation molecular ion

$C_4H_{10} \rightarrow [C_4H_{10}]^{+\cdot} + e^-$ m/z 58

Equations for formation of fragment ions from molecular ions

$[C_4H_{10}]^{+\cdot} \rightarrow [CH_3CH_2CH_2]^+ + \cdot CH_3$ m/z 43

$[C_4H_{10}]^{+\cdot} \rightarrow [CH_3CH_2]^+ + \cdot CH_2CH_3$ m/z 29



Equation for formation molecular ion

$CH_3CH_2COCH_3 \rightarrow [CH_3CH_2COCH_3]^{+\cdot} + e^-$ m/z 72

Equations for formation of fragment ions from molecular ions

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CH_2CO]^+ + \cdot CH_3$ m/z 57

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CO]^+ + \cdot CH_2CH_3$ m/z 43

$[CH_3CH_2COCH_3]^{+\cdot} \rightarrow [CH_3CH_2]^+ + \cdot COCH_3$ m/z 29

Chromatography

Chromatography is an analytical technique that separates components in a mixture between a mobile phase and a stationary phase.

The mobile phase may be a liquid or a gas. The stationary phase may be a solid (as in thin-layer chromatography, TLC) or either a liquid or solid on a solid support (as in gas chromatography, GC)

Separation by column chromatography depends on the balance between solubility in the moving phase and retention in the stationary phase.

If the stationary phase was polar and the moving phase was non- polar e.g. Hexane. Then non-polar compounds would pass through the column more quickly than polar compounds as they would have a greater solubility in the non-polar moving phase.
(Think about intermolecular forces)

A solid stationary phase separates by adsorption,
A liquid stationary phase separates by relative solubility

HPLC stands for high performance liquid chromatography.
HPLC: **stationary** phase is a **solid** silica
HPLC: **mobile** phase a **liquid**

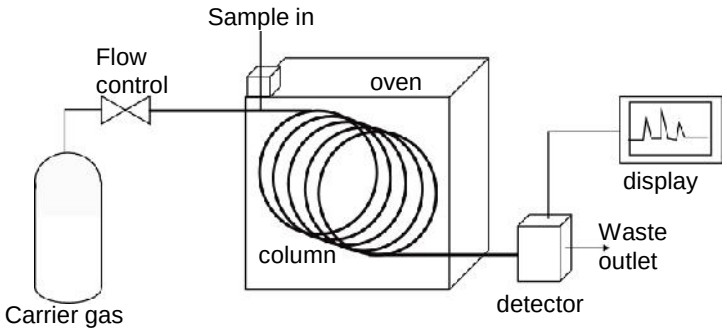
In gas-liquid chromatography GC the **mobile** phase is a inert **gas** such as nitrogen, helium, argon.
The **Stationary** phase is a **liquid** on an inert solid.

Gas-Liquid Chromatography

Gas-liquid chromatography can be used to separate mixtures of volatile liquids.

In gas-liquid chromatography, the mobile phase is a gas such as helium and the stationary phase is a high boiling point liquid absorbed onto a solid.

The time taken for a particular compound to travel from the injection of the sample to where it leaves the column to the detector is known as its **retention time.** This can be used to identify a substance.



Some compounds have similar retention times so will not be distinguished.

Basic gas-liquid chromatography will tell us how many components there are in the mixture by the number of peaks. It will also tell us the abundance of each substance. The area under each peak will be proportional to the abundance of that component.

It is also possible for gas-liquid chromatography machine to be connected to a mass spectrometer, IR or NMR machine, enabling all the components in a mixture to be identified.

Most commonly a mass spectrometer is combined with GC to generate a mass spectra which can be analysed or compared with a spectral database by computer for positive identification of each component in the mixture.

GC-MS is used in analysis, in forensics, environmental analysis, airport security and space probes.

TLC Chromatography (thin-layer chromatography)

A mixture can be separated by chromatography and identified from the amount they have moved. (Can be used with mixtures of amino acids)

Method: **Thin-layer chromatography**

a) **Wearing gloves**, draw a **pencil line** 1 cm above the bottom of a TLC plate and mark spots for each sample, equally spaced along line.
b) Use a capillary tube to add a **tiny drop** of each solution to a different spot and allow the plate to air dry.
c) Add solvent to a chamber or large beaker with a lid so that is no more than **1cm in depth**
d) Place the TLC plate into the chamber, **making sure that the level of the solvent is below the pencil line**. Replace the **lid to get a tight** seal.
e) When the level of the solvent **reaches about 1 cm from the top of the plate**, remove the plate and mark the solvent level with a pencil. Allow the plate to **dry in the fume cupboard.**
f) Place the plate under a **UV lamp** in order to see the spots. Draw around them lightly in pencil.
g) Calculate the Rf values of the observed spots.

Wear plastic gloves to prevent contamination from the hands to the plate

pencil line –will not dissolve in the solvent

tiny drop – too big a drop will cause different spots to merge

Depth of solvent– if the solvent is too deep it will dissolve the sample spots from the plate

lid– to prevent evaporation of toxic solvent

Will get more accurate results if the solvent is allowed to rise to near the top of the plate but the Rf value can be calculated if the solvent front does not reach the top of the plate

dry in **a fume** cupboard as the solvent is toxic

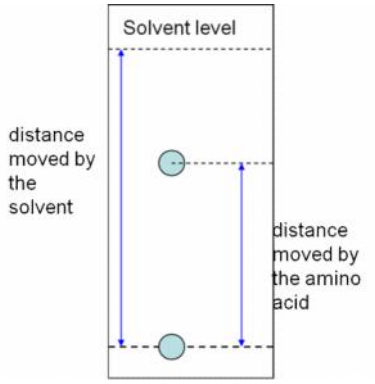
UV lamp used if the spots are colourless and not visible

If using amino acids then ninhydrin spray can be used instead of UV lamp to locate the spots

R_f value = $\frac{\text{distance moved by amino acid}}{\text{distance moved by the solvent}}$

Each substance has its own R_f value

Measure how far each spot travels relative to the solvent front and calculate the Rf value.
Compare Rf values to those for known substances.



Some substances won't separate because similar compounds have similar Rf values. So some spots may contain more than one compound

Bringing it all together

1. Work out empirical formula

Elemental analysis C 66.63% H 11.18% O 22.19%

C	H	O
66.63/12	11.18/1	22.19/16
=5.5525	=11.18	=1.386875
=4	=8	=1

2. Using molecular ion peak m/z value from mass spectrum calculate molecular formula

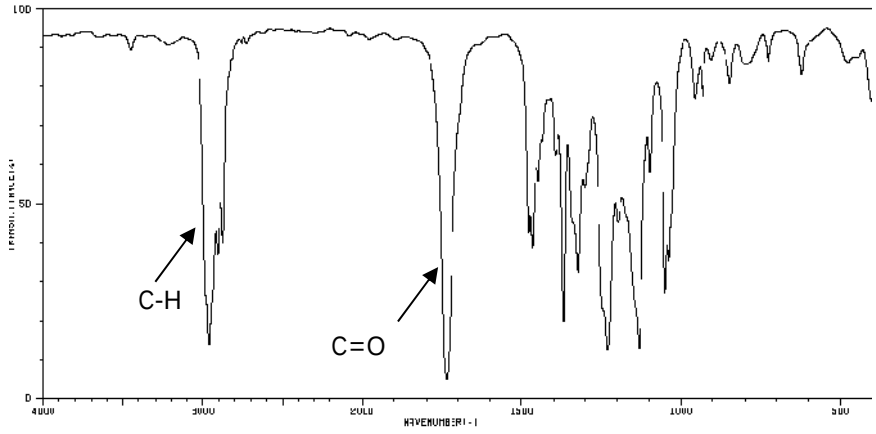
molecular ion peak m/z value= 144

*M*r empirical formula C_4H_8O = 72

If *M*r molecular formula 144 then compound is $C_8H_{16}O_2$

3. Use IR spectra to identify main bonds/functional group

$C_8H_{16}O_2$ could be an ester, carboxylic acid or combination of alcohol and carbonyl. Look for IR spectra for C=O and O-H bonds

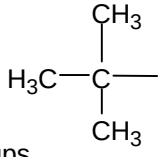


There is a C=O but no O-H absorptions, so must be an ester.

4. Use NMR spectra to give details of carbon chain

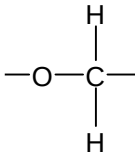
4 peaks – only 4 different environments.

singlet of area 9
At δ =0.9
Means 3 CH_3 groups



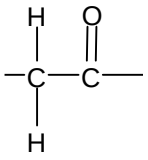
Peak at δ 4 shows H–C–O

Area 2 suggests CH_2
Quartet means next to a CH_3



Peak at δ 2.2 shows H–C=O

Area 2 suggests CH_2
Singlet means adjacent to C with no hydrogens



Peak at δ 1.2 shows R-CH_3
Area 3 means CH_3
Triplet means next to a CH_2

Put all together to give final structure