

A Level Chemistry OCR

YOUR NOTES



6. Organic Chemistry & Analysis (A Level Only)

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6.1 Benzene & Aromatic Compounds

6.1.1 Benzene

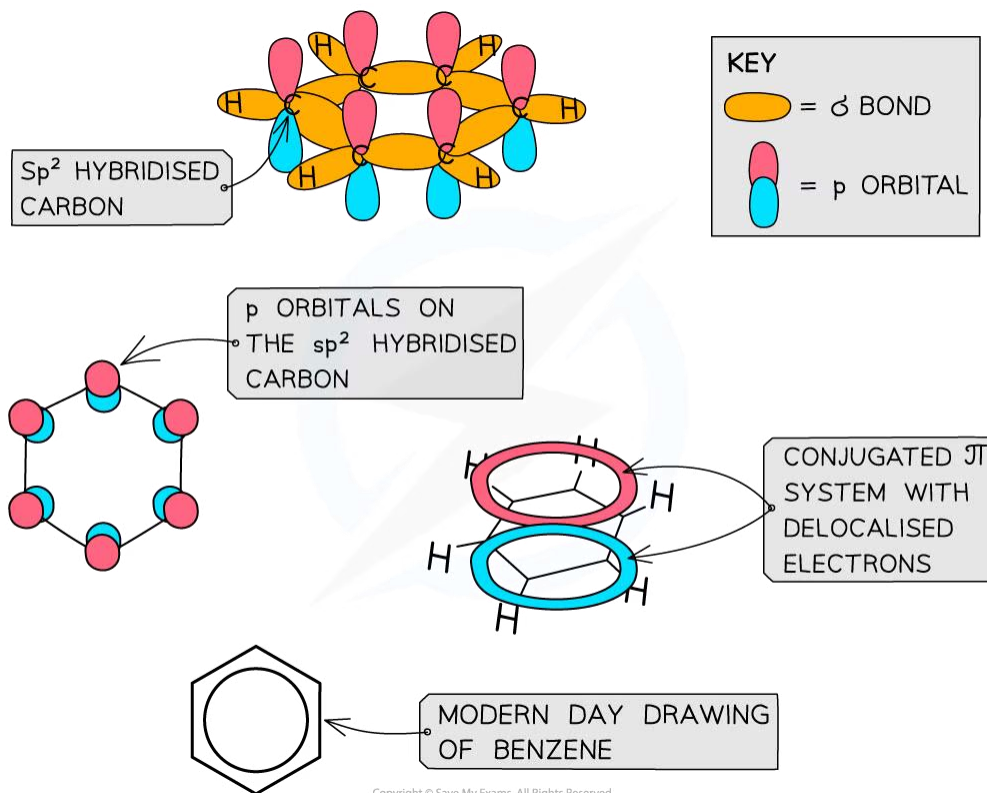
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Comparing Models of Benzene

Structure of Benzene

- The structure of benzene was determined many years ago, by a chemist called Kekule
- The structure consists of 6 carbon atoms in a hexagonal ring, with alternating single and double carbon-carbon bonds
 - This suggests that benzene should react in the same way that an unsaturated alkene does
 - However, this is not the case



Like other aromatic compounds, benzene has a planar structure due to the sp^2 hybridisation of carbon atoms and the conjugated π system in the ring

- Each carbon atom in the ring forms three σ bonds using the sp^2 orbitals
- The remaining **p orbitals** overlap laterally with p orbitals of neighbouring carbon atoms to form a π system
- This extensive sideways overlap of p orbitals results in the electrons being delocalised and able to freely spread over the entire ring causing a π system
 - The π system is made up of two ring shaped clouds of electron density – one above the plane and one below it

- Benzene and other aromatic compounds are **regular** and **planar** compounds with bond angles of 120°
- The delocalisation of electrons means that all of the carbon-carbon bonds in these compounds are identical and have both **single** and **double bond** character
- The bonds all being the same length is evidence for the delocalised ring structure of benzene

Evidence for delocalisation

- This evidence of the bonding in benzene is provided by data from enthalpy changes of hydrogenation and carbon-carbon bond lengths
- Hydrogenation of cyclohexene
 - Each molecule has one C=C double bond
 - The enthalpy change for the reaction of cyclohexene is -120 kJ mol^{-1}



- Hydrogenation of benzene
 - The Kekule structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds
 - It would be expected that the enthalpy change for the hydrogenation of this structure would be three times the enthalpy change for the one C=C bond in cyclohexene



- When benzene is reacted with hydrogen, the enthalpy change obtained is actually far less exothermic, $\Delta H^\ominus = -208 \text{ kJ mol}^{-1}$

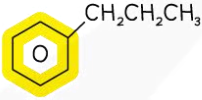
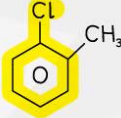
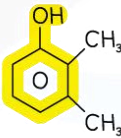
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Nomenclature of Aromatic Compounds

- In normal, everyday conversation the word 'aromatic' is used to refer to pleasant, fragrant smells
- However, in chemistry, it is used to describe molecules that contain one or more **benzene rings**, i.e. a ring with **conjugated π systems**
- **Conjugated π systems** arise from alternating double and single bonds in which the electrons are **delocalised**
- Benzene is found in many useful compounds, for example in pharmaceuticals, pesticides, polymers and dyes
 - The common painkillers aspirin, paracetamol, ibuprofen and morphine all contain benzene rings

Examples of aromatic compounds including benzene table

| Functional Group | Example | Name |
|------------------|---|-----------------------|
| Arene |  | propylbenzene |
| Chlorobenzene |  | 2-methylchlorobenzene |
| Phenol |  | 2,3-dimethyl phenol |

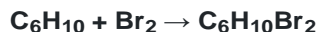
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Benzene Resistance to Halogenation

- Alkenes tend to undergo bromination easily which can be observed in cyclohexene



- As the π bond contains localised electrons, it produces an area of high electron density allowing it to repel the electron in the bromine molecule
- Therefore a dipole is introduced making one bromine atom δ^+ and one δ^- bromine atom
- The δ^+ bromine is attracted to the π bond in the cyclohexane
- This then leaves a carbocation in the intermediate molecule which the negative bromide ion is attracted to, hence forming 1,2-dibromocyclohexane by electrophilic addition
- In benzene, there are no localised areas of high electron density, preventing it from being able to polarise the bromine molecule
- In order for benzene to undergo electrophilic substitution with bromine, a halogen carrier must be present in the reaction e.g. AlBr_3

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6.1.2 Electrophilic Substitution

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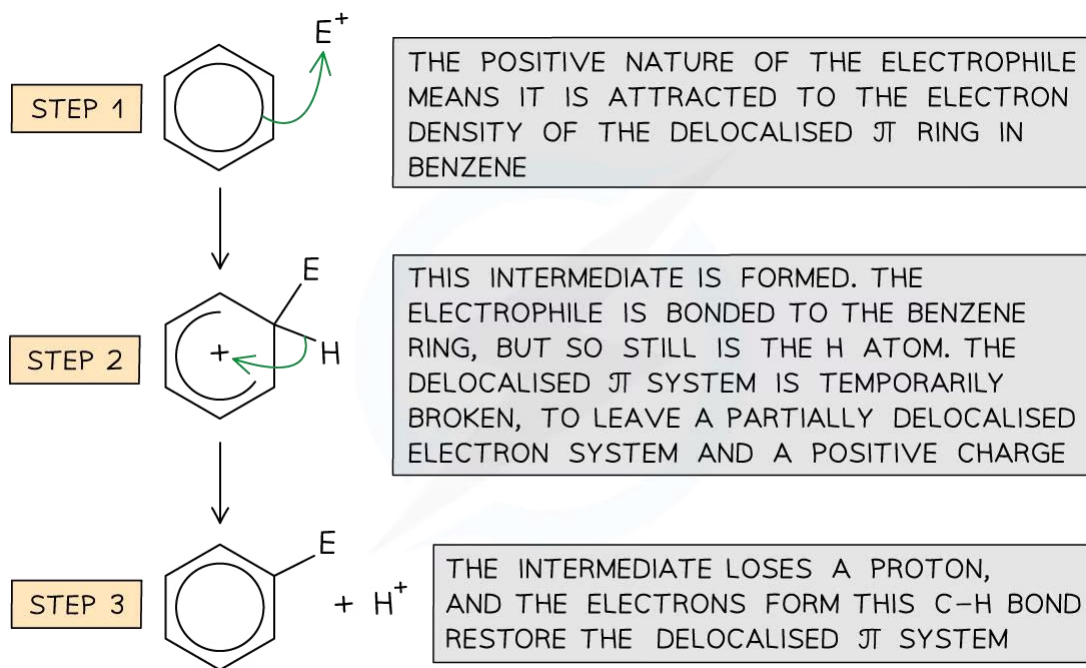


Electrophilic Substitution Reactions

Reactions of Benzene

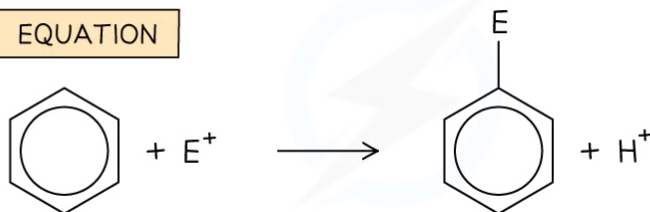
- The main reactions which benzene will undergo include the replacement of one of the 6 hydrogen atoms from the benzene ring
 - This is different to the reactions of unsaturated alkenes, which involve the double bond breaking and the electrophile atoms 'adding on' to the carbon atoms
- These reactions where at least one of the H atoms from benzene are replaced, are called electrophilic substitution reactions
 - The hydrogen atom is substituted by the electrophile
- You must be able to provide the mechanisms for specific examples of the electrophilic substitution of benzene

General Electrophilic Substitution Mechanism:



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OVERALL EQUATION



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- The delocalised π system is extremely stable and is a region of high electron density
- Electrophilic substitution reactions involve an electrophile, which is either a positive ion or the positive end of a polar molecule
- There are numerous electrophiles which can react with benzene
 - However, they usually cannot simply be added to the reaction mixture to then react with benzene
 - The electrophile has to be produced in situ, by adding appropriate reagents to the reaction mixture

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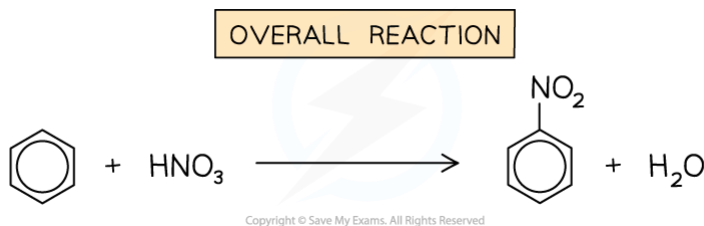


Benzene Nitration

- The **electrophilic substitution** reaction in arenes consists of **three steps**:
 - Generation of an **electrophile**
 - **Electrophilic attack**
 - Regenerating **aromaticity**

Mechanism of electrophilic substitution

- The nitration of benzene is one example of an **electrophilic substitution reaction**
 - A hydrogen atom is replaced by a nitro ($-\text{NO}_2$) group



The overall reaction of nitration of arenes

- In the **first** step, the **electrophile** is generated
 - The electrophile NO_2^+ ion is generated by reacting **concentrated** nitric acid (HNO_3) and **concentrated** sulfuric acid (H_2SO_4)
- Once the electrophile has been generated, it will carry out an **electrophilic attack** on the benzene ring
 - The nitrating mixture of HNO_3 and H_2SO_4 is **refluxed** with the arene at $25 - 60^\circ\text{C}$

Nitration of Benzene Mechanism:

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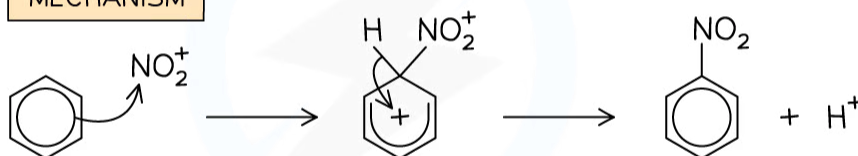


FORMATION OF ELECTROPHILE

ELECTROPHILE

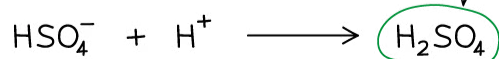


MECHANISM



REFORMING THE CATALYST

CATALYST



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Addition reactions of arenes

- The **delocalisation of electrons** (also called **aromatic stabilisation**) in arenes is the main reason why arenes predominantly undergo **substitution** reactions over **addition** reactions
- In substitution reactions,
- In addition reactions, on the other hand, the aromaticity is **not restored** and is in some cases **completely lost**
 - The **hydrogenation** of arenes is an example of an addition reaction during which the aromatic stabilisation of the arene is completely lost
 - The cyclohexane formed is **energetically less stable** than the benzene



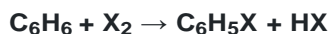
Benzene Halogenation

Halogenation

- The nature of benzene is different to other unsaturated compounds such as alkenes and halogenation via electrophilic addition is not possible
- Therefore aromatic compounds will react with halogens in the presence of a **metal halide carrier**
 - iron(III) bromide
 - aluminium chloride
- The reaction of the metal halide carrier acts as catalyst and creates the electrophile, X^+ (where X represents a halogen atom)
- At the end of the reaction it is regenerated

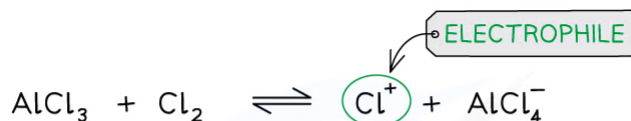


- The overall equation for halogenation is

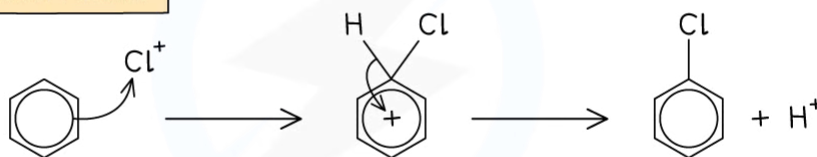


- Remember that one hydrogen atom on the benzene ring has been substituted for one halogen atom, therefore HX will be a product
- The electrophilic substitution reactions follows the same pattern as the general mechanism

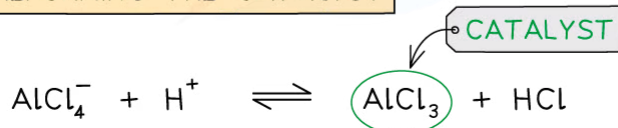
FORMATION OF ELECTROPHILE



MECHANISM



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The different stages in the chlorination of benzene

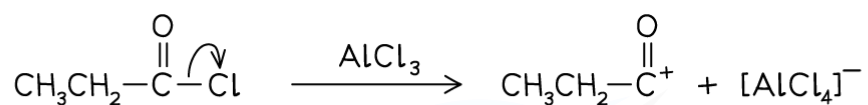
Friedel-Crafts Acylation

- In the Friedel-Crafts acylation reaction, an **acyl group** is substituted into the benzene ring



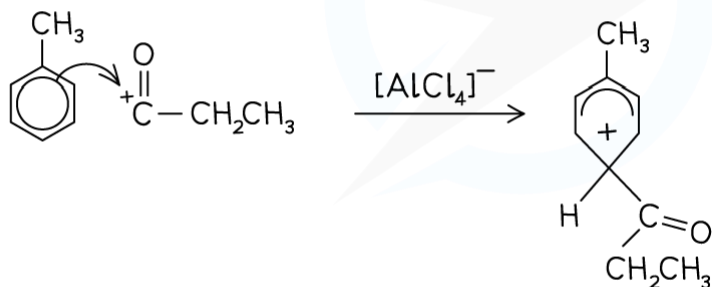
- An acyl group is an alkyl group containing a carbonyl, C=O group
- A metal halide catalyst is needed to generate the necessary alkyl electrophile
- The benzene ring is reacted with an acyl chloride in the presence of an AlCl_3 catalyst
- This complex then reacts with the benzene ring in a similar manner as we have seen before
- An example of an acylation reaction is the reaction of methylbenzene with propanoyl chloride to form an acyl benzene
 - Note that the acyl group is on the 4 position due to the $-\text{CH}_3$ group on the benzene

STEP 1: GENERATING THE ELECTROPHILE



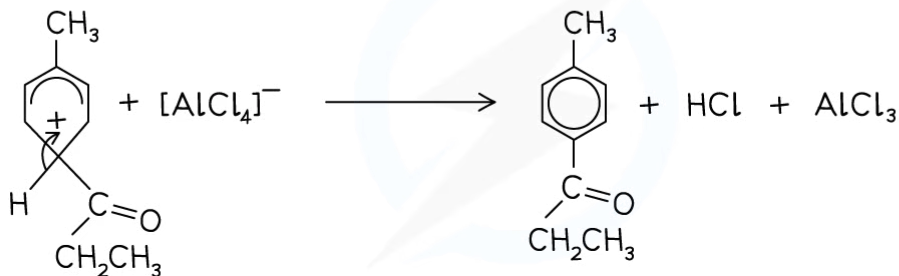
PROPANOYL CHLORIDE

STEP 2: ELECTROPHILIC ATTACK



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STEP 3: RESTORING AROMATICITY



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Example of a Friedel-Crafts acylation reaction



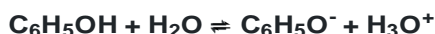
Acidity of Phenol



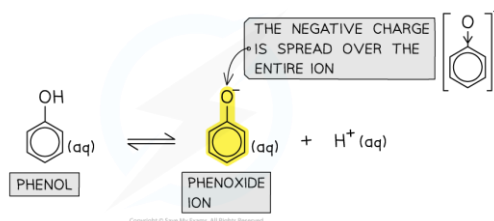
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The structure of phenol

- In phenol the OH group is directly bonded to the benzene ring
- Phenol can behave as a **very weak** acid
- Depending on the concentration, the typical pH of a solution of phenol will be 5–6
- A hydrogen ion can break away from the –OH group and transfer to a base



- Phenol is able to lose a hydrogen ion because the phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$) formed is fairly stable
- The more stable the ion is, the more likely it is to form
- One of the lone pairs of electrons on the oxygen is delocalised with the electron cloud of the whole phenoxide ion
- Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen



Delocalisation in the phenoxide ion

- Oxygen is the most electronegative element in the ion and the delocalised electrons will be drawn towards it
- That means that there will still be a lot of charge around the oxygen which will tend to attract the hydrogen ion back again
- This is why phenol behaves as just a weak acid
- This behaviour is demonstrated by the reactions of phenol with sodium hydroxide and sodium metal
- Phenols dissolve in alkaline solutions and undergo acid–base reactions with bases to form a soluble salt and water

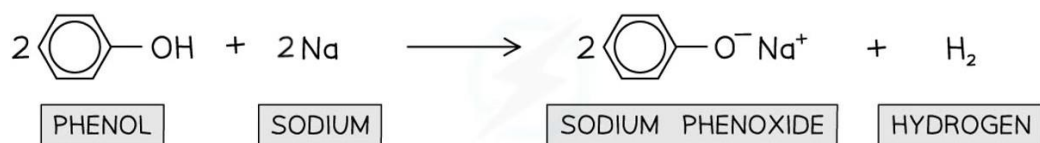


Reaction of phenol with sodium NaOH

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- Phenols react **vigorouslly** with reactive metals such as sodium (Na)
- A soluble salt is formed and hydrogen gas is given off



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Reaction of phenol with Na

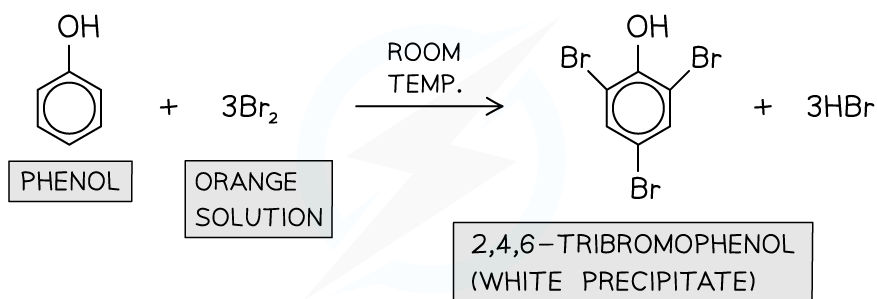
Reactions of Phenol

Reactions of the aromatic ring in phenols

- Phenols react more readily with electrophiles compared to benzene
- This is because one of the lone pairs of electrons on the oxygen atom in $-OH$ overlaps with the π bonding system
- This **increases the electron density** of the benzene ring making it more susceptible to electrophilic attack
- The $-OH$ group in phenols is activating and directs incoming electrophiles to the **2, 4, and 6 positions**

Bromination

- Phenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperature
- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol
- This is also known as the **bromination of phenol**



Phenols undergo bromination when reacted with bromine water at room temperature

Nitration

- Phenols can undergo electrophilic substitution reactions when reacted with dilute nitric acid (HNO_3) at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol
 - When concentrated HNO_3 is used, the product will be 2,4,6-trinitrophenol instead
- A hydrogen atom in the benzene ring is substituted by a nitro ($-NO_2$) group
- This is also known as the **nitration** of phenol

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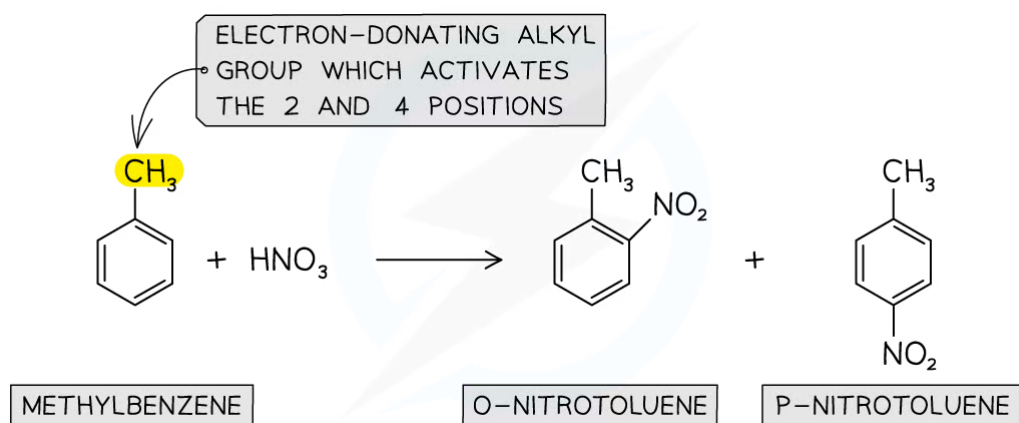


6.1.4 Directing Effects

Directing Effects in Electrophilic Substitution

Electron donating and electron withdrawing sides groups

- Side groups on a benzene ring can affect the position on the ring of substitution reactions
- Groups which are **electron donating** such as $-\text{CH}_3$, $-\text{OH}$ and $-\text{NH}_2$ will force further substitutions to occur in the **2-** and **4-** positions on the benzene ring
- Groups that are **electron withdrawing** such as $-\text{NO}_2$ will force substitution in the **3-** position
- We can use the directing effect of substitute the groups when planning an **organic synthesis**
- If a $-\text{OH}$ group, a Cl atom or an $-\text{NH}_2$ group is directly bonded to a benzene ring, the delocalisation in the ring will extend to include the lone pairs from the N, O and Cl atoms
- This changes the properties and the reactions of the side group
- Due to the **electron donating** alkyl group in methylbenzene, nitration of methylbenzene will occur on the 2 and 4 position



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Nitration of methylbenzene

Chlorobenzene

- Typical halogenoalkane and elimination reactions do not occur
- Electron rich benzene ring will repel nucleophiles

Phenol

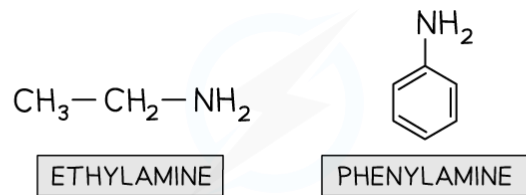
- Delocalisation makes the C–O bond stronger and the O–H bond weaker
- It is more acidic than alcohols and also will not oxidise

Phenylamine

- Phenylamine is less basic than aliphatic amines as lone pair is delocalised
- Therefore the lone pair is less available for accepting a proton

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Phenylamine is less basic than an amine such as ethylamine due to the lone pair involvement of the delocalised electron ring

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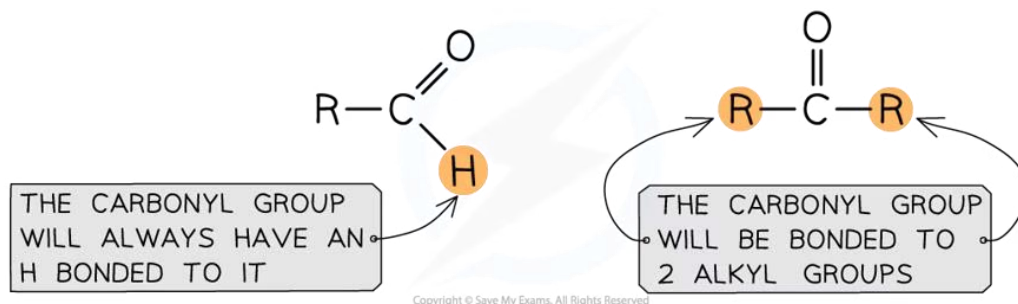


6.2 Carbonyl Compounds

6.2.1 Reactions of Carbonyl Compounds

Oxidation of Aldehydes

- Aldehydes and ketones contain the carbonyl functional group, C=O
- This is why aldehydes and ketones are also known as carbonyls
- The difference between aldehydes and ketones is the groups bonded to the carbon of the carbonyl group

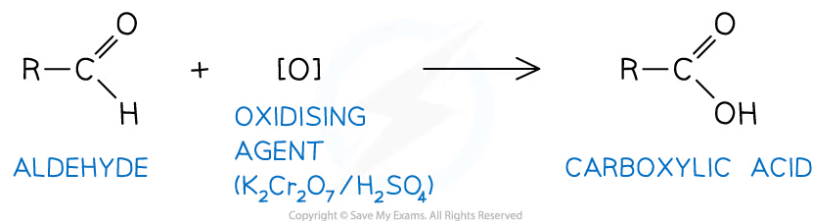


- The carbonyl group in an aldehyde is always situated at the end of the chain
 - When naming aldehydes, you do not include the '1' in the name, the carbonyl carbon is always number 1 on the chain
 - The simplest aldehyde is methanal, HCHO, with the only carbon being that of the carbonyl group
- The carbonyl group in a ketone is always situated in the middle of the chain
 - The simplest ketone is propan-2-one, CH₃COCH₃, as you need an alkyl group either side of the carbonyl carbon in a ketone
- During the oxidation of a primary alcohol to an aldehyde, the apparatus must be set up to **distill off** the aldehyde as it is produced
- Further oxidation of primary alcohols can then take place
 - Aldehydes can be easily oxidised to form carboxylic acids
- To oxidise a primary alcohol straight to a carboxylic acid, you would heat the reaction mixture under **reflux**
 - The aldehyde would still be produced, but as it evaporates it would condense and drop back into the reaction mixture, to be further oxidised to the carboxylic acid
- The oxidising agent used for **all** of the oxidation reactions be acidified potassium dichromate
 - K₂Cr₂O₇ with sulfuric acid, H₂SO₄
- Ketones are very resistant to being oxidised, so no further oxidation reaction will take place with secondary alcohols
 - This is because ketones do not have a readily available hydrogen atom, in the same way that aldehydes (or alcohols) do

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- An extremely strong oxidising agent would be needed for oxidation of a ketone to take place
- The oxidation will likely oxidise a ketone in a destructive way, breaking a C-C bond



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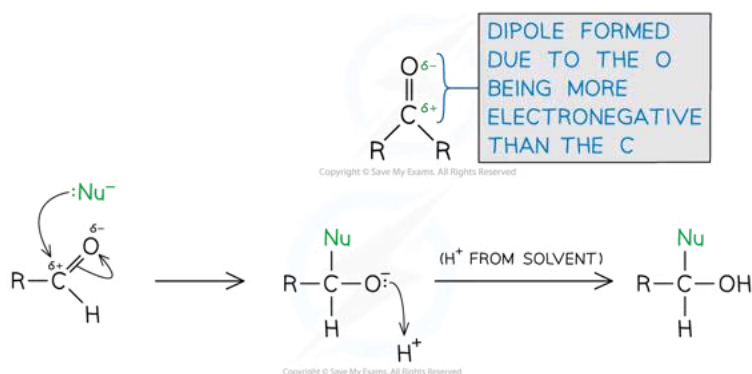




Nucleophilic Addition Reactions

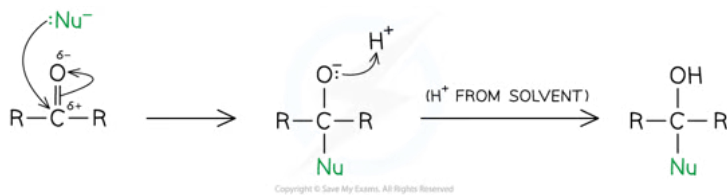
- Many of the reactions which carbonyl compounds undergo are nucleophilic addition reactions
- The carbonyl group -C=O , in aldehydes and ketones is polarised
- The oxygen atom is more electronegative than carbon drawing electron density towards itself
- This leaves the carbon atom slightly positively charged and the oxygen atom slightly negatively charged
- The carbonyl carbon is therefore susceptible to attack by a nucleophile, such as the cyanide ion

The carbonyl group here has a dipole with a delta positive carbon and a delta negative oxygen



General Mechanism with an aldehyde:

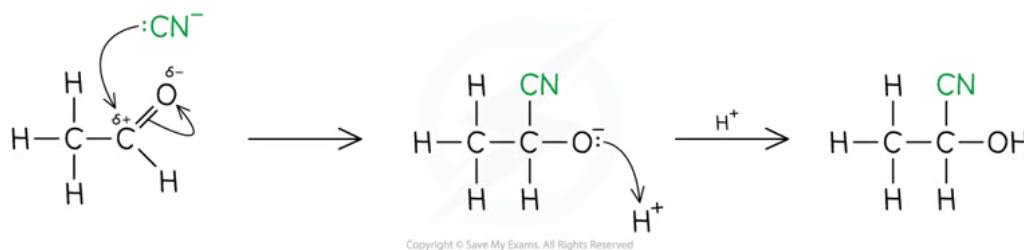
General Mechanism with a ketone:



In both reactions, the nucleophile (Nu) attacks the carbonyl carbon to form a negatively charged intermediate which quickly reacts with a proton

Addition of HCN to carbonyl compounds

The nucleophilic addition of hydrogen cyanide to carbonyl compounds is a two-step process, as shown below



- In **step 1**, the cyanide ion attacks the carbonyl carbon to form a negatively charged intermediate



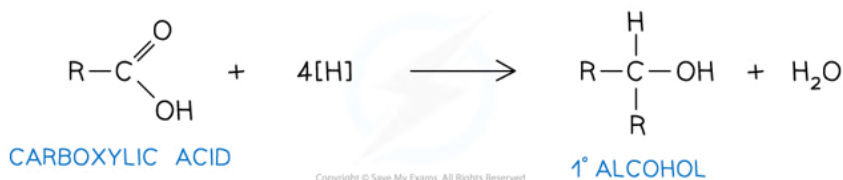
- In **step 2**, the negatively charged oxygen atom in the reactive intermediate quickly reacts with aqueous H^+ (either from HCN , water or dilute acid) to form 2-hydroxynitrile compounds,
 - e.g. 2-hydroxypropanenitrile
- This reaction is important in organic synthesis, because it adds a carbon atom to the chain, increasing the chain length
- The products of the reaction are hydroxynitriles
 - The nitrile group is the priority functional group so it is attached to carbon 1 and results in the suffix -nitrile
 - The hydroxyl group is not the priority functional group so the hydroxyl group is named using the hydroxy- prefix, rather than the -ol suffix

Reduction of Carbonyls

- There are a large number of reducing agents which will reduce both an aldehyde and a ketone to an alcohol
- Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols
- Possibly the most common reducing agent for this is sodium tetrahydridoborate, NaBH_4
 - You may also see this named as sodium borohydride in some sources
- In an aqueous solution, NaBH_4 generates the hydride ion nucleophile, $:\text{H}^-$
- The hydride ion will reduce a carbonyl group in an aldehyde or a ketone, but is not strong enough to reduce a $\text{C}=\text{C}$ double bond
 - This is because it is attracted to the C in the $\text{C}=\text{O}$ bond, but is repelled by the high electron density of the $\text{C}=\text{C}$ bond
- When this reaction takes place, it is an example of a nucleophilic addition reaction

Reduction Reactions

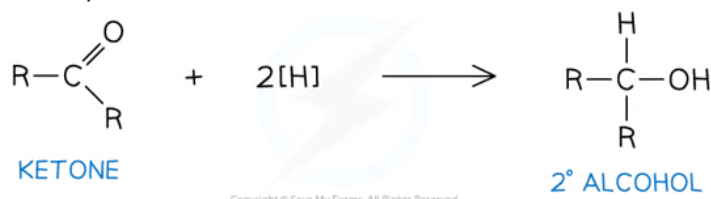
- Carboxylic acid to a primary alcohol:



- Aldehyde to a primary alcohol:



- Ketone to a secondary alcohol:





Exam Tip

In theory the reduction of a carboxylic acid is a two stage process, from the carboxylic acid to the aldehyde and then further reduction from the aldehyde to the primary alcohol. In reality however, the reaction would really go from the carboxylic acid straight to the primary alcohol. Be careful and check the wording of the question when asked about the reduction of a carboxylic acid!

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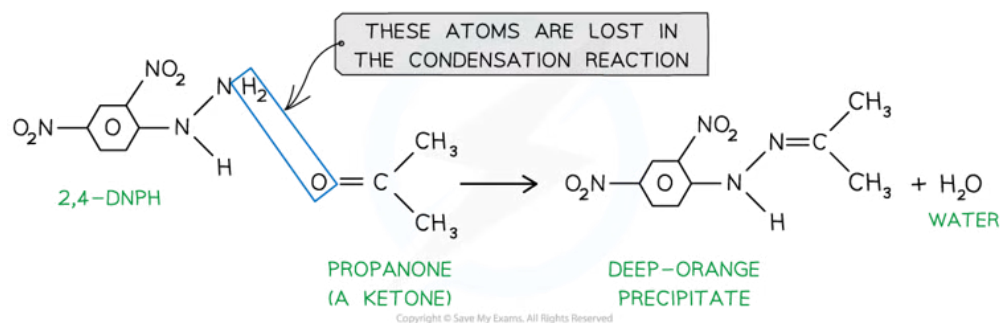
6.2.2 Testing for Carbonyl Compounds

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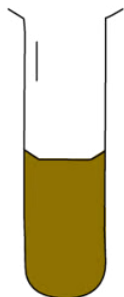


Using 2,4-Dinitrophenylhydrazine

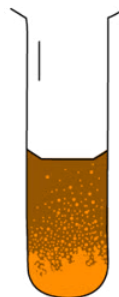
- 2,4-dinitrophenylhydrazine (also known as **2,4-DNPH**) is a reagent which detects the presence of **carbonyl compounds** (compounds with $-C=O$ group)
- The carbonyl group of **aldehydes** and **ketones** undergoes a **condensation** reaction with 2,4-dinitrophenylhydrazine
 - A condensation reaction is a reaction in which two molecules join together and a small molecule (such as H_2O or HCl) is eliminated
- The **product** formed when 2,4-DNPH is added to a solution that contains an aldehyde or ketone is a **deep-orange precipitate** which can be purified by recrystallisation
- The **melting point** of the formed precipitate can then be measured and compared to literature values to find out which specific aldehyde or ketone had reacted with 2,4-DNPH



Ketones and aldehydes react with 2,4-DNPH in a condensation reaction



NEGATIVE TEST WITH 2,4-DNPH
(UNKNOWN SUBSTANCE IS NOT
AN ALDEHYDE/KETONE)



POSITIVE TEST WITH 2,4-DNPH
(UNKNOWN SUBSTANCE IS
AN ALDEHYDE/KETONE)

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The test tube on the left shows a negative 2,4-DNPH test and the tube on the right shows a positive test



Exam Tip

The 2,4-DNPH test is especially useful as other carbonyl compounds such as carboxylic acids and esters do not give a positive result

YOUR NOTES

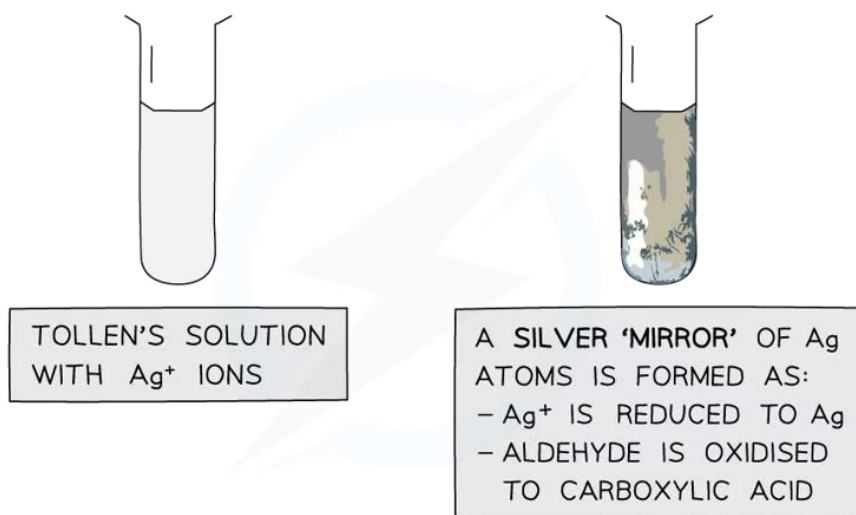


Using Tollens' Reagent

- Tollens' reagent contains the silver(I) complex ion $[\text{Ag}(\text{NH}_3)_2]^+$
- This is formed when aqueous ammonia is added to a solution of silver nitrate
 - Tollens' reagent is also known as ammoniacal silver nitrate
- If gently warmed with Tollens' reagent, an aldehyde will become oxidised
- The silver(I) complex ion solution, $[\text{Ag}(\text{NH}_3)_2]^+$, is colourless
- As the aldehyde is oxidised, it causes the $[\text{Ag}(\text{NH}_3)_2]^+$ ions to become reduced to solid metallic silver, Ag
- This is why a positive test result is called a "silver mirror"

Positive Test Result:

- When Tollens' reagent is gently warmed with an aldehyde, the silver mirror is formed
 - This is the positive test result
- When Tollens' reagent is gently warmed with a ketone, no silver mirror will be seen, as the ketone cannot be oxidised by Tollens' reagent, so no reaction takes place
 - This is a negative test result



The Ag^+ ions in Tollens' reagent are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms



Exam Tip

Use 2,4-DNP to identify if the compound is a carbonyl

Then to differentiate an aldehyde from a ketone use Tollen's reagent.

YOUR NOTES



6.3 Carboxylic Acids & Esters

6.3.1 Carboxylic Acids

Properties of Carboxylic Acids

- **Carboxylic acid** is the name given to the family of compounds that contain the **carboxyl** functional group, **-COOH**
- The general formula of a carboxylic acid is **C_nH_{2n+1}COOH** which can be shortened to just **RCOOH**
 - (In some countries, this family is also called alkanolic acid)
- The nomenclature of **carboxylic acid** follows the pattern **alkan + oic acid**, e.g. propanoic acid
- There is no need to use numbers in the name as the carboxyl group, COOH, is always on the number 1 carbon atom

Carboxylic Acids Examples Table

| Structural Formula | Name | Molecular Formula |
|---|---|--------------------------------------|
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{O}-\text{H} \end{array}$ | methanoic acid (also known as formic acid) | HCOOH |
| $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$ | ethanoic acid (also known as acetic acid) | CH ₃ COOH |
| $\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ \quad \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | propanoic acid | CH ₃ CH ₂ COOH |

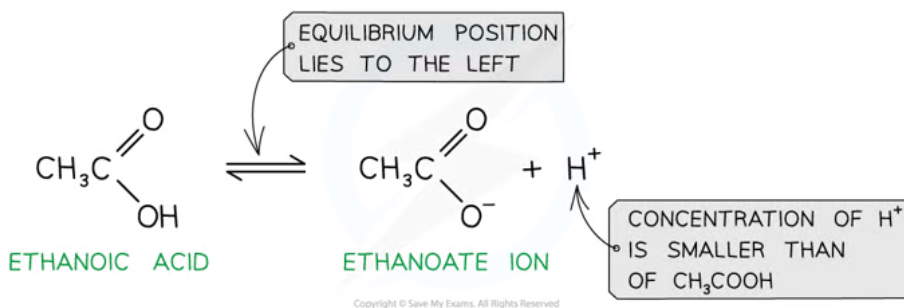
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Weak Acids

- Carboxylic acids with fewer than six carbon atoms per molecule are water-soluble
 - This is because water molecules can hydrogen-bond with the functional group
- In aqueous solution they are only slightly ionised, to give low concentrations of hydronium ions and alkanoate ions (often called carboxylate ions)

YOUR NOTES



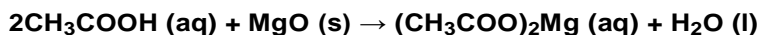


Carboxylic acids are weak acids that do not fully dissociate in water, the position of the equilibrium lies to the left

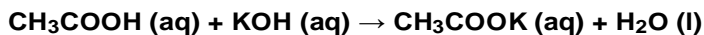
- This **partial ionisation** in solution means that carboxylic acids are **weak acids**

Reactions of Carboxylic Acids

- Carboxylic acids can form salts with metals, alkalis and carbonates.
- In the reaction with **metal oxides**, a metal salt and water are produced
 - For example in reaction with magnesium the salt magnesium ethanoate is formed:



- In the reaction with **alkalis** a salt and water are formed in a neutralisation reaction
 - For example in reaction with potassium hydroxide the salt potassium ethanoate is formed:



- In the reaction with **carbonates** a metal salt, water and carbon dioxide gas are produced
 - For example in reaction with potassium carbonate the salt potassium ethanoate is formed:



Exam Tip

The effervescence caused by the 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

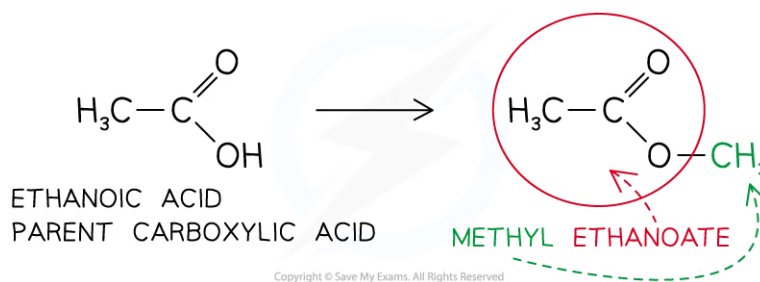
YOUR NOTES



6.3.2 Esters

Esterification of Carboxylic Acids & Acid Anhydrides

- **Esters** are a **carboxylic acid derivative** which contains the **ester group, -COO-**
- An ester is named after the parent carboxylic acid from which it is derived
- The nomenclature of esters follows the pattern:
 - Remove the **-oic acid** suffix from the parent carboxylic acid and replace with **-oate**
 - The **alkyl** chain attached to the oxygen atom of the **-COO-** group is then added as the first word in the name
 - This part of the name comes from the alcohol, e.g. propanol becomes propyl
- Ester names are confusing because the name is written backwards from the way the structure is drawn



Structure of methyl ethanoate

Esters Examples Table

YOUR NOTES



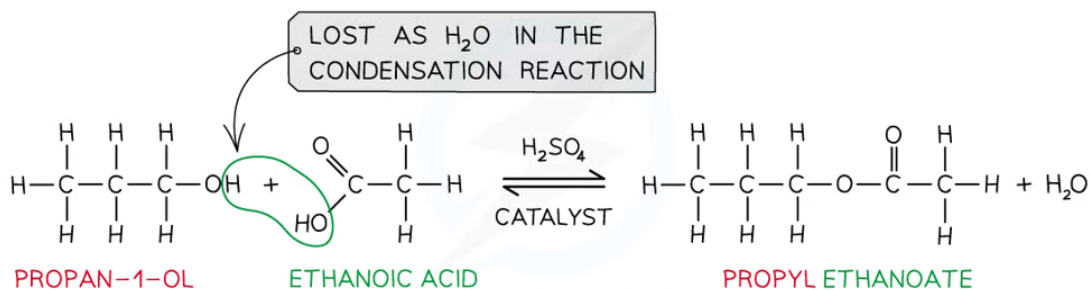


| Structural Formula | Name | Molecular Formula |
|---|-------------------|--|
| $\begin{array}{c} \text{O} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\ & & \\ & & \text{H} \end{array}$ | methyl methanoate | HCO_2CH_3 |
| $\begin{array}{c} \text{H} & \text{O} & \text{H} \\ & & \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\ & & \\ \text{H} & & \text{H} \end{array}$ | methyl ethanoate | $\text{CH}_3\text{CO}_2\text{CH}_3$ |
| $\begin{array}{c} \text{H} & \text{O} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$ | ethyl ethanoate | $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ |

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Esterification

- **Esters** are characterised by their **sweet** and **fruity** smells
- They are prepared from the **condensation** reaction between a **carboxylic acid** and **alcohol** with **concentrated H_2SO_4** as **catalyst**
 - This is also called **esterification**
- A condensation reaction involves the elimination of a small molecule **not** always water
 - Esterification is **one** example of a condensation reaction as water is eliminated from the acid and alcohol reacting together
- The reaction is reversible
- The reaction is quite slow and needs heating under reflux, (often for several hours or days).
- Low yields(50% ish) tend to be achieved by this route

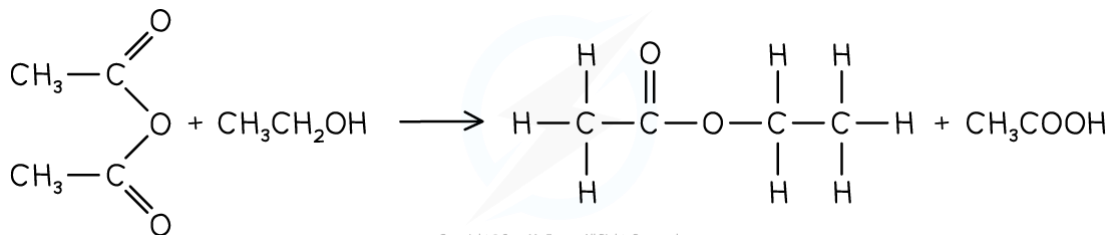


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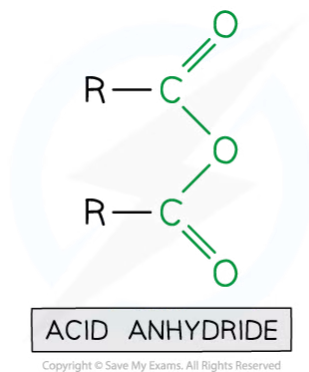
Esters are formed from the condensation reaction between carboxylic acids and alcohols

- Esterification can also take place by reacting **acid anhydrides** with **alcohols** at **room temperature**



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- Acid anhydrides are also **derivatives of carboxylic acids** formed by substitution of the $-\text{OH}$ group by an alkanoate
 - Acid anhydrides are named by identifying the parent hydrocarbon chain and adding the suffix *-oic anhydride*
 - They can also be named by removing the $-\text{oic acid}$ from the carboxylic acid and adding *-oic anhydride*



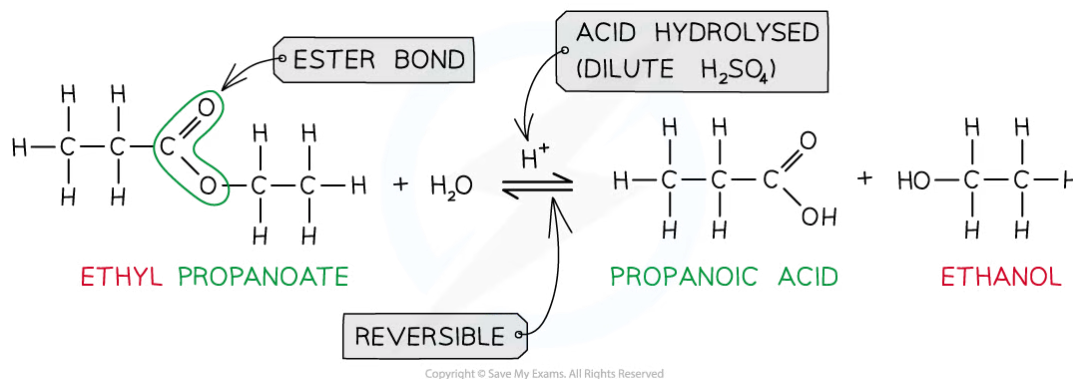
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- The acid anhydrides are more reactive than carboxylic acids
- The reaction is not reversible and a higher yield is achieved.



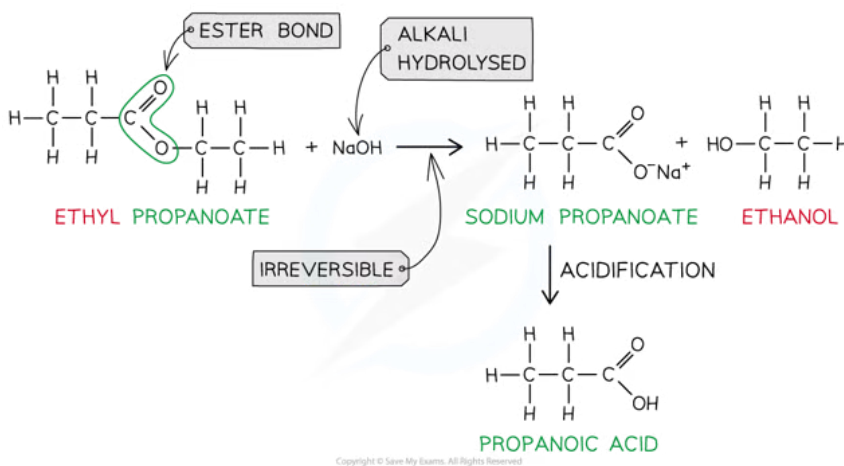
Hydrolysis of Esters

- Esters can be **hydrolysed** to reform the carboxylic acid and alcohol by either **dilute acid** or **dilute alkali** and **heat**
- When an ester is **heated under reflux** with **dilute acid** (eg. sulfuric acid) an equilibrium mixture is established as the reaction is **reversible**



Ester hydrolysis by dilute acid is a reversible reaction forming carboxylic acid and alcohol

- However, **heating** the ester **under reflux** with **dilute alkali** (eg. sodium hydroxide) is an **irreversible** reaction as the ester is fully hydrolysed
- This results in the formation of a **sodium carboxylate** salt which needs further **acidification** to turn into a **carboxylic acid**
 - The sodium carboxylate ($-\text{COO}^-$) ion needs to get protonated by an acid (such as HCl) to form the carboxylic acid ($-\text{COOH}$)



Ester hydrolysis by dilute alkali is an irreversible reaction forming a sodium carboxylate salt and alcohol

Table showing differences in hydrolysis of esters



| Acid hydrolysis | Alkaline hydrolysis |
|---|---|
| Equilibrium established / does not go to completion | Reaction is irreversible / goes to completion |
| Reflux, heat and dilute acid (HCl or H ₂ SO ₄) | Reflux, heat and dilute alkali (NaOH) |
| Carboxylic acid and alcohol produced | Carboxylate salt and alcohol produced |

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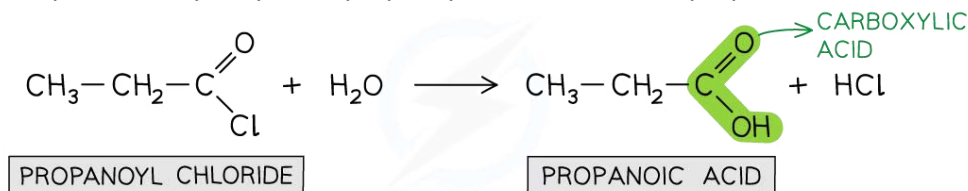


Uses of Acyl Chlorides

- **Acyl chlorides** are **reactive** organic compounds that undergo many reactions such as **addition-elimination reactions**
- In addition-elimination reactions, the **addition** of a small molecule across the C=O bond takes place followed by **elimination** of a small molecule
- Examples of these addition-elimination reactions include:
 - **Hydrolysis**
 - Reaction with alcohols and phenols to form **esters**
 - Reaction with ammonia and amines to form **amides**

Hydrolysis

- The **hydrolysis** of acyl chlorides results in the formation of a **carboxylic acid** and **HCl** molecule
- This is an **addition-elimination** reaction
 - A **water molecule** adds across the C=O bond
 - A hydrochloric acid (HCl) molecule is **eliminated**
- An example is the hydrolysis of propanoyl chloride to form propanoic acid and HCl



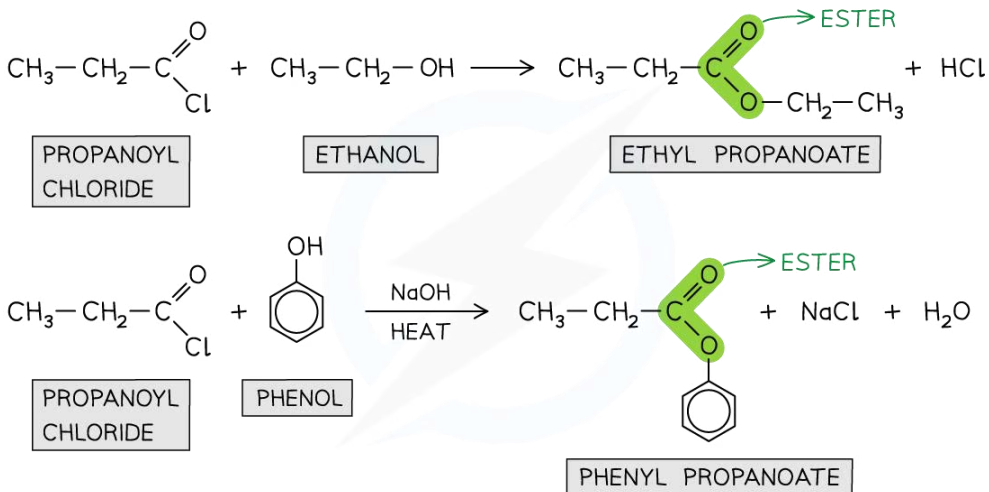
Acyl chlorides are hydrolysed to carboxylic acids

Formation of esters

- Acyl chlorides can react with **alcohols** and **phenols** to form esters
 - The reaction with phenols requires **heat** and a **base**
- Esters can also be formed from the reaction of **carboxylic acids** with phenol and alcohols however, this is a **slower** reaction as carboxylic acids are less reactive and the reaction does **not go to completion** (so less product is formed)
- Acyl chlorides are therefore more useful in the synthesis of esters
- The esterification of acyl chlorides is also an **addition-elimination** reaction
 - The alcohol or phenol adds across the C=O bond
 - A HCl molecule is eliminated

YOUR NOTES





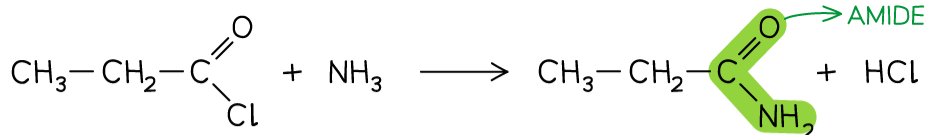
YOUR NOTES



Acyl chlorides undergo esterification with alcohols and phenols to form esters

Formation of amides

- Acyl chlorides can form **amides** from their **condensation reaction** with **amines** and **ammonia**
- The nitrogen atom in ammonia and amines has a lone pair of electrons which can be used to attack the carbonyl carbon atom in the acyl chlorides
- The product is a **non-substituted** amide (when reacted with ammonia) or **substituted** amide (when reacted with primary and secondary amines)
- This is also an example of an **addition-elimination** reaction as
 - The amine or ammonia molecule adds across the C=O bond
 - A HCl molecule is eliminated

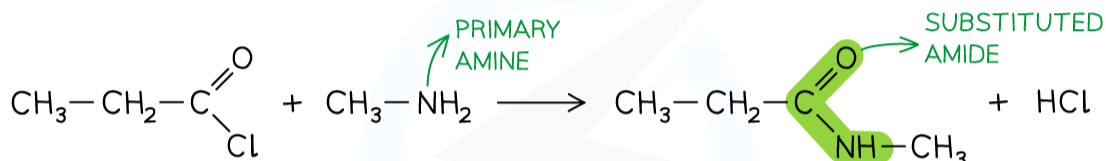


PROPANOYL
CHLORIDE

AMMONIA

PROPANAMIDE

AMIDE



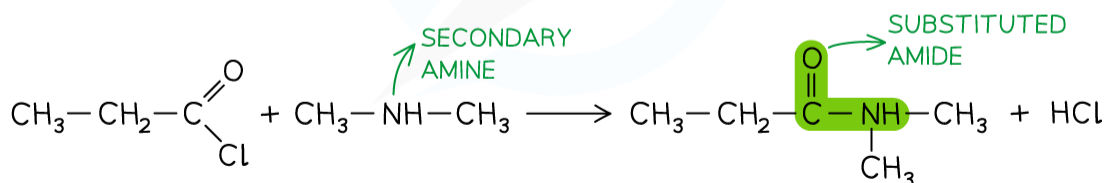
PROPANOYL
CHLORIDE

METHYLAMINE

METHYL PROPANAMIDE

SUBSTITUTED
AMIDE

PRIMARY
AMINE



PROPANOYL
CHLORIDE

DIMETHYL
AMINE

DIMETHYL PROPANAMIDE

SUBSTITUTED
AMIDE

SECONDARY
AMINE

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Acyl chlorides undergo condensation reactions with ammonia and amines to form amides

6.4 Nitrogen Compounds

6.4.1 Amines

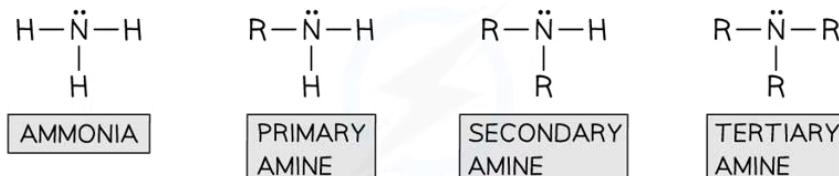
YOUR NOTES



Amine Basicity

Amines

- **Amines** can be thought of as derivatives of ammonia, in which one or more of the hydrogens is replaced by an alkyl or aryl group
- The number of substituted hydrogens is the basis of classifying amines



Classification of amines

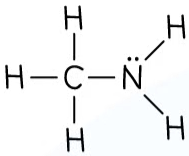
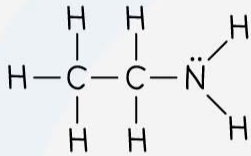
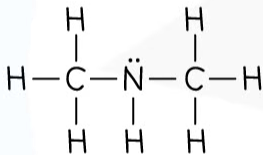
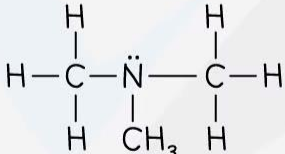
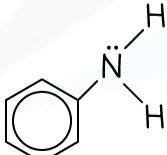
- Notice the classification is not the same as in alcohols and haloalkanes, where the designation primary, secondary and tertiary is based on the substituents on the *carbon* atom rather than the *nitrogen* atom
- If the R group is an alkyl group (methyl, ethyl, etc) then then it is an **aliphatic amine**; if it is an aryl group (benzene ring or phenyl) then it is an **aromatic amine**
- Aliphatic and aromatic amines share similar chemical reactions and the aryl group can strongly influence the chemistry and reactivity of the amine group

Naming Amines

- Amines can be named using common names or IUPAC systematic names
- The common way to name amines is to use the alkyl (or aryl) prefix followed by **-amine**
- The IUPAC systematic name uses the numbered prefix **amino-** followed by the alkane (or aromatic) stem

Nomenclature of aliphatic and aromatic amines table



| Structural Formula | Name | Molecular Formula |
|---|--|---------------------------------|
|  | methylamine or aminomethane | CH ₅ N |
|  | ethylamine or aminoethane | C ₂ H ₇ N |
|  | dimethylamine or N-methyl aminomethane | C ₂ H ₇ N |
|  | trimethylamine or N,N-dimethyl aminomethane | C ₃ H ₉ N |
|  | phenylamine or aminobenzene | C ₆ H ₇ N |

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Basic properties

- The nitrogen atom in ammonia and amine molecules can **accept** a **proton** (H⁺ ion)
- They can therefore act as **bases** in aqueous solutions by **donating** its lone pair of electrons to a proton and form a **dative bond**
 - For example, ammonia undergoes an **acid–base** reaction with dilute hydrochloric acid (HCl) to form a salt



base acid salt

- Amines react with HCl to form amine salts, such as ethylammonium chloride



For more help, please visit www.exampaperspractice.co.uk

base acid salt

YOUR NOTES

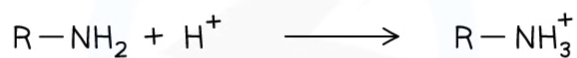


- Like ammonium salts, amine salts are soluble ionic compounds, so when the alkyl group is small they are water soluble but become less so as the carbon chain increases
- We can show the reaction in **Brønsted–Lowry terms**, where ammonia or the amine acts as a **proton acceptor**:

AMMONIA



PRIMARY AMINE



SECONDARY AMINE



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The nitrogen atom in ammonia and amines can donate its lone pair of electrons to form a bond with a proton and therefore act as a base

6.4.2 Preparing Amines

YOUR NOTES



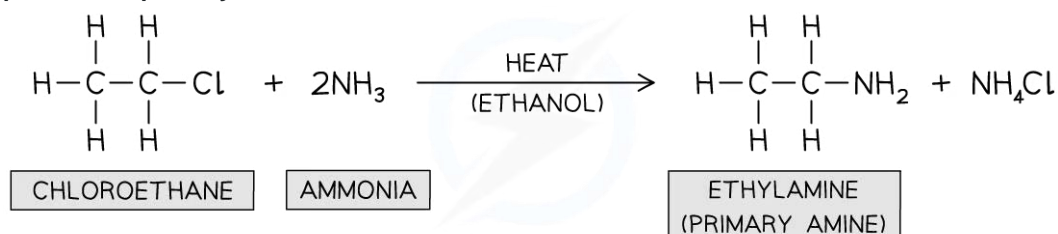
Preparing Aliphatic Amines

Preparing Amines

- Primary amines can be prepared from different reactions including:
 - The reaction of halogenoalkanes with ammonia
 - The reduction of nitriles

Reaction of halogenoalkanes with ammonia

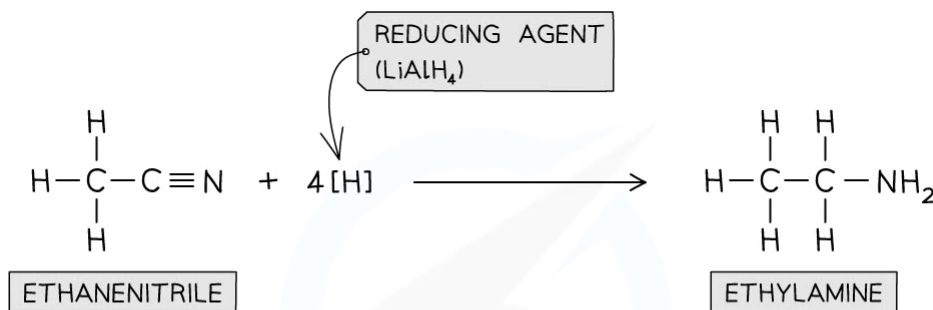
- This is a **nucleophilic substitution** reaction in which the nitrogen lone pair in ammonia acts as a **nucleophile** and **replaces** the halogen in the halogenoalkane
- When a halogenoalkane is reacted with **excess, hot ethanolic ammonia under pressure** a **primary amine** is formed



Formation of primary amine

Reduction of nitriles

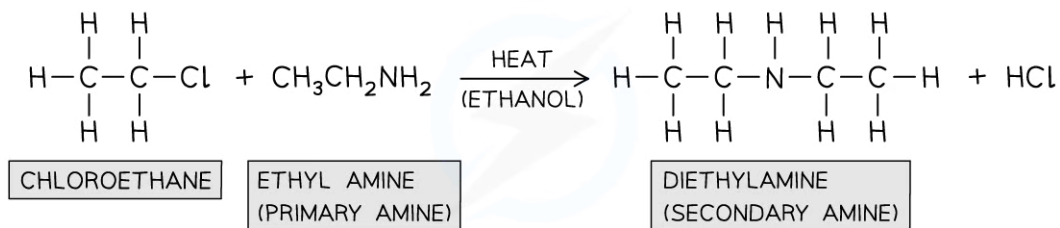
- Nitriles contain a $-\text{CN}$ functional group which can be **reduced** to an $-\text{NH}_2$ group
- The nitrile vapour and **hydrogen gas** are passed over a **nickel catalyst** or LiAlH_4 in **dry ether** can be used to form a **primary amine**



Nitriles can be reduced with LiAlH_4 or H_2 and Ni catalyst

Reaction of halogenoalkanes with primary amine

- This is also a **nucleophilic substitution** reaction in which the nitrogen in the primary amine acts as a **nucleophile** and **replaces** the halogen in the halogenoalkane
- When a halogenoalkane is reacted with a **primary amine** in **ethanol** and **heated in a sealed tube, under pressure** a **secondary amine** is formed



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Formation of secondary amine

- Tertiary amines can also be formed by further reaction of the secondary amine
- In this example, further substitution would form triethylamine ($\text{CH}_3\text{CH}_2\text{N}$)

YOUR NOTES

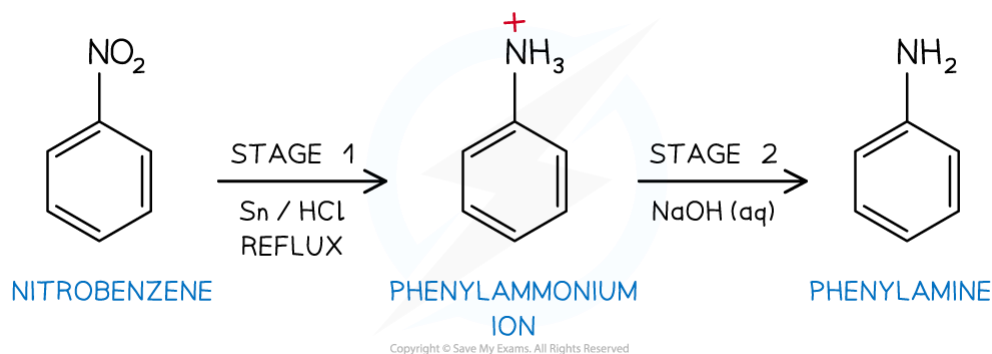


Preparing Aromatic Amines

YOUR NOTES



- **Phenylamine** is an organic compound consisting of a benzene ring and an **amine** (NH_2) functional group
- Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, according to the following two-stage reaction:



The two-stage reduction reaction of nitrobenzene to phenylamine

Stage 1 - Reduction of nitrobenzene

- Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, is reacted with tin, Sn, and concentrated hydrochloric acid, HCl
 - Tin and hydrochloric acid act as reducing agents
- The reaction mixture is heated under reflux in a boiling water bath
- The phenylammonium ions, $\text{C}_6\text{H}_5\text{NH}_3^+$, are protonated due to the acidic conditions

Stage 2 - Formation of phenylamine

- The phenylammonium ions, $\text{C}_6\text{H}_5\text{NH}_3^+$, are deprotonated by the addition of excess sodium hydroxide solution, NaOH (aq)

6.4.3 Amino acids

YOUR NOTES

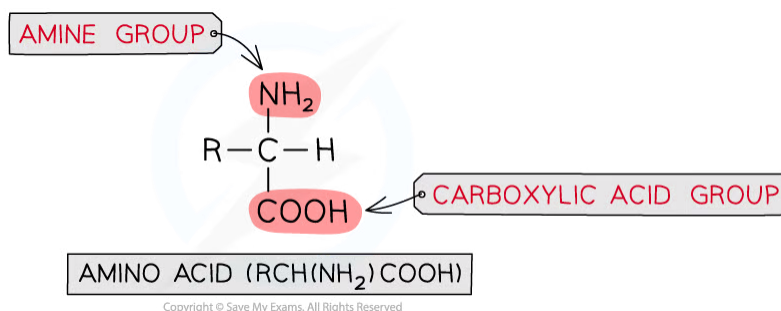


Reactions of Amino Acids

- **Amino acids** are organic compounds that contain two functional groups:
 - A basic **amino** ($-\text{NH}_2$) group
 - An acidic **carboxylic acid** ($-\text{COOH}$) group
- Due to the presence of both a basic and acidic group in amino acids, they are said to be amphoteric
 - They can act as both acids and bases

Naturally occurring amino acids

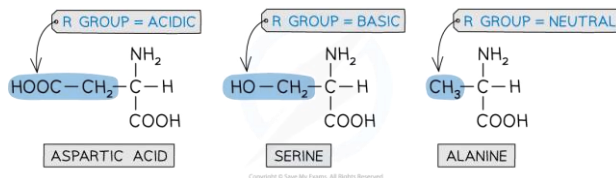
- 2-aminocarboxylic acids are a type of amino acids in which the amine ($-\text{NH}_2$) group is bonded to the carbon atom next to the $-\text{COOH}$ group
- These type of amino acids form the 'building blocks' that make up **proteins**
- There are 20 naturally occurring amino acids with the general structural formula of **$\text{RCH}(\text{NH}_2)\text{COOH}$**



General structural formula of amino acids

General structural formula of amino acids

- The **R** group varies in different amino acids and can be:
 - Acidic
 - Basic
 - Neutral



The R group varies in different amino acids

Acid / base properties of amino acids

- Amino acids will undergo most reactions of amines and carboxylic acids including acid-base reactions of:
 - Amines with acids
 - Carboxylic acids with bases

Reactions of the amine group

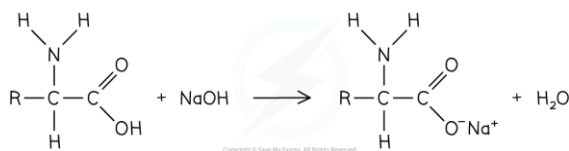
- The amine group is basic and reacts with acids to make salts
- For example, a general amino acid reacts with hydrochloric acid to form the ammonium salt:



Reactions of the carboxylic acid group

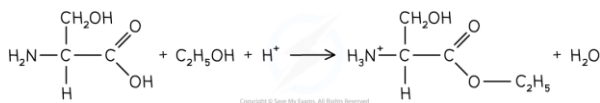
Reaction with aqueous alkalis

- An amino acid reacts with aqueous alkali such as sodium or potassium hydroxide to form a salt and water
- For example, a general amino acid reacts with sodium hydroxide to form a sodium salt:



Esterification with alcohols

- Amino acids, like carboxylic acids, can be esterified by heating with alcohol in the presence of concentrated sulfuric acid
- The carboxylic acid group is esterified whilst the basic amine group is protonated due to the acidic conditions:



YOUR NOTES



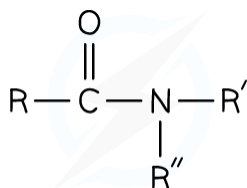
6.4.4 Amides

YOUR NOTES



Amides

- **Amides** are formed from the **condensation reaction** of **carboxylic acids** or **acyl chlorides** with **ammonia** or **amines**
- Amides are common in nature such as in proteins where the amine and carboxylic acid groups of amino acids bond together
- Amides have a general structure of RCONR_2



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The general structure of an amide

- Amides can be classified as primary, secondary or tertiary amides
- Like amines, this is done as a comparison to ammonia, depending on the number of substitutions on the amide nitrogen
 - Primary amide – one carbon bonded to the amide nitrogen
 - R' and R'' are both hydrogen atoms so one "ammonia" hydrogen has been substituted with the carbonyl group from the RCO portion of the molecule
 - Secondary amide – two carbons bonded to the amide nitrogen (one MUST be the carbonyl carbon)
 - Tertiary amide – three carbons bonded to the amide nitrogen (one MUST be the carbonyl carbon)

Naming primary amides

- For primary amides, we simply add -amide to the stem name
 - e.g. CH_3CONH_2
 - Contains two carbons with a C-C (ethan-) and an amide group (-amide)
 - This gives us ethanamide

Naming secondary amides

- For secondary amides, the alkyl chain attached to the nitrogen is added at the start of the chemical name
- This alkyl chain is prefixed with N-
- The chain containing the carbonyl group is named the same as a primary amide
 - e.g. $\text{CH}_3\text{CONH}(\text{C}_3\text{H}_7)$
 - Contains a propyl group on the nitrogen (N-propyl)
 - Contains two carbons with a C-C (ethan-) and an amide group (-amide)
 - This gives us N-propylethanamide

Naming tertiary amides

- For tertiary amides, there are two alkyl chains attached to the nitrogen
- The naming of these chains is the same as secondary amides

- ♦ As with standard nomenclature, these chains are listed in alphabetical order and the prefix 'di-' is used if necessary
 - e.g. $\text{CH}_3\text{CONCH}_3(\text{C}_3\text{H}_7)$
 - Contains a methyl group on the nitrogen (N-methyl)
 - Contains a propyl group on the nitrogen (N-propyl)
 - Contains two carbons with a C-C (ethan-) and an amide group (-amide)
 - This gives us N-methyl-N-propylethanamide

YOUR NOTES



6.5 Optical Isomerism

6.5.1 Optical Isomers

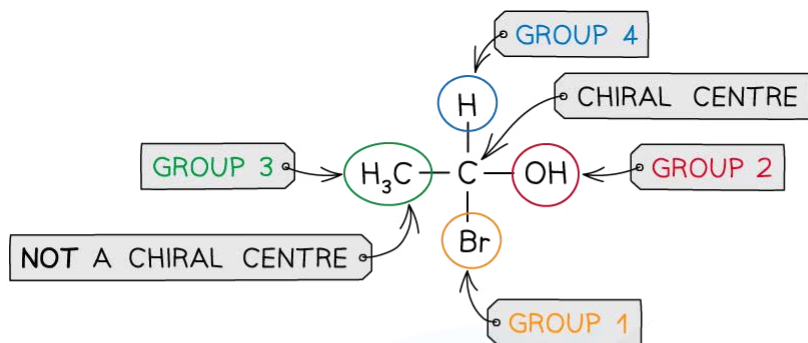
Optical Isomers & Chirality

Optical isomerism

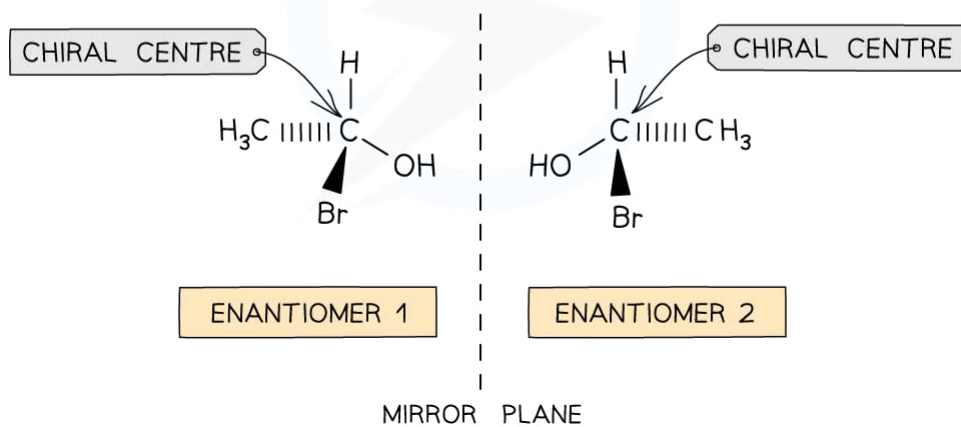
- **Stereoisomers** are molecules that have the same **structural formula** but have the atoms arranged differently in space
- There are two types of stereoisomerism
 - Geometrical (*E/Z*)
 - Optical
- A carbon atom that has **four different atoms** or **groups of atoms** attached to it is called a **chiral carbon** or **chiral centre**
 - Chira comes from a Greek word meaning hand, so we talk about these molecules having a handedness
- Compounds with a chiral centre (**chiral molecules**) exist as two **optical isomers** which are also known as **enantiomers**
- The enantiomers are **non-superimposable mirror images** of each other just like your left and right hand

YOUR NOTES





THIS CHIRAL CENTRE GIVES RISE TO TWO ENANTIOMERS (MIRROR IMAGES WHICH ARE NON-SUPERIMPOSABLE)



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A molecule has a chiral centre when the carbon atom is bonded to four different atoms or group of atoms; this gives rises to enantiomers

6.5.2 Identification of Chiral Centres

YOUR NOTES



Identification of Chiral Centres

- Identifying chiral centres in a molecule takes a bit of practice whether it is from a formula, a 2D drawing or a 3D drawing
- To be successful you need to differentiate the carbon atoms and determine one of the following:
 - Whether a particular carbon is bonded to four different atoms or groups of atoms and therefore is chiral
 - Whether a particular carbon is bonded to two of the same atoms or groups of atoms and therefore cannot be chiral
- If you are given a molecular formula you need to either draw the molecule as a condensed structural formula or a displayed formula so you can see all the bonds and groups



Worked Example

Determine which isomers of C_4H_9Br contain chiral carbons

Answer

$CH_3CH_2CH_2CH_2Br$
1-BROMOBUTANE
X NOT OPTICALLY ACTIVE

C 3 Hs AROUND IT NOT CHIRAL
C 2 Hs AROUND IT NOT CHIRAL
C 2 Hs AROUND IT NOT CHIRAL
C 2 Hs AROUND IT NOT CHIRAL

$CH_3CH_2CHBrCH_3$
2-BROMOBUTANE
✓ OPTICALLY ACTIVE

C 3 Hs AROUND IT NOT CHIRAL
C 2 Hs AROUND IT NOT CHIRAL
C H, CH_3 , Br AND C_2H_5 AROUND CHIRAL
C 3 Hs AROUND IT NOT CHIRAL

$(CH_3)_2CHCH_2Br$
1-BROMO-2-METHYLPROPANE
X NOT OPTICALLY ACTIVE

C 3 Hs AROUND IT NOT CHIRAL
C 2 CH_3 s AROUND IT NOT CHIRAL
C 2 Hs AROUND IT NOT CHIRAL

$(CH_3)_3CBr$
2-BROMO-2-METHYLPROPANE
X NOT OPTICALLY ACTIVE

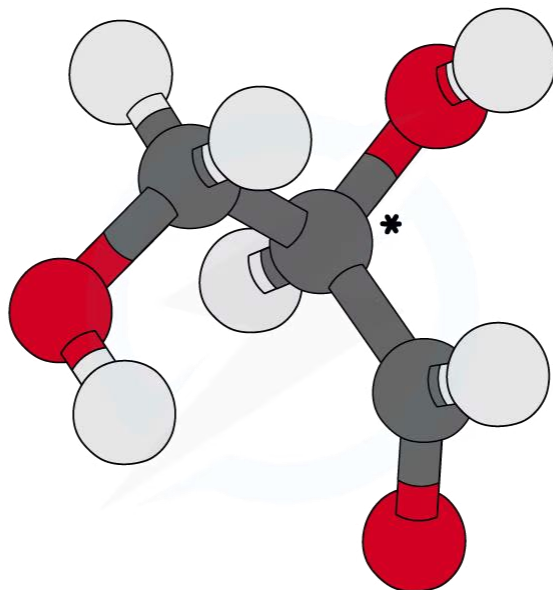
C 3 Hs AROUND IT NOT CHIRAL
C 3 CH_3 s AROUND IT NOT CHIRAL

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Recognising chiral centres in 3D drawings

- You should be able to spot chiral centres in 3D drawings

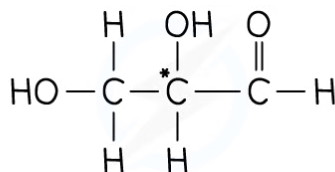
- Chiral centres are marked with an asterisk (*)
- For example, glyceraldehyde contains a chiral centre on the middle carbon:



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A 3D drawing space filling model of glyceraldehyde

- You can show the chiral carbon in a displayed formula like this



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A displayed formula for glyceraldehyde showing the the chiral centre

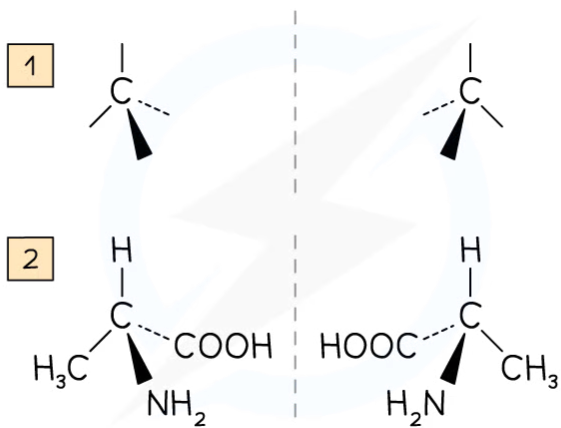
Drawing optical isomers

- You need to use stereochemical drawing conventions to represent optical isomers
- In the convention:
 - a solid line is a bond in the same plane as the paper
 - a dotted line is a bond receding behind the plane of the paper (this can also be hatched or shaded wedges)
 - a solid wedge is a bond coming out of the paper
- For example, suppose you are asked to draw the optical isomers of the amino acid alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$
 - Start by drawing a vertical dotted line to represent a line of symmetry in the centre of your page
 - Next draw the chiral carbon with four bonds in a tetrahedral arrangement
 - Make sure two bond lie in the plane of the paper, one comes out and one recedes

YOUR NOTES



- Add the four groups, but be careful to show the mirror image sequence of atoms



Drawing optical isomers

YOUR NOTES



6.6 Polymers

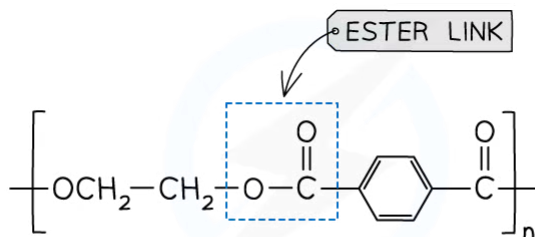
6.6.1 Condensation Polymers

Condensation Polymers

- Addition polymerisation has been covered in reactions of alkenes
 - They are made using monomers that have C=C double bonds joined together to form polymers such as polyethene
- Condensation polymerisation is another type of reaction whereby a polymer is produced by repeated condensation reactions between monomers
- Natural condensation polymers are all formed by **elimination of water**
 - Although the process of **condensation** polymerisation involves the **elimination of a small molecule**
- **Condensation polymers** can be identified because the monomers are linked by **ester or amide bonds**
- Condensation polymers can be formed by:
 - dicarboxylic acids and diols
 - dicarboxylic acids and diamines
 - amino acids

Polyester

- Is formed by the reaction between **dicarboxylic acid monomers** and **diol monomers**
- Polyester is produced by linking these monomers with **ester bonds / links**



THE POLYMER STRUCTURE FOR A POLYESTER

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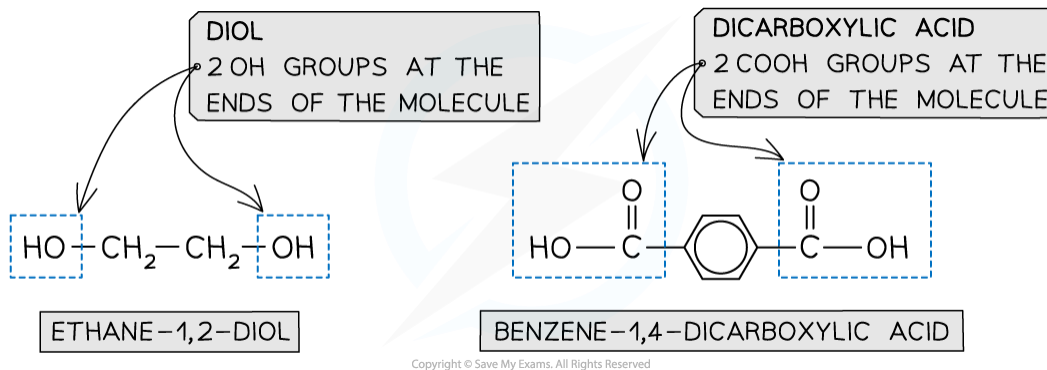
This polymer structure shows an ester functional group linking monomers together

Formation of polyesters

- A diol and a dicarboxylic acid are required to form a polyester
 - A diol contains 2 -OH groups
 - A dicarboxylic acid contains 2 -COOH groups

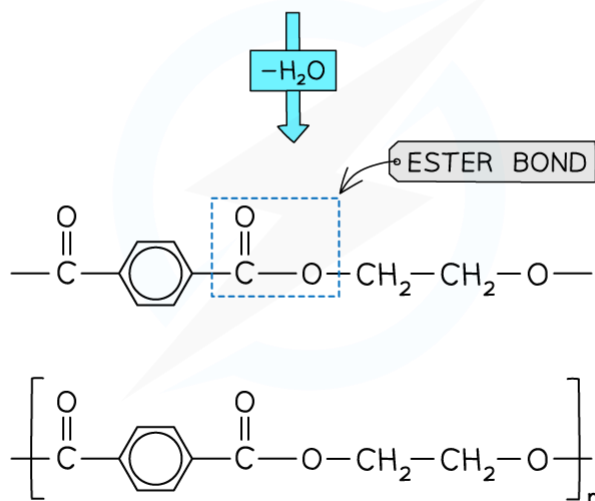
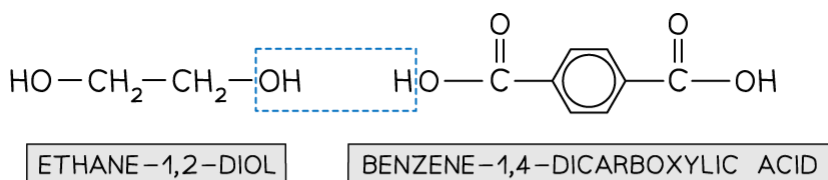
YOUR NOTES





The position of the functional groups on both of these molecules allows condensation polymerisation to take place effectively

- When the polyester is formed, one of the -OH groups on the diol and the hydrogen atom of the -COOH are expelled as a water molecule (H₂O)
- The resulting polymer is a polyester
 - In this example, the polyester is **poly(ethylene terephthalate)** or PET, which is sometimes known by its brand names of Terylene or Dacron



THE POLYMER STRUCTURE FOR POLY(ETHYLENE TEREPHTHALATE) (PET)

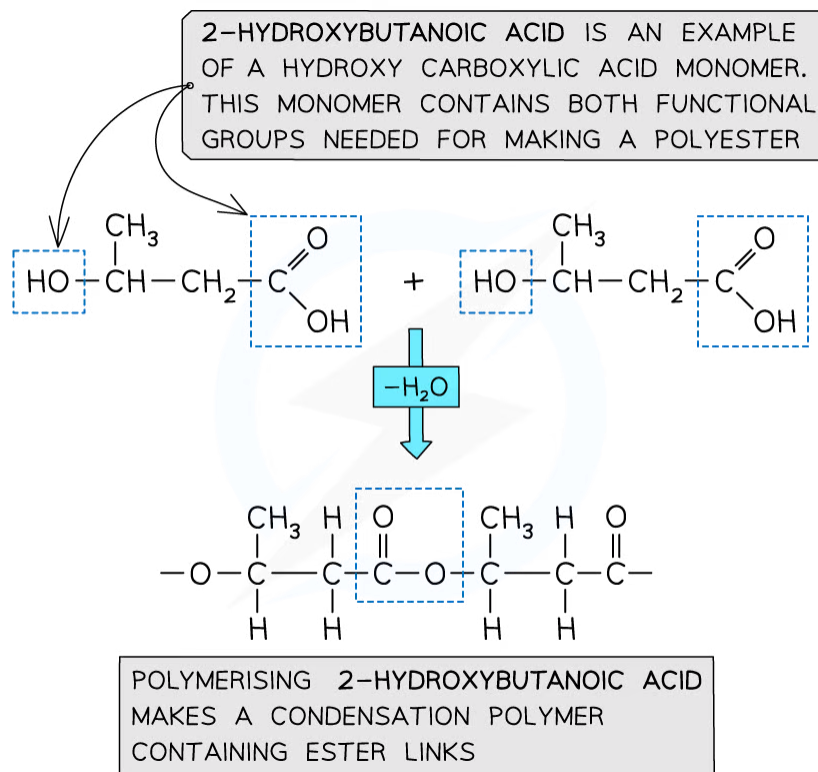
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Expulsion of a water molecule in this condensation polymerisation forms the polyester called (ethylene terephthalate) (PET)

Formation of polyesters – hydroxycarboxylic acids



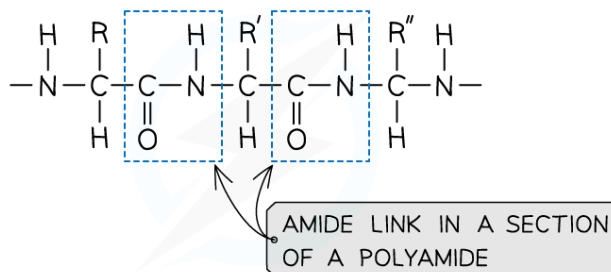
- So far the examples of making polyesters have focused on using 2 separate monomers for the polymerisation
- There is another route to making polyesters
- A single monomer containing both of the key functional groups can also be used
- These monomers are called hydroxycarboxylic acids
 - They contain an alcohol group (-OH) at one end of the molecule while the other end is capped by a carboxylic acid group (-COOH)



Both functional groups that are needed to make the polyester come from the same monomer

Polyamides

- Polyamides are polymers where repeating units are bonded together by amide links
- The formula of an amide group is -CONH



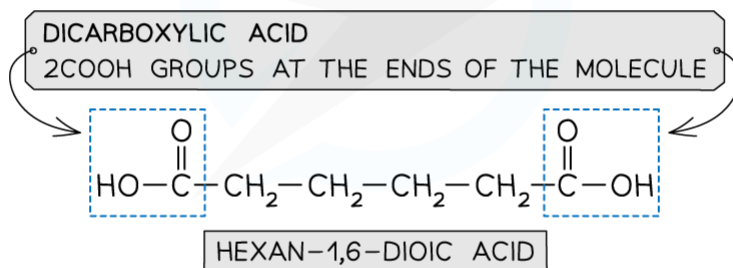
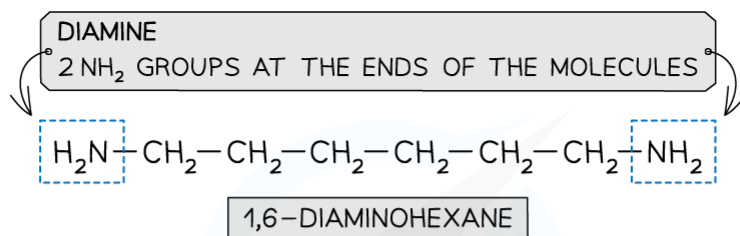
An amide link - also known as a peptide link - is the key functional group in a polyamide

YOUR NOTES

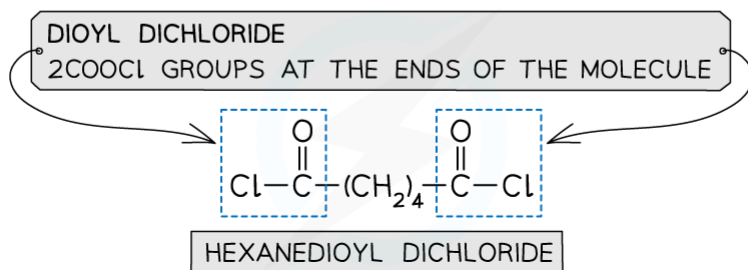


Polyamide monomers

- A diamine and a dicarboxylic acid are required to form a polyamide
 - A diamine contains 2 -NH_2 groups
 - A dicarboxylic acid contains 2 -COOH groups
- Dioyl dichlorides can also be used to react with the diamine instead of the acid
 - A dioyl chloride contains 2 -COCl groups
 - This is a more reactive monomer but more expensive than dicarboxylic acid



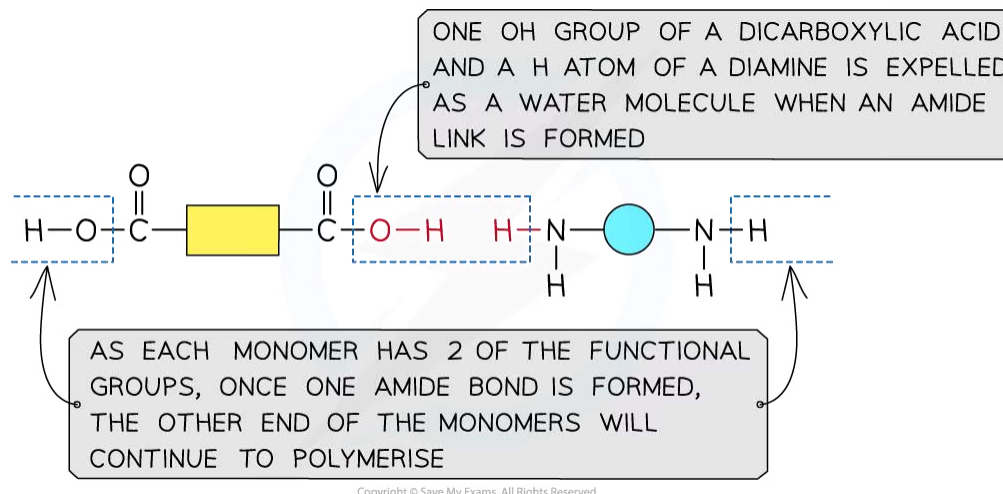
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The monomers for making polyamides

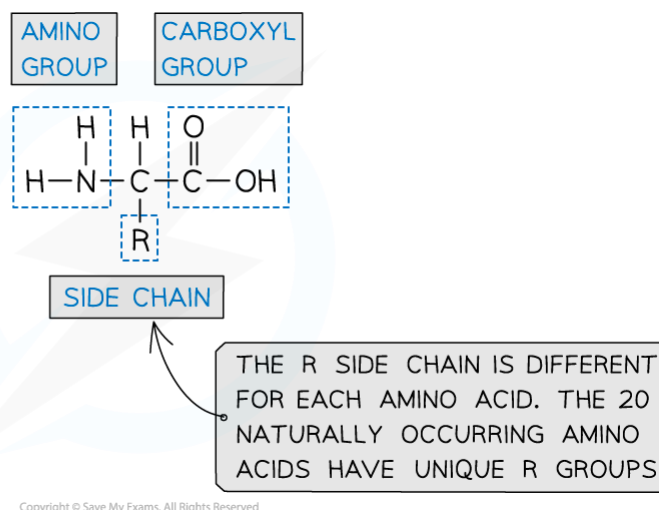
Formation of polyamides



This shows the expulsion of a small molecule as the amide link forms

Amino acids - formation of proteins

- Proteins are vital biological molecules with varying functions within the body
- They are essentially polymers made up of amino acid monomers
- Amino acids have an aminocarboxylic acid structure
- Their properties are governed by a branching side group – the R group

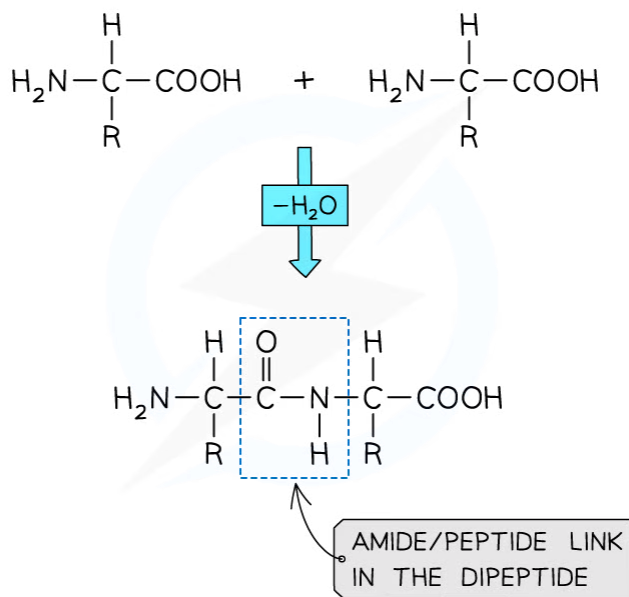


Amino acids contain an amine group, an acid group and a unique R group

- Different amino acids are identified by their unique R group
- The names of each amino acid is given using 3 letters
- For example Glutamine is known as 'Gln'
- Dipeptides can be produced by polymerising 2 amino acids together
 - The amine group ($-\text{NH}_2$) and acid group ($-\text{COOH}$) of each amino acid is used to polymerise with another amino acid

- Polypeptides are made through polymerising more than 2 amino acids together

2 AMINO ACIDS REACT TOGETHER TO FORM A DIPEPTIDE



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Dipeptides and polypeptides are formed by polymerising amino acid molecules together

YOUR NOTES



Acid & Base Hydrolysis

YOUR NOTES



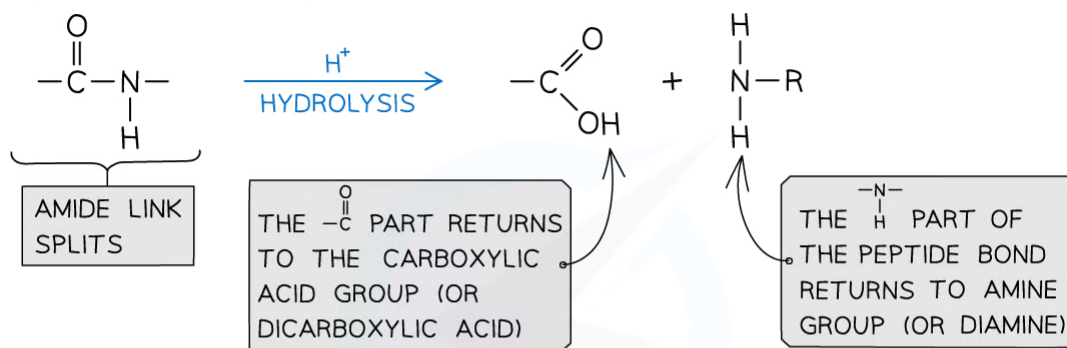
Biodegradable polymers

- Both polyesters and polyamides can be broken down using hydrolysis reactions
- This is a major advantage over the polymers produced using alkene monomers (polyalkenes)
- When polyesters and polyamides are taken to landfill sites, they can be broken down easily and their products used for other applications

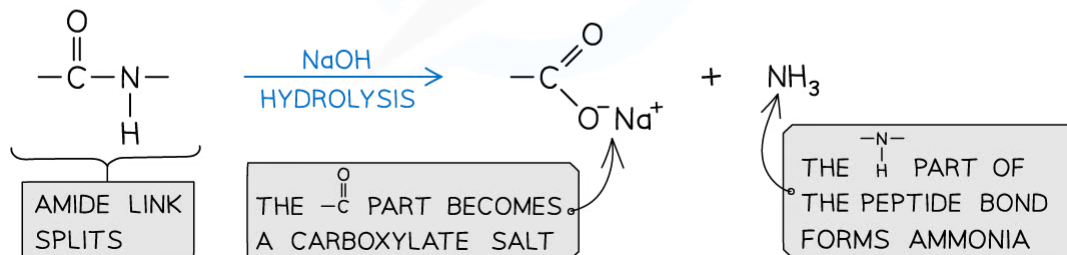
Hydrolysis of polyamides

- Hydrolysis is a breaking up of a molecules using water
- In **acidic hydrolysis**, acid (such as hydrochloric acid) acts as the catalyst
 - Polyamides are heated with dilute acid
 - This reaction breaks the polyamide into carboxylic acid molecules and ammonium chloride ions
- Alkaline hydrolysis
 - The polyamide is heated with a species containing hydroxide ions (eg. sodium hydroxide)
 - This breaks the polymer into the sodium salts of its monomers (dicarboxylic acids and diamines)
 - If the poly amide link used an aminocarboxylic acid as the monomer, then a sodium salt of the original amino acid is reformed

ACID HYDROLYSIS



ALKALINE HYDROLYSIS

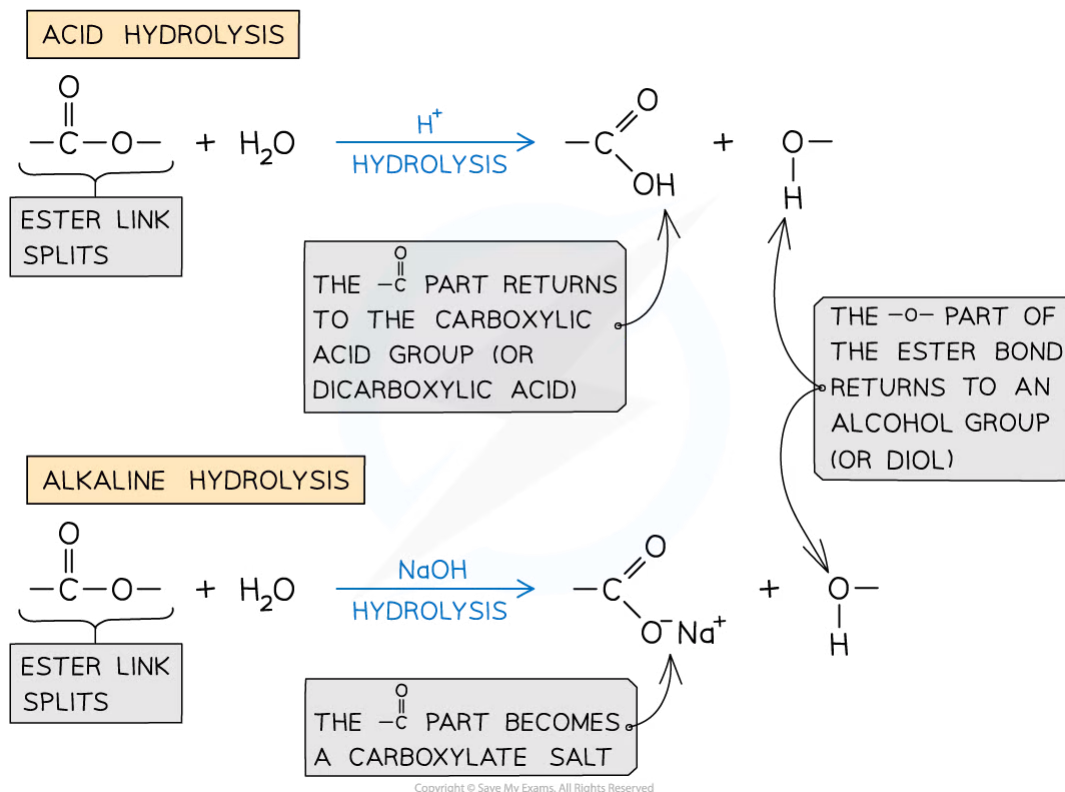


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When polyamides are degraded by hydrolysis, carboxylic acids and amines are formed

Hydrolysis of polyesters

- Ester linkages can also be degraded through hydrolysis reactions
- Acid hydrolysis forms the alcohols and carboxylic acids that were used to form the polyesters



When polyesters are degraded by hydrolysis, carboxylic acids and alcohols are formed

YOUR NOTES



6.6.2 Polymer Repeat Units

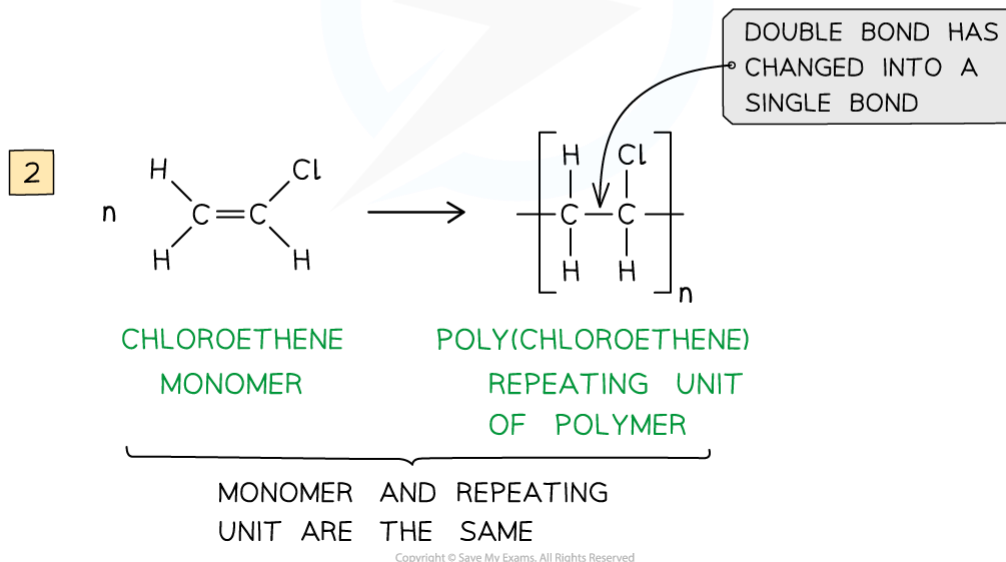
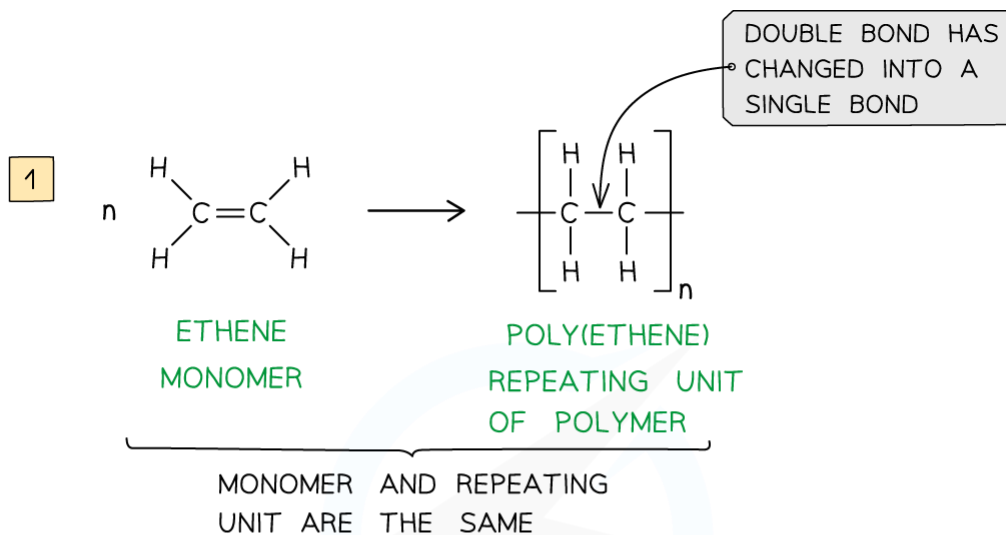
YOUR NOTES



Polymer Repeat Units

Repeat units for addition polymers

- A **repeat unit** is the smallest group of atoms that when connected one after the other make up the polymer chain
 - It is represented by **square brackets** in the displayed and general formula
- In **poly(alkenes)** (such as poly(ethene)) and **substituted poly(alkenes)** (such as PVC) made of **one type of monomer** the repeating unit is the same as the monomer except that the C=C double bond is changed to a C-C single bond

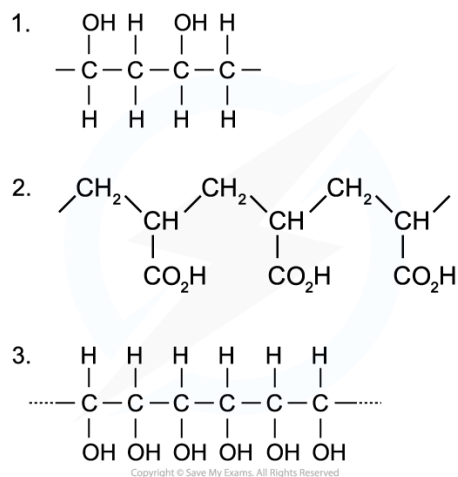


The repeating units of poly(ethene) and poly(chloroethene) are similar to their monomer except that the C=C bond has changed into a C-C bond



? Worked Example

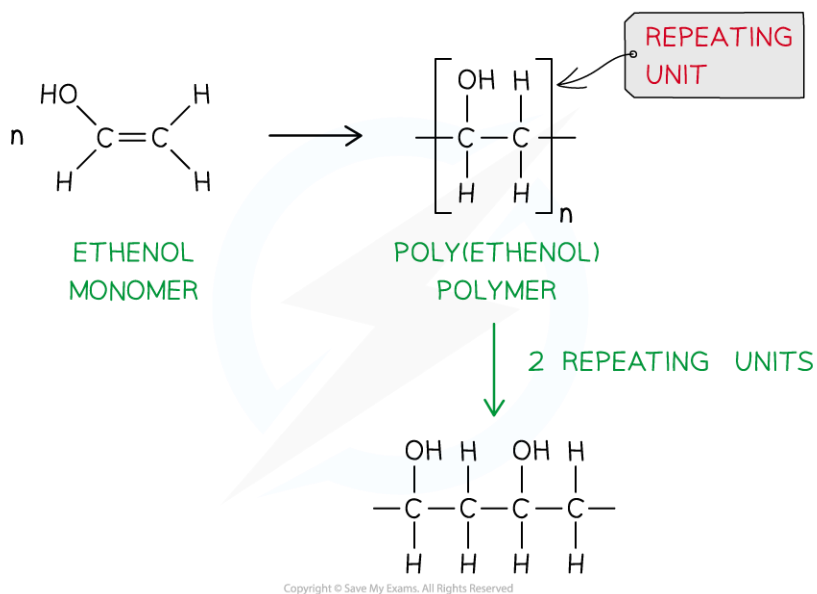
Identify the monomers present in the given sections of addition polymer molecules:



Answers:

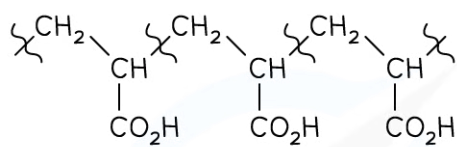
Answer 1:

When ethenol ($\text{CH}(\text{OH})=\text{CH}_2$) is polymerised, the C-C double bond opens to produce a repeating unit of $\text{CH}(\text{OH})-\text{CH}_2$. This gives the polymer poly(ethenol)

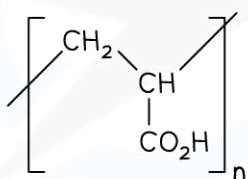


Answer 2:

- To find the monomer, first the repeating unit should be deduced. Repeating units have only 2 carbons in the polymer main chain



ONE REPEATING UNIT

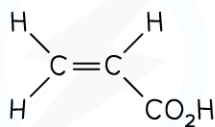


POLY(PROP-2-ENOIC ACID)

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- Since the repeating unit is now found, it can be concluded that the monomer is prop-2-enoic acid

MONOMER

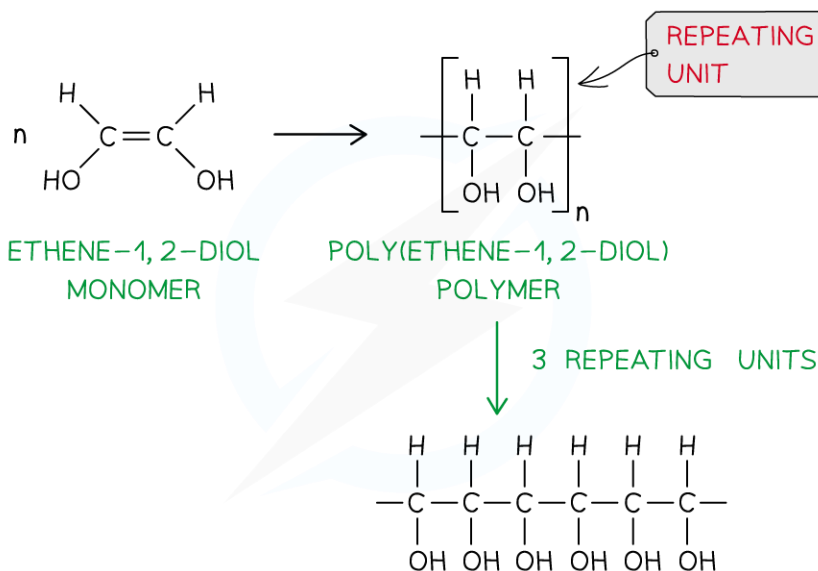


PROP-2-ENOIC ACID

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Answer 3:

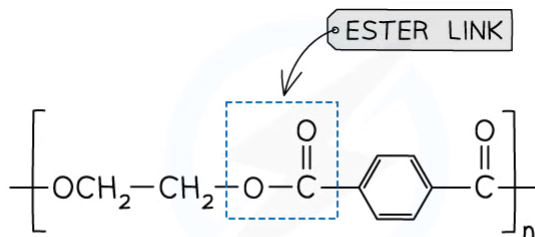
- Again, the repeating unit only has 2 carbons in the polymer chain which in this case are two carbon atoms that each contain one OH group
- Thus, when ethene-1,2-diol (CH(OH)=CH(OH)) is polymerised, the C=C double bond opens to produce a repeating unit of CH(OH)-CH(OH) which gives the polymer poly(ethene-1,2-diol)



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Repeat units for condensation polymers

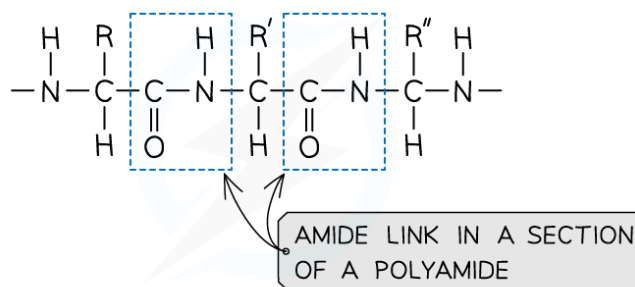
- Remember we can tell the type of polymerisation by identifying the linking between the monomers
- If a chain of carbon atoms is present, the polymer is an addition polymer
- If there is an ester link, the polymer is a polyester (formed by condensation polymerisation)
- If there is an amide link, the polymer is a polyamide (formed by condensation polymerisation)



THE POLYMER STRUCTURE FOR A POLYESTER

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This polymer structure shows an ester functional group linking monomers together



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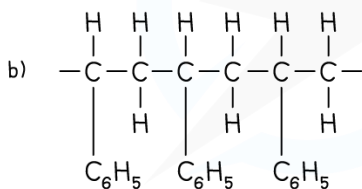
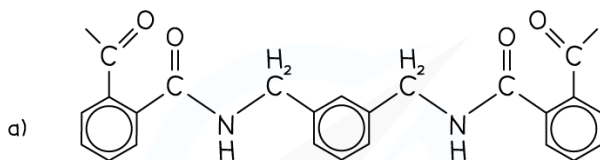
An amide link - also known as a peptide link - is the key functional group in a polyamide

YOUR NOTES



Worked Example

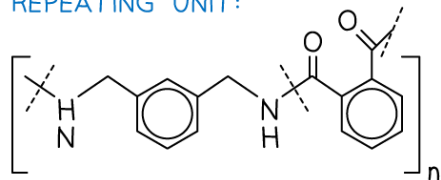
Draw the repeating unit and identify the monomers used to make the following polymers



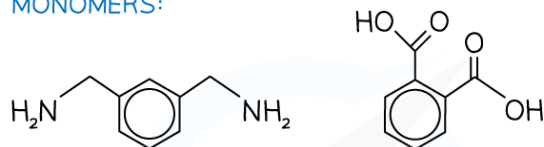
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Answer:

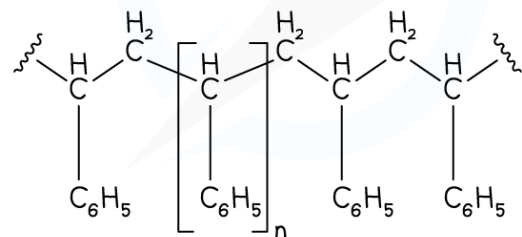
a) REPEATING UNIT:



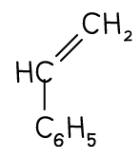
a) MONOMERS:



b) REPEATING UNIT:



b) MONOMERS:



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YOUR NOTES



6.7 Extending Carbon Chains

6.7.1 Nitriles

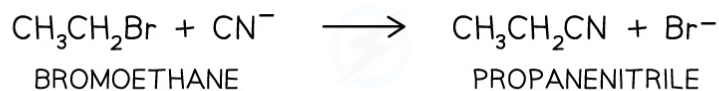
Formation of Nitriles

Carbon-carbon bond forming

- **Carbon-carbon bond forming** reactions are organic reactions in which a new carbon-carbon bond is formed
- They are important in the production of many man-made chemicals such as pharmaceuticals and plastics
- Carbon-carbon bonds can be formed via the following reactions
 - Formation of nitriles to extend the carbon chain
 - Friedel-Crafts alkylation and acylation

Formation of nitriles

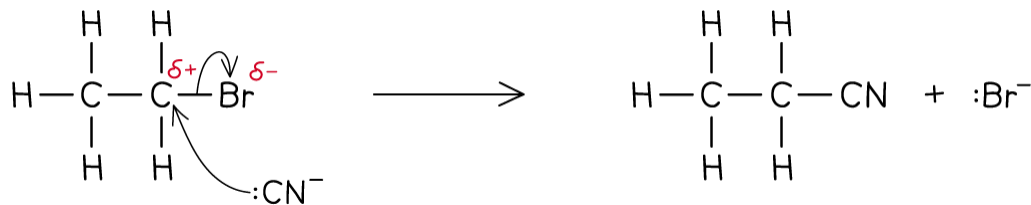
- The **nucleophile** in this reaction is the **cyanide**, CN^- ion
- **Ethanol solution of potassium cyanide** (KCN in ethanol) is **heated under reflux** with the halogenoalkane
- The product is a **nitrile**
 - Eg. bromoethane reacts with ethanolic potassium cyanide when heated under reflux to form propanenitrile



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The halogen is replaced by a cyanide group, CN^-

- The nucleophilic substitution of halogenoalkanes with KCN adds an **extra** carbon atom to the carbon chain
- This reaction can therefore be used by chemists to make a compound with one more carbon atom than the best available organic starting material

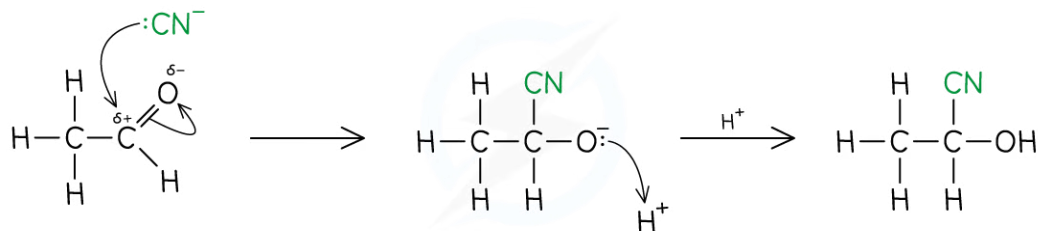


Nucleophilic substitution of a haloalkane with CN^-

Addition of HCN to carbonyl compounds

- The nucleophilic addition of hydrogen cyanide to carbonyl compounds is a two-step process, as shown below





- In **step 1**, the cyanide ion attacks the carbonyl carbon to form a negatively charged intermediate
- In **step 2**, the negatively charged oxygen atom in the reactive intermediate quickly reacts with aqueous H^+ (either from HCN, water or dilute acid) to form 2-hydroxynitrile compounds,
 - e.g. 2-hydroxypropanenitrile

YOUR NOTES



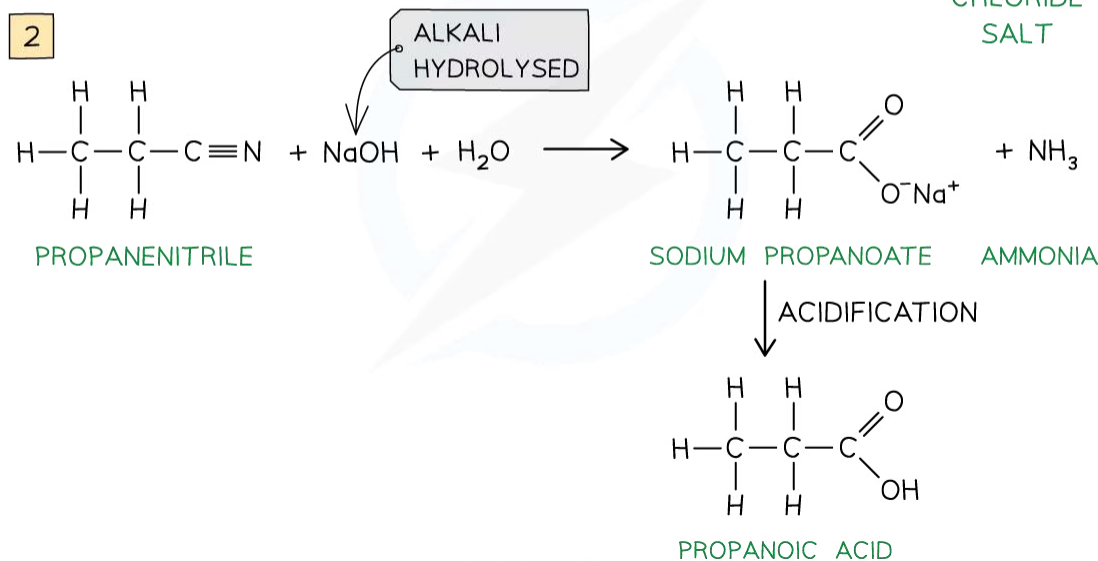
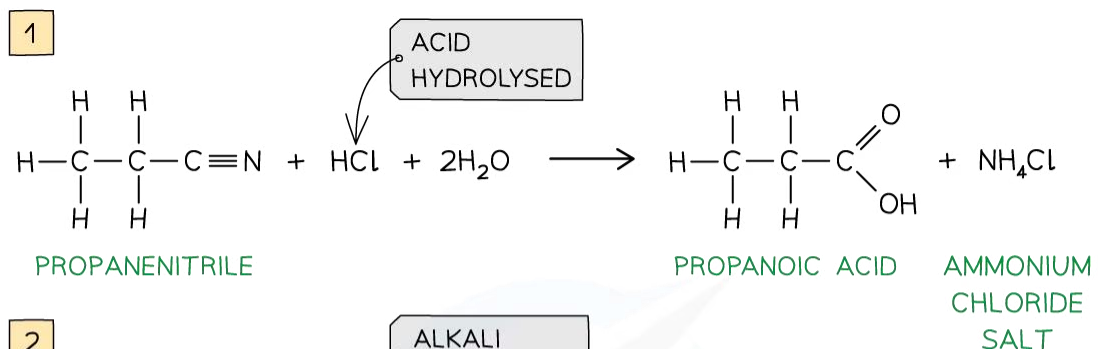
Reactions of Nitriles

YOUR NOTES



Hydrolysis of nitriles

- Nitriles are **hydrolysed** by either **dilute acid** or **dilute alkali followed by acidification**
 - Hydrolysis by dilute acid results in the formation of a carboxylic acid and ammonium salt
 - Hydrolysis by dilute alkali results in the formation of a sodium carboxylate salt and ammonia; **Acidification** is required to change the carboxylate ion into a carboxylic acid
- The $-CN$ group at the end of the hydrocarbon chain is converted to a $-COOH$ group



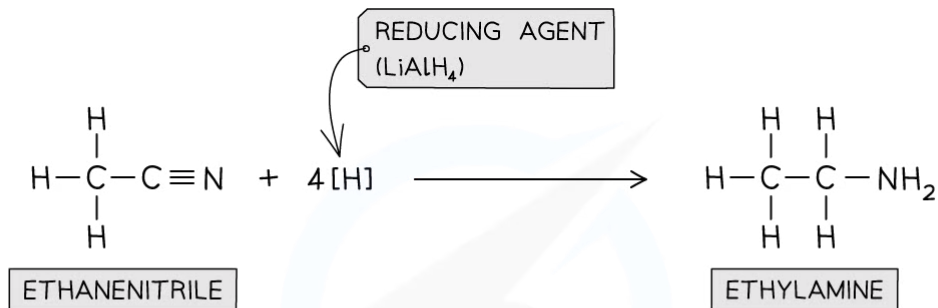
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Hydrolysis of nitriles by either dilute acid (1) or dilute alkali and acidification (2) will form a carboxylic acid

Reduction of Nitriles

- Nitriles contain a $-CN$ functional group which can be **reduced** to an $-NH_2$ group
- The nitrile vapour and **hydrogen gas** are passed over a **nickel catalyst** or LiAlH_4 in **dry ether** can be used to form a **primary amine**

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Nitriles can be reduced with LiAlH₄ or H₂ and Ni catalyst

6.7.2 Substituted Aromatic Carbon-carbon Bond Formation

YOUR NOTES



Alkylation & Acylation

Friedel-Crafts Reactions

- Friedel-Crafts reactions are also **electrophilic substitution** reactions
- Due to the aromatic stabilisation in arenes, they are often **unreactive**
- To use arenes as **starting materials** for the synthesis of other organic compounds, their structure, therefore, needs to be changed to turn them into more reactive compounds
- Friedel-Crafts reactions can be used to substitute a hydrogen atom in the benzene ring for an **alkyl group** (Friedel-Crafts alkylation) or an **acyl group** (Friedel-Crafts acylation)
- Like any other electrophilic substitution reaction, the Friedel-Crafts reactions consist of three steps:
 - Generating the electrophile
 - Electrophilic attack on the benzene ring
 - Regenerating aromaticity of the benzene ring

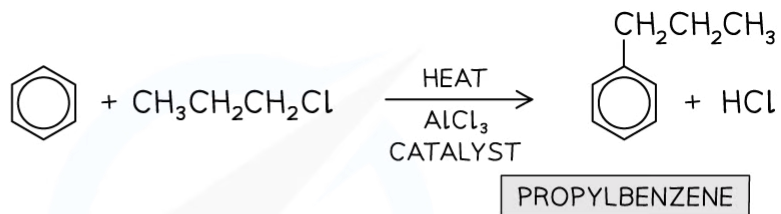
Friedel-Crafts Alkylation

- In the Friedel-Crafts alkylation, an **alkyl group** is substituted into the benzene ring
- The benzene ring is reacted with a chloroalkane (e.g. chloroethane) in the presence of an AlCl_3 catalyst
- An example of alkylation is the reaction of benzene with chloropropane to form propylbenzene
- The Friedel-Crafts alkylation reaction is a method of generating alkylbenzenes by using alkyl halides as reactants

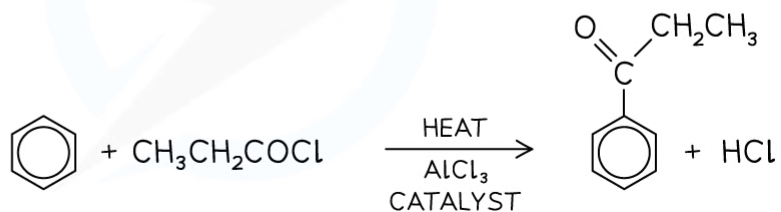
Friedel-Crafts Acylation

- In the Friedel-Crafts acylation reaction, an **acyl group** is substituted into the benzene ring
 - An acyl group is an alkyl group containing a carbonyl, $\text{C}=\text{O}$ group
- The benzene ring is reacted with an acyl chloride in the presence of an AlCl_3 catalyst
- An example of an acylation reaction is the reaction of benzene with propanoyl chloride to form phenylpropanone
 - The Friedel-Crafts acylation reaction is a method of generating ketones

FRIEDEL-CRAFTS
ALKYLATION



FRIEDEL-CRAFTS
ACYLATION



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Examples of Friedel-Crafts alkylation and acylation reactions

YOUR NOTES



6.8 Organic Synthesis

6.8.1 Techniques

Preparation of an Organic Solid

- This preparation and purification covers a number of key laboratory skills:
 - use appropriate apparatus to record a range of measurements
 - use water bath or electric heater or sand bath for heating
 - use laboratory apparatus for a variety of experimental techniques
 - purify a solid product by recrystallisation
 - use melting point apparatus
 - safely and carefully handle solids and liquids
- There are a few choices of experiments that are commonly done in schools which cover these laboratory skills and three which can be done are:
 - The preparation of aspirin
 - The preparation of benzoic acid
 - The nitration of methyl benzoate
 - These are covered in more detail in Unit 1. Development of practical skills in chemistry

YOUR NOTES



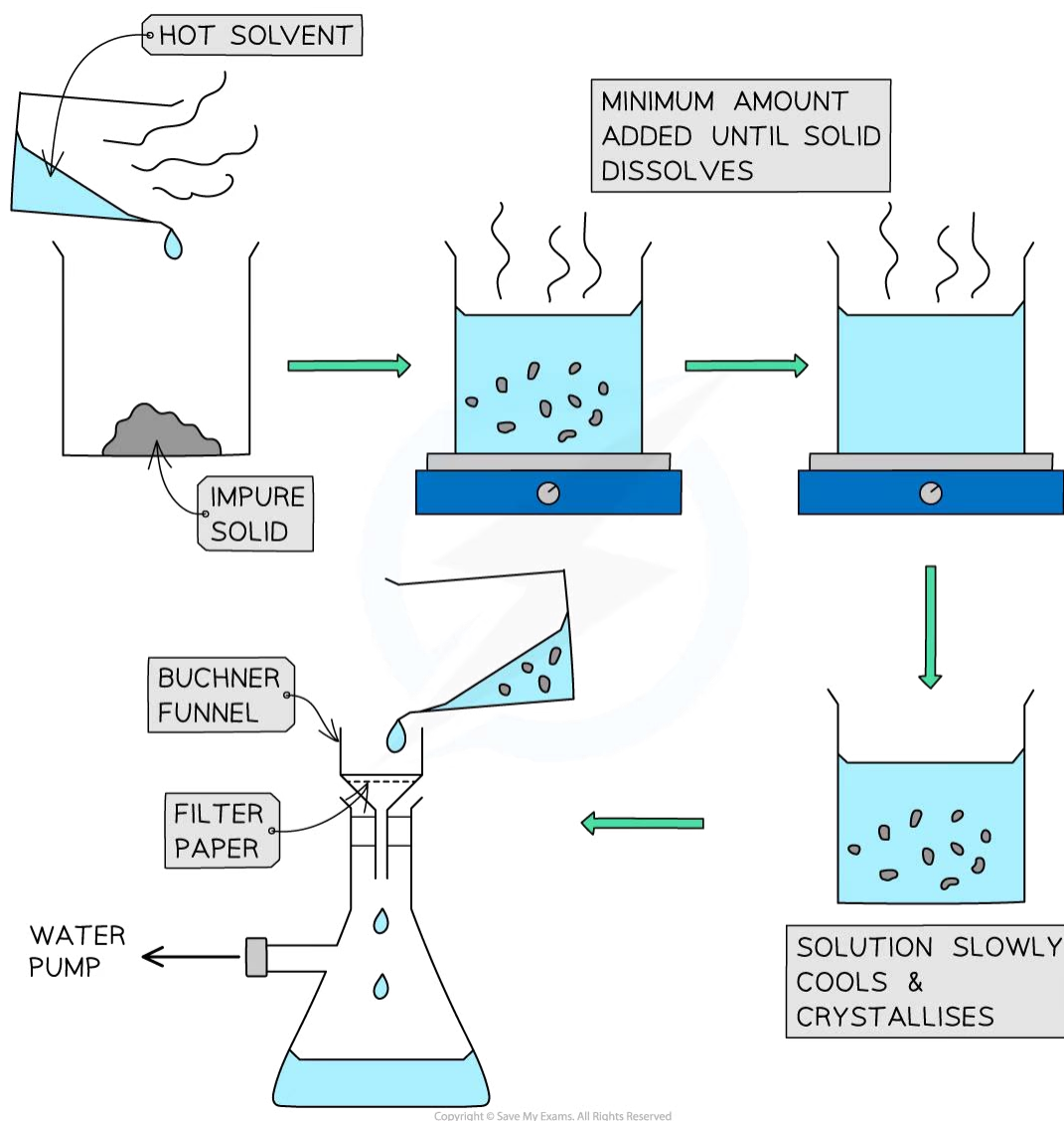
Purification of an Organic Solid

YOUR NOTES



Recrystallisation

- Recrystallisation is used to purify impure solids
- The principle is that a hot solvent is used to dissolve both the organic solid and the impurities and then as the solution cools the solid crystallises out and leaves behind the impurities in the solution
- The key is using the minimum amount of solvent to dissolve the solid and avoid loss of the product
- If any solid impurities remain in the solution, a hot filtration can be carried out
- Once the solution has cooled down to room temperature and crystallised then the product crystals can be recovered by filtration
- This is faster using Buchner apparatus in which filtration occurs under reduced pressure



Recrystallisation and Buchner filtration

YOUR NOTES



- After filtration the product is washed with fresh cold solvent and then allowed to dry on filter paper

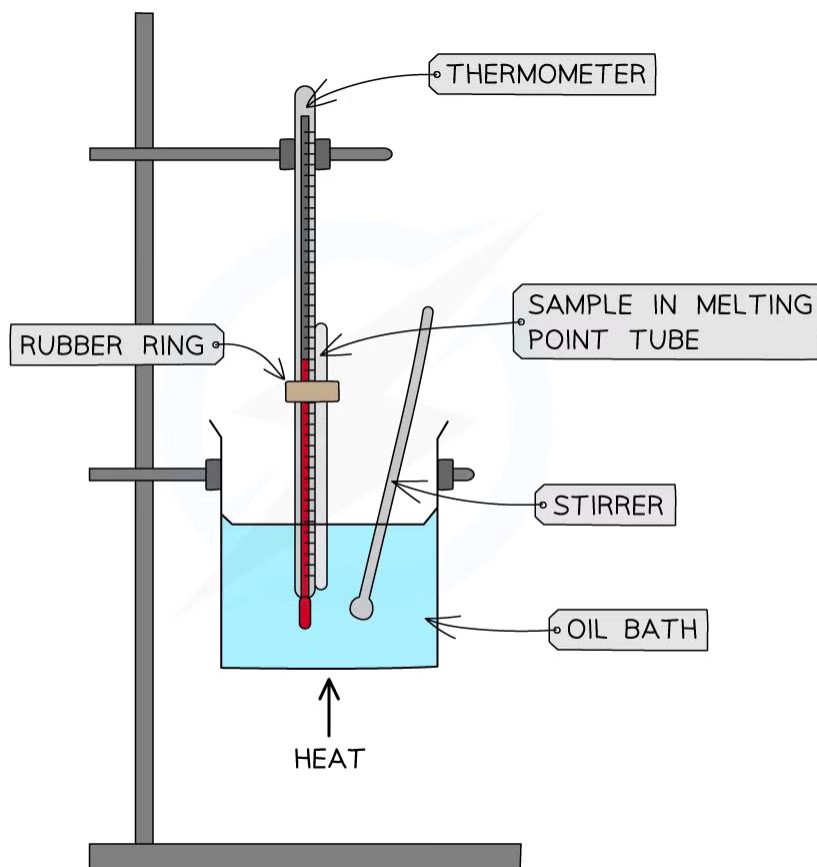


Exam Tip

Recrystallisation can be repeated more than once to ensure a very pure product, but each time the yield of product will decrease. Slow cooling results in bigger well defined crystals which are easier to filter and dry.

Determination of Melting point

- The melting point of a solid is indicative of its purity and identity
- A melting point can be matched to a known substance as a means of identification or confirmation of a desired product
- The proximity of a melting point to the actual data book value can express purity
 - Impurities tend to lower the melting point of a solid
- The melting point range also reveals the degree of purity
 - Pure substances have sharp well defined melting points
 - Impure substances have a broad melting point range, i.e. a large difference between when the substance first melts until it completely melts
- The skills needed in performing a melting point test are largely dependent on the specific melting point apparatus you are using
- However, there are some common key skills:
 - Correctly preparing the melting point tubes
 - Heating the tubes very slowly
 - Repeating to get a range of measurements (three would be normal)
- The sample solid must be totally dry and finely powdered – this can be achieved by crushing it with the back of a spatula onto some filter paper or the back of a white tile (this absorbs any moisture)
- Use the first tube to find the approximate melting point range and then repeat using a much slower heating rate



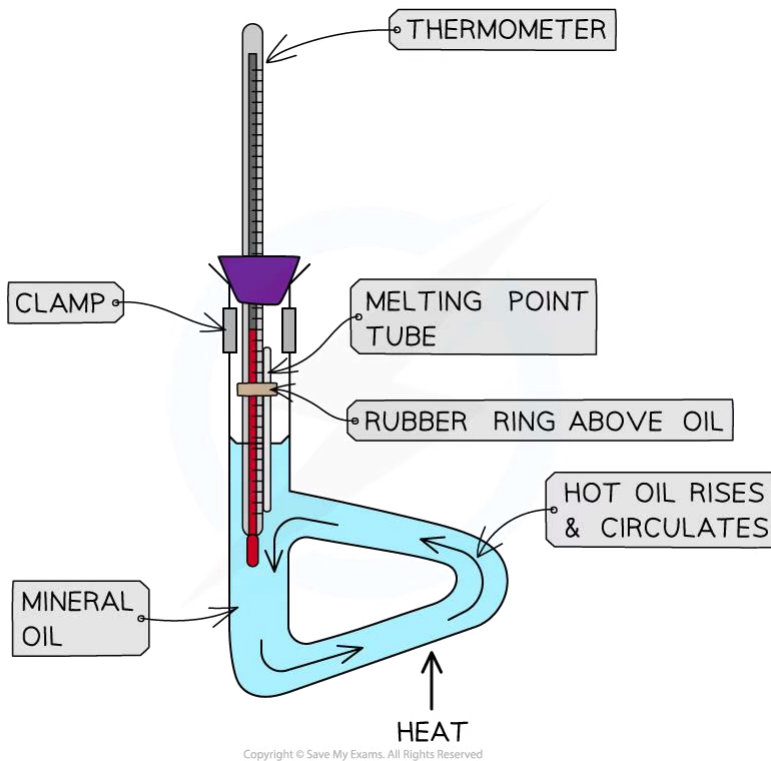
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Melting point test using an oil bath

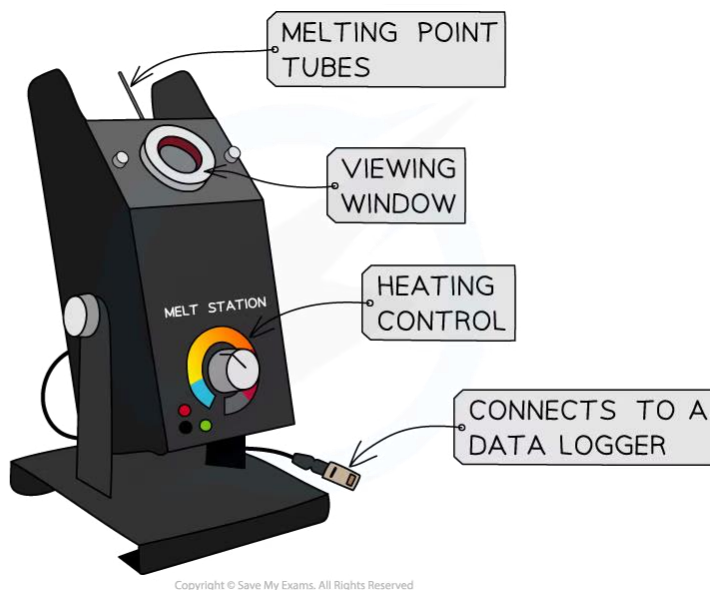
YOUR NOTES



YOUR NOTES



Melting point test using a Thiele tube



Melting point test using a melt station



Exam Tip

Always quote a melting point as a range + or - and reference a data book value if you have one.

YOUR NOTES



6.8.2 Synthetic Routes

Multi-Stage Organic Synthetic Routes

- A large number of organic products are made from a few starting compounds using appropriate reagents and conditions
- Knowing how organic functional groups are related to each other is key to the synthesis of a given molecule
- The main functional groups you need to know are
 - Alkanes
 - Alkenes
 - Haloalkanes
 - Nitriles
 - Amines
 - Alcohols
 - Carbonyls (aldehydes & ketones)
 - Hydroxynitriles
 - Carboxylic acids
 - Esters
 - Acyl chlorides
 - Primary and secondary amides



Exam Tip

You also need to be able to identify the functional groups of these chemicals in structures that are given to you

Aliphatic Reaction Pathways

- The key interconversions between functional groups are summarised here:

Aliphatic Reactions Table

YOUR NOTES





YOUR NOTES



| Reactant | Product | Reagents | Reaction |
|-------------------|------------------------------|--|--|
| Alkene | Haloalkane | Hydrogen halide | Electrophilic addition |
| Alkene | Alcohol | Steam + H ₂ SO ₄ / heat | Hydration |
| Alkene | Alkane | Hydrogen + Ni catalyst / 150 °C | Electrophilic addition / hydrogenation |
| Alcohol | Alkene | Al ₂ O ₃ or conc. acid / heat | Elimination / dehydration |
| Alcohol | Haloalkane | NaX + H ₂ SO ₄ / heat under reflux | Nucleophilic substitution |
| Haloalkane | Alcohol | NaOH (aq) / heat under reflux | Nucleophilic substitution |
| Alkane | Haloalkane | Halogen / UV light | Free radical substitution |
| Primary alcohol | Aldehyde | K ₂ Cr ₂ O ₇ / H ₂ SO ₄ / Distillation | Oxidation |
| Secondary alcohol | Ketone | K ₂ Cr ₂ O ₇ / H ₂ SO ₄ / Heat | Oxidation |
| Primary alcohol | Carboxylic acid | K ₂ Cr ₂ O ₇ / H ₂ SO ₄ / Heat under reflux | Oxidation |
| Aldehyde | Primary alcohol | NaBH ₄ / H ₂ O | Reduction |
| Ketone | Secondary alcohol | NaBH ₄ / H ₂ O | Reduction |
| Haloalkane | Nitrile | NaCN | Nucleophilic substitution |
| Haloalkane | Amine | NH ₃ / ethanol | Nucleophilic substitution |
| Nitrile | Carboxylic acid | H ₂ O / HCl | Hydrolysis |
| Aldehyde | Hydroxynitrile | NaCN / H ⁺ | Nucleophilic addition |
| Alcohol | Ester | Carboxylic acid / H ₂ SO ₄ | Esterification |
| Carboxylic acid | Ester | Alcohol / H ₂ SO ₄ | Esterification |
| Ester | Carboxylate salt and alcohol | NaOH (aq) | Alkaline hydrolysis |
| Ester | Carboxylic acid | Dilute acid | Acid hydrolysis |



| | | | |
|-----------------|-----------------|-------------------|--------------------------------------|
| Carboxylic acid | Acyl chloride | SOCl ₂ | Chlorination |
| Acyl chloride | Carboxylic acid | H ₂ O | Hydrolysis |
| Acyl chloride | Primary amide | NH ₃ | Nucleophilic addition elimination |
| Acyl chloride | Secondary amide | Primary amine | Nucleophilic addition elimination |

Aromatic Reaction Pathways

- The key aromatic reactions are summarised here:

Aromatic Reactions Table

| Reactant | Product | Reagents | Reaction |
|----------------|---|---|--|
| Benzene | Methylbenzene / toluene | CH ₃ Cl / AlCl ₃ | Alkylation / Electrophilic substitution |
| Benzene | Bromobenzene | Br ₂ / FeBr ₃ | Bromination / Electrophilic substitution |
| Benzene | Chlorobenzene | Cl ₂ / AlCl ₃ | Chlorination / Electrophilic substitution |
| Benzene | Nitrobenzene | HNO ₃ / H ₂ SO ₄ | Nitration / Electrophilic substitution |
| Nitrobenzene | Aminobenzene / phenylamine / aniline | Sn / HCl | Reduction |
| Aminobenzene | 2,4,6-tribromoaminobenzene / 2,4,6-tribromoaniline | Bromine | Electrophilic substitution |
| Benzene | Phenylethanone | CH ₃ COCl / AlCl ₃ | Acylation / Electrophilic substitution |
| Phenylethanone | 1-phenylethanol | NaBH ₄ | Reduction |

Designing a Reaction Pathway

- The given molecule is usually called the **target molecule** and chemists try to design a synthesis as efficiently as possible
- Designing a reaction pathway starts by drawing the structures of the **target molecule** and the **starting molecule**
- Determine if they have the **same number** of carbon atoms
 - If you need to lengthen the carbon chain you will need to put on a **nitrile group** by nucleophilic substitution
- Work out all the compounds that can be made from the starting molecule and all the molecules that can be made into the target molecule
 - Match the groups they have in common and work out the reagents and conditions needed



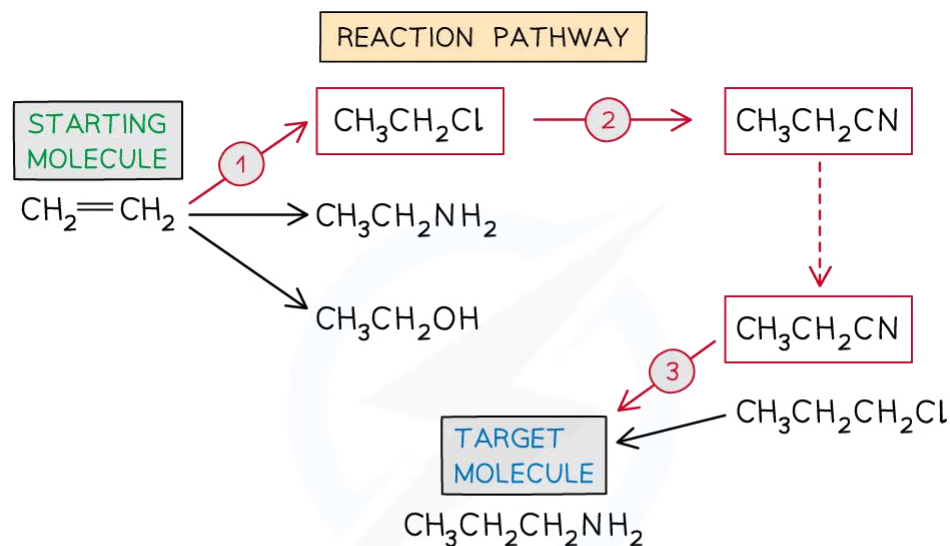
Worked Example

Suggest how the following synthesis could be carried out:

Ethene to 1-aminopropane

Answer

YOUR NOTES



1. REACT WITH HCl AT ROOM TEMPERATURE
2. REACT WITH KCN IN ETHANOL + HEAT UNDER REFLUX
3. REDUCE WITH LiAlH_4 IN DRY ETHER + HEAT

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Exam Tip

Sound knowledge of all of the different reactions is beneficial as the A-level course simply states that you should be able to design a multistage synthesis

Past papers generally go to four steps in a multistep reaction although there is no clear limit stated

6.9 Analytical Techniques

6.9.1 Thin Layer Chromatography, TLC

Thin-Layer Chromatography Practical

- ♦ Thin-layer chromatography (TLC) is a technique used to analyse small samples via separation
 - For example, we could separate a dye out to determine the mixture of dyes in a forensic sample
- ♦ There are 2 phases involved in TLC:
 - **Stationary phase**
 - This phase is commonly thin metal sheet coated in alumina (Al_2O_3) or silica (SiO_2)
 - The solute molecules **adsorb** onto the surface
 - Depending on the strength of interactions with the stationary phase, the separated components will travel particular distances through the plate
 - The more they interact with the stationary phase, the more they will 'stick' to it
 - **Mobile phase**
 - Flows over the stationary phase
 - It is a polar or non-polar liquid (solvent) that carries components of the compound being investigated
 - Polar solvents – water or alcohol
 - Non-polar solvents – alkanes
- ♦ If the sample components are coloured, their spots are easily identifiable on the chromatogram
- ♦ If the sample components are not coloured, then we can **locate** the spots on the chromatogram and draw around them in pencil
 - To **locate** the spots we can use:
 - UV light
 - Ninhydrin (carcinogenic)
 - Iodine vapour

Conducting a TLC analysis

- ♦ **Step 1:**
Prepare a beaker with a small quantity of solvent
- ♦ **Step 2:**
On a TLC plate, draw a horizontal line at the bottom edge (in pencil)

This is called the **baseline**
- ♦ **Step 3:**

Place a spot of pure reference compound on the left of this line, then a spot of the sample to be analysed to the right of the baseline and allow to air dry

YOUR NOTES





The reference compounds will allow identification of the mixture of compounds in the sample

• **Step 4:**

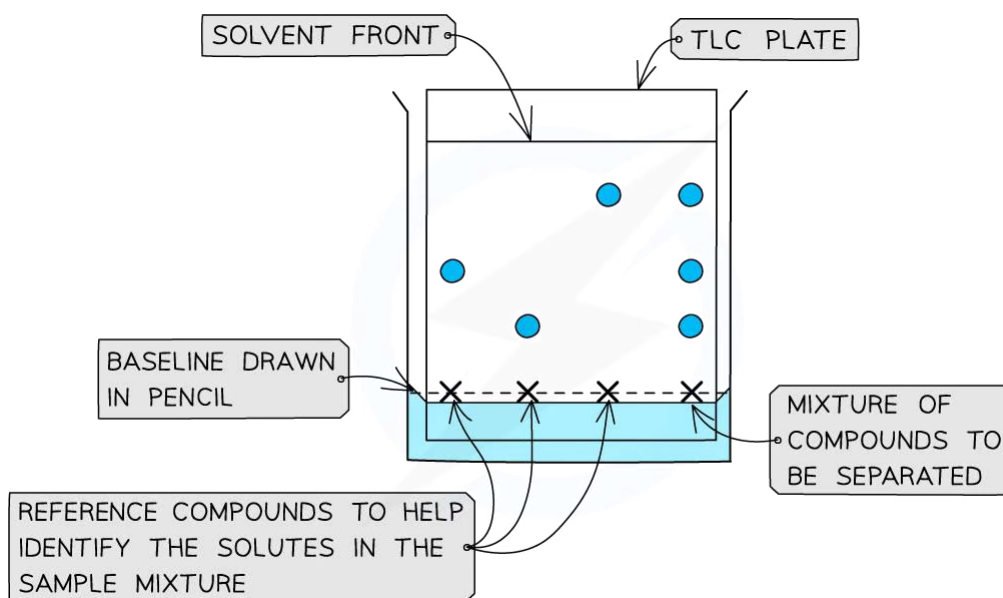
Place the TLC plate inside the beaker with solvent – making sure that the solvent does not cover the spot – and place a lid to cover the beaker

The solvent will begin to travel up the plate, dissolving the compounds as it does

• **Step 5:**

As solvent reaches the top, remove the plate and draw another pencil line where the solvent has reached, indicating the **solvent front**

The sample's components will have separated and travelled up towards this solvent front



A dot of the sample is placed on the baseline and allowed to separate as the mobile phase flows through the stationary phase; The reference compound/s will also move with the solvent

TLC & R_f Values

YOUR NOTES

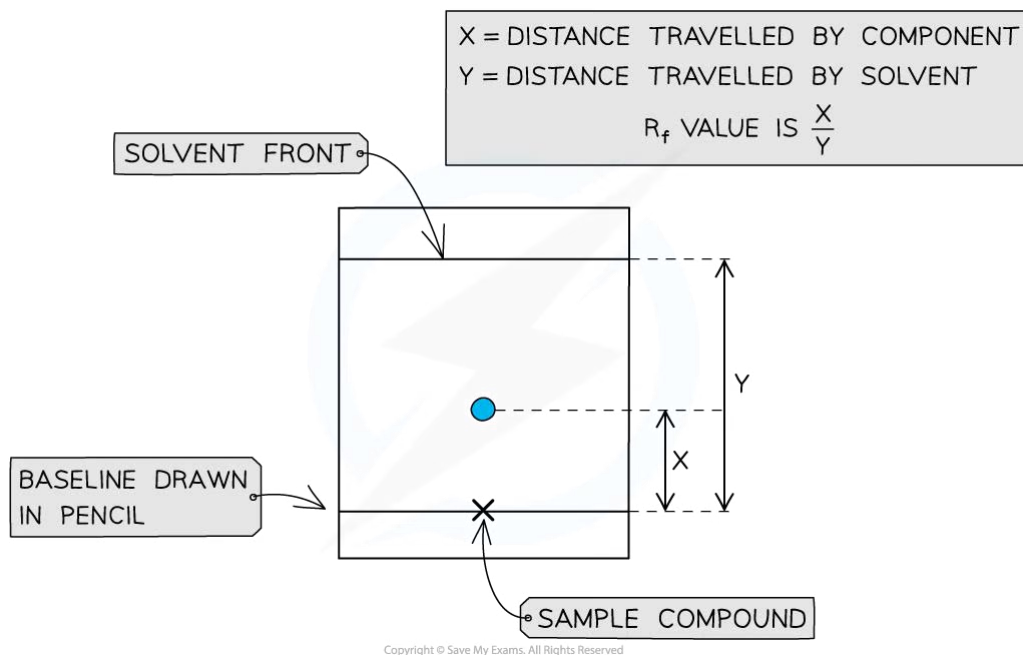


R_f values

- A TLC plate can be used to calculate R_f values for compounds

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

- These values can be used alongside other analytical data to deduce composition of mixtures



R_f values can be calculated by taking 2 measurements from the TLC plate



Exam Tip

The baseline on a TLC plate must be drawn in pencil. Any other medium would interact with the sample component and solvents used in the analysis process.

- The less polar components travel further up the TLC plate
 - Their **R_f values are higher** than those closer to the baseline
 - They are **more soluble** in the mobile phase and get carried forwards with the solvent
- More polar components do not travel far up the plate
 - They are more attracted to the polar stationary phase
- The extent of separating molecules in the investigated sample depends on the solubility in the mobile and stationary phases

- Knowing the R_f values, of compounds being analysed, helps to compare the polarity of various molecules

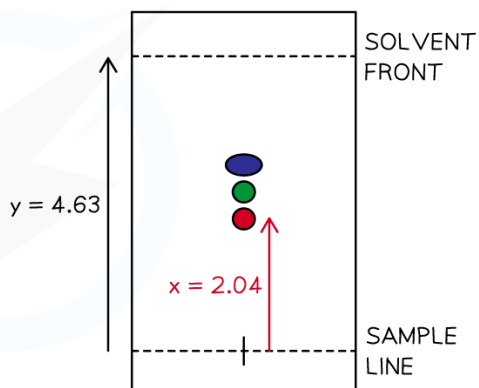
YOUR NOTES



? Worked Example

A mixture of amino acids is analysed by thin layer chromatography (TLC). The TLC plate produced is shown below. Identify the amino acids in the sample using the table of values for R_f .

| Amino acid | R_f value |
|---------------|-------------|
| Alanine | 0.33 |
| Aspartic acid | 0.24 |
| Valine | 0.44 |
| Leucine | 0.61 |
| Cysteine | 0.37 |
| Isoleucine | 0.53 |



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Answers:

Blue spot R_f value = $2.82 \div 4.63 = 0.61 =$ Leucine

Green spot R_f value = $2.45 \div 4.63 = 0.536 =$ Isoleucine

Red spot R_f value = $2.04 \div 4.63 = 0.44 =$ Valine

6.9.2 Gas Chromatography, GC

Interpreting Gas Chromatograms

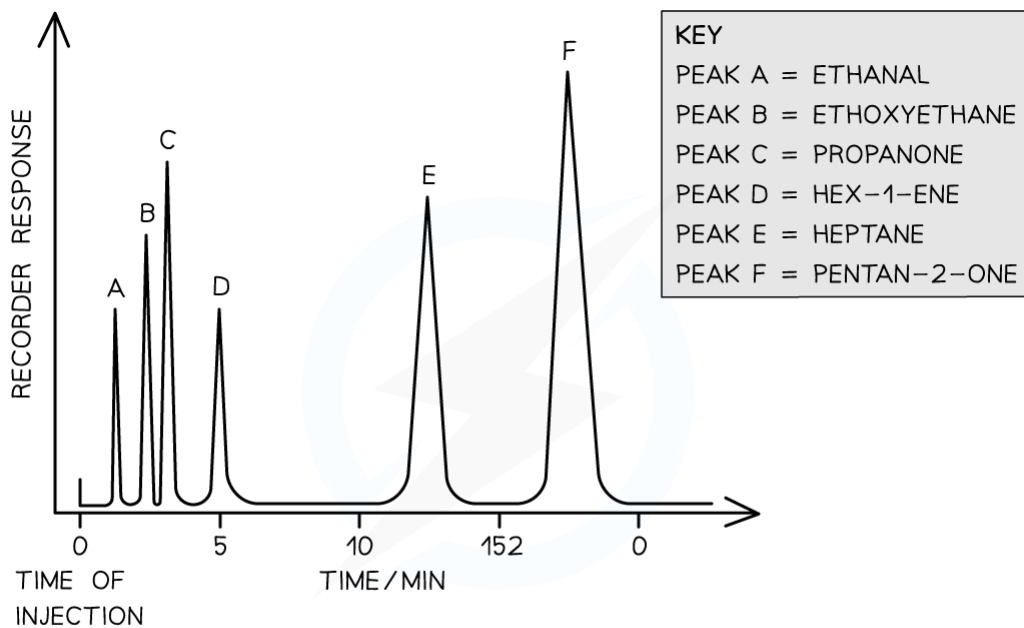
- ♦ Gas-Liquid Chromatography (GLC) is used for analysing:
 - Gases
 - Volatile liquids
 - Solids in their vapour form
- ♦ The stationary phase:
 - This method uses a long coiled column for the stationary phase
 - Normally a non-volatile liquid is the stationary phase in GLC
- ♦ The Mobile phase
 - An **inert** carrier gas (e.g. helium, nitrogen) moves the sample molecules through the stationary phase
- ♦ The sample is injected into the column through a self-sealing disc and the vapour formed is carried through the stationary phase using the inert-gas mobile phase

Retention times

- ♦ Once sample molecules reach the detector, their **retention times** are recorded
 - This is the time taken for a component to travel through the column
 - It depends upon the attraction between the solute and the stationary and mobile phases as well as the volatility and nature of the solute
- ♦ The retention times are recorded on a chromatogram where each peak represents a volatile compound in the analysed sample
 - The relative sizes (i.e. areas) of the peaks are related to how much of each compound is present in the mixture
- ♦ Retention times are then compared with data book values to identify unknown molecules

YOUR NOTES





THE RETENTION TIME OF EACH PEAK IS DEPENDANT ON THE TIME TAKEN FOR THE SAMPLE MOLECULES TO TRAVEL THROUGH THE GLC COLUMN

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A gas chromatogram of a volatile sample compound has six peaks. Depending on each molecule's interaction with the stationary phase, each peak has its own retention time

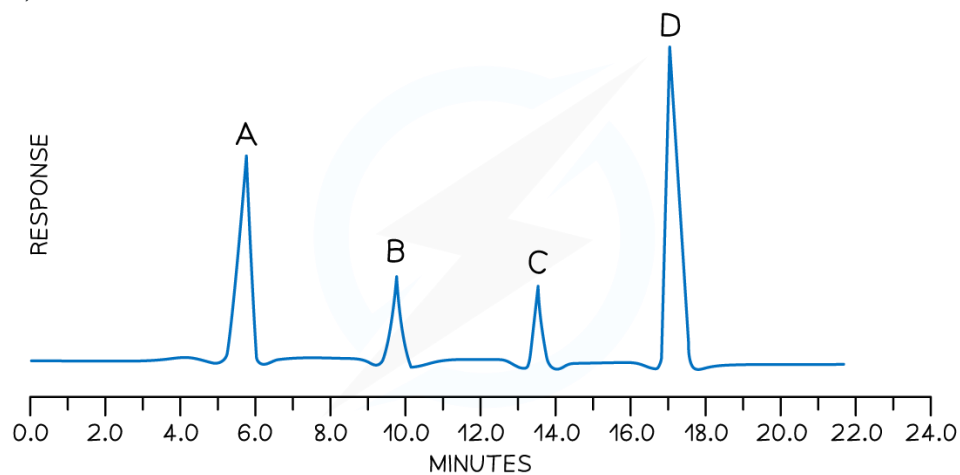
YOUR NOTES





Worked Example

Analysis of a compound by GLC shows the presence of four components, **A**, **B**, **C** and **D**.



- Which compound is present in the greatest quantity?
- Which compounds were present in equal amounts?
- Which compound had the strongest interaction with the stationary phase?

Answers:

- D** (the larger the relative size of the peak, the greater the quantity of that substance present)
- B** and **C** (the peak sizes are equal)
- D** (the larger the retention time, the greater the interaction of that component with the stationary phase)

6.9.3 Qualitative Analysis

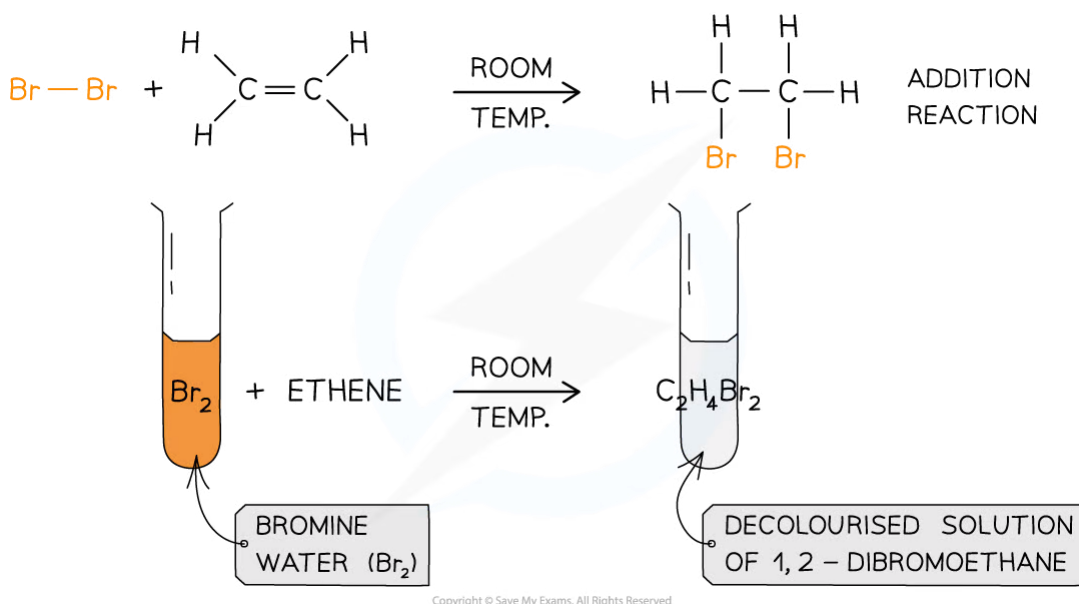
Testing for Alkenes & Haloalkanes

YOUR NOTES



Testing for an Alkene

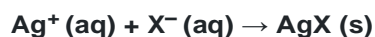
- Halogens can be used to test if a molecule is **unsaturated** (i.e. contains a double bond)
- $\text{Br}_2(\text{aq})$ is an orange-yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise



The bromine water test is the standard test for unsaturation in alkenes

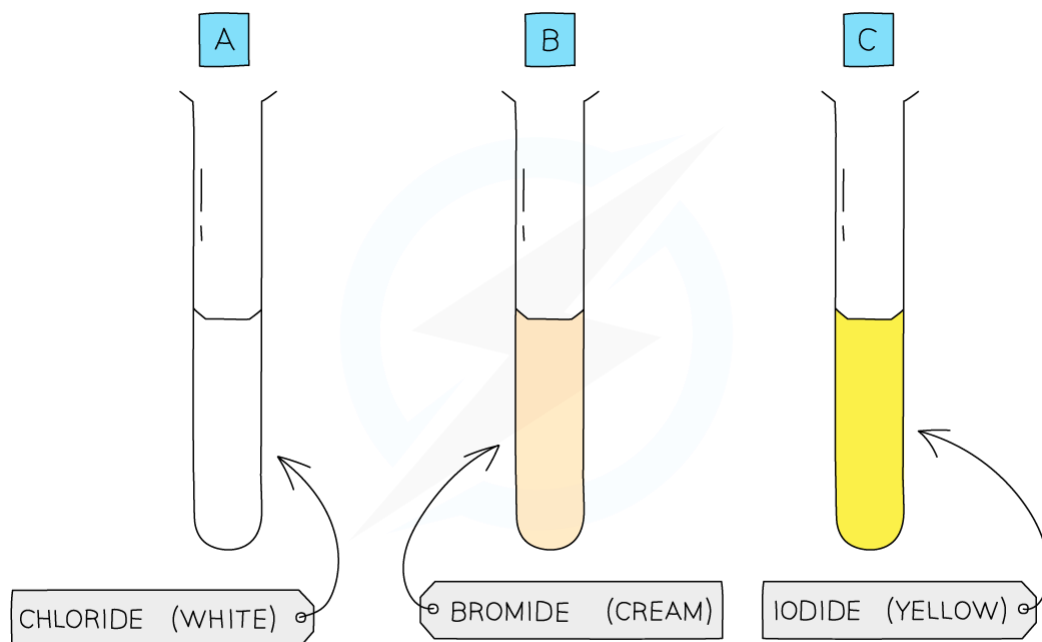
Testing for a haloalkane

- The haloalkane must first be warmed with sodium hydroxide in a mixture of ethanol and water
- The haloalkane will undergo nucleophilic substitution releasing the halide ion into solution, which can then be tested
- The released halide ion is tested for using the silver nitrate test:
 - Acidify the sample with dilute nitric acid (HNO_3) followed by the addition of silver nitrate solution, AgNO_3
 - The acidification is done to remove carbonate ions that might give a false positive result
 - If a halide is present it forms a silver halide precipitate:



- Depending on the halide present, a **different coloured precipitate** is formed, allowing for identification of the halide ion
 - Silver chloride is **white**, silver bromide is **cream** and silver iodide is **yellow**

Each silver halide produces a precipitate of a different colour



Exam Tip

The acidification step in the halide ion test must be done with nitric acid rather than hydrochloric acid, as HCl contains chloride ions which would interfere with the results.

YOUR NOTES



Testing for Carbonyls & Alcohols

Testing for a carbonyl

2,4-dinitrophenylhydrazine or Brady's reagent

- 2,4-dinitrophenylhydrazine (2,4-DNP or 2,4-DNPH) is used to test for the presence of a carbonyl group, C=O
 - 2,4-DNP is usually dissolved in methanol and sulfuric acid
 - It is a pale orange solution
- A few drops of the unknown sample are added to 5.0 cm³ of 2,4-DNP and it left to stand
- A few drops of sulfuric acid are then added to the mixture
 - The formation of an orange / yellow precipitate of 2,4-dinitrophenylhydrazone confirms the presence of an aldehyde or ketone



Exam Tip

It is more common to use other chemical tests to more specifically check for the presence of an aldehyde or a ketone because:

1. Brady's reagent / 2,4-DNP only confirms the presence of a carbonyl group, it does not distinguish between an aldehyde and a ketone
2. Friction or sudden impacts can cause solid 2,4-DNP to explode

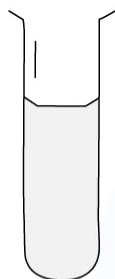
Testing for an Aldehyde

Tollens' reagent

- Tollens' reagent is an aqueous alkaline solution of silver nitrate in excess ammonia solution
 - Tollens' reagent is also called **ammoniacal silver nitrate solution**
- When **warmed** with an aldehyde, the aldehyde is oxidised to a carboxylic acid and the Ag⁺ ions are reduced to Ag atoms
 - In the alkaline conditions, the carboxylic acid will become a carboxylate ion and form a salt
- The Ag atoms form a silver 'mirror' on the inside of the tube
- **Ketones** cannot be oxidised and therefore give a **negative test** when warmed with Tollens' reagent

YOUR NOTES





TOLLEN'S SOLUTION
WITH Ag^+ IONS



A SILVER 'MIRROR' OF Ag
ATOMS IS FORMED AS:
- Ag^+ IS REDUCED TO Ag
- ALDEHYDE IS OXIDISED
TO CARBOXYLIC ACID

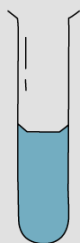
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The Ag^+ ions in Tollens' reagent are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms

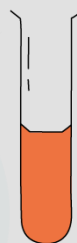


Exam Tip

- Fehling's solution can also be used to test for an aldehyde
- An aldehyde cause a change from a blue solution to a orange / brick-red precipitate
- There is no visible change for a ketone



CLEAR BLUE FEHLING'S
SOLUTION WITH Cu^{2+} IONS



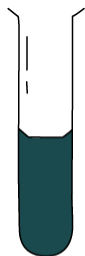
OPAQUE RED PRECIPITATE OF Cu_2O AS:
- Cu^{2+} IS REDUCED TO Cu^+
- ALDEHYDE IS OXIDISED TO
CARBOXYLIC ACID

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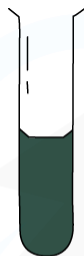
Testing an Alcohol

- Alcohols can be classified as either primary, secondary or tertiary, depending on the placement of the $-\text{OH}$ group
- Primary and secondary alcohols can both be oxidised, but tertiary alcohols cannot
- To test for the alcohol functional group, add a small amount (1 cm^3) of the substance to a test tube using a pipette
- Then, add a small amount (1 cm^3) of a suitable oxidising agent to the sample using a different pipette

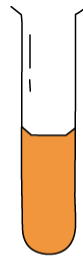
- The most commonly used oxidising agent for this test is acidified potassium dichromate solution ($K_2Cr_2O_7$, acidified with H_2SO_4)
- Add a stopper to the test tube and shake well
- Place in a hot water bath (heated to around $60\text{ }^\circ\text{C}$) for a few minutes
- If a primary or secondary alcohol are present, then the colour will change from orange to green
 - If a tertiary alcohol is present, then nothing will happen – the solution will remain orange



PROPAN-1-OL
(PRIMARY ALCOHOL)



PROPAN-2-OL
(SECONDARY ALCOHOL)



2-METHYL-PROPAN-2-OL
(TERTIARY ALCOHOL)

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Positive test results of the oxidation of a primary, secondary and tertiary alcohol



Exam Tip

When heated with acidified potassium dichromate, an aldehyde will also cause a colour change from orange to green

YOUR NOTES



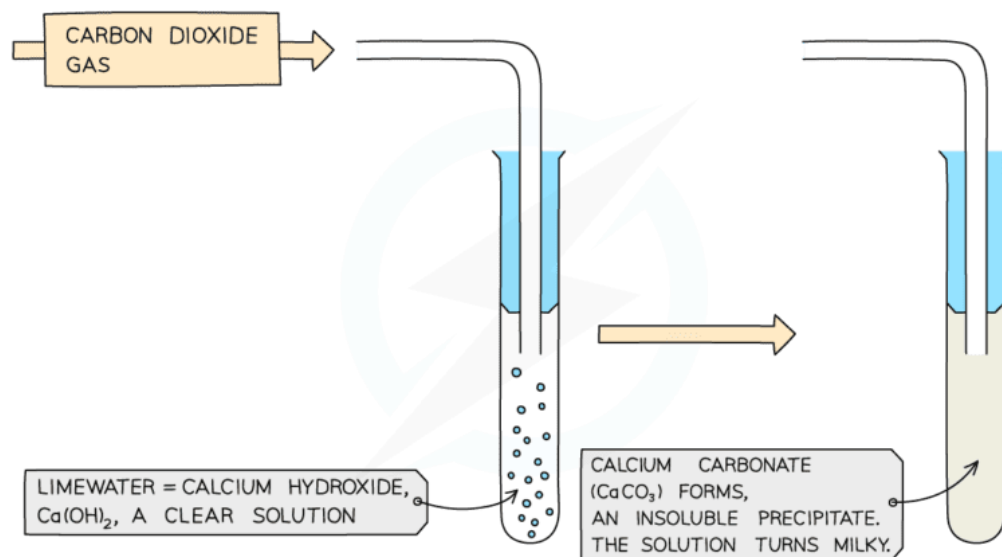
Testing for Carboxylic Acids & Phenols

YOUR NOTES



Testing for a Carboxylic Acid

- Carboxylic acids in solution have a pH of around 3, so measuring the pH is a way of testing for the presence of the carboxylic acid functional group in an organic sample
- The end of a glass rod could be dipped into the solution and then carefully dripped onto indicator paper
- Or, a pH probe could be used, which would give you an exact pH
- Since carboxylic acids are acids, they will react with a carbonate solution to produce carbon dioxide gas
- 1–2 cm³ of sodium carbonate (Na₂CO₃) or sodium hydrogen carbonate (NaHCO₃) could be added using a pipette
- If bubbles of gas are seen, this is a good indicator that the solution is a carboxylic acid
 - If an exam question asks you to simply distinguish between different types of organic compound, and the carboxylic acid is the only organic compound present which would react in this way with a carbonate solution, then this is enough
- The gas produced could then be bubbled into limewater
- If the limewater turns milky or cloudy, then this proves that the gas produced was carbon dioxide



Testing for Phenols

- **Bromine water** can be used to test if a molecule is **phenolic** (i.e. contains phenol)
- The unknown compound is **shaken** with the bromine water

- ♦ If the compound contains phenol, a substitution reaction will take place and the coloured bromine water will decolourise and then a white precipitate will form

YOUR NOTES



6.9.4 Carbon-13 NMR

YOUR NOTES



Carbon-13 NMR

- Nuclear Magnetic Resonance (NMR) spectroscopy is used for analysing organic compounds
- Atoms with odd mass numbers usually show signals on NMR
 - For example, isotopes of atoms
 - Many of the carbon atoms on organic molecules are carbon-12
 - A small quantity of organic molecules will contain the isotope carbon-13 atoms
 - These will show signals on a ^{13}C NMR
- In ^{13}C NMR, the magnetic field strengths of carbon-13 atoms in organic compounds are measured and recorded on a spectrum
- Just as in ^1H NMR, all samples are measured against a reference compound – Tetramethylsilane (TMS)
- On a ^{13}C NMR spectrum, non-equivalent carbon atoms appear as peaks with different chemical shifts

Chemical shift values (relative to the TMS) for ^{13}C NMR analysis table

| Environment of carbon | Groups | Chemical shift range δ / ppm |
|-----------------------------------|----------------------------|-------------------------------------|
| $-\text{CH}_2-\text{CH}_2-$ | Alkyl | 5–40 |
| RCH_2Cl or Br | Halogenoalkanes | 10–70 |
| RCOCH_2- | Carbonyls | 20–50 |
| RCH_2NH_2 | Amines | 25–60 |
| $-\text{CH}_2-\text{O}-$ | Alcohols, ethers or esters | 50–90 |
| $-\text{CH}=\text{CH}-$ | Alkenyl | 90–150 |
| $\text{R}-\text{C}\equiv\text{N}$ | Nitriles | 110–125 |
| C_6H_6 | Benzene | 110–160 |
| $\text{R}-\text{COO}-$ | Ester or acids | 160–185 |
| $\text{R}-\text{CO}-$ | Aldehyde or ketones | 190–220 |

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Features of a ^{13}C NMR spectrum

- ^{13}C NMR spectrum displays sharp single signals
 - There are no complicated splitting patterns like ^1H NMR spectra

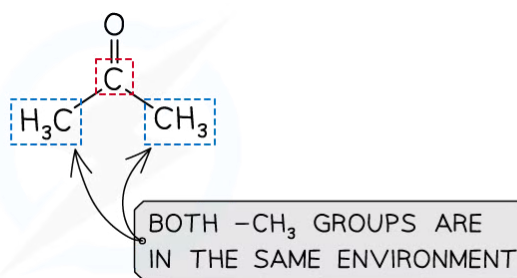
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- The height of each signal is **not proportional** to the number of carbon atoms present in a single molecular environment
- Carbon atoms in different chemical environments will give resonances at different chemical shifts in a ^{13}C spectrum
- As with ^1H NMR, tetramethylsilane is used as the standard reference point for ^{13}C at 0 ppm

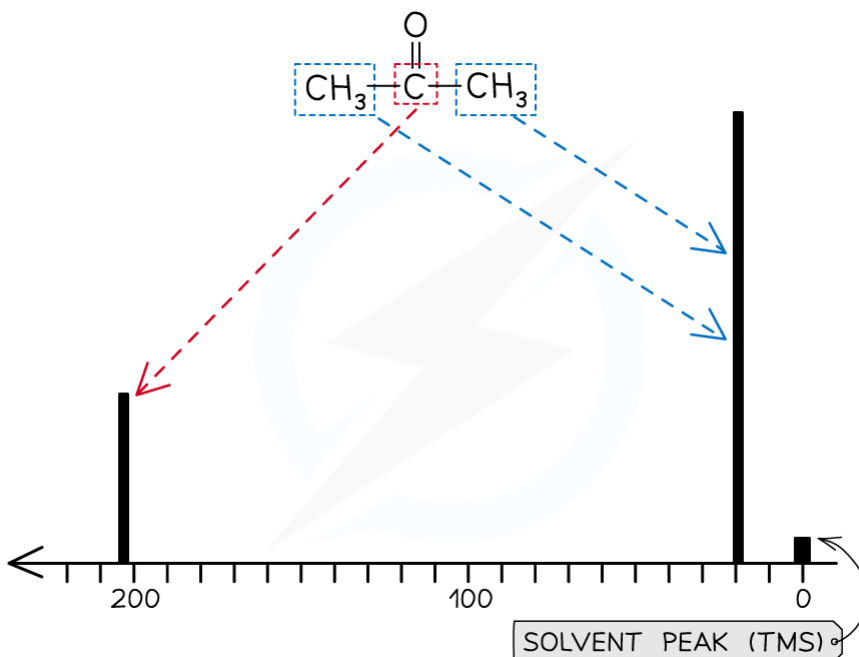
Identifying ^{13}C molecular environments

- On an organic molecule, the carbon-13 environments can be identified in a similar way to the proton environments in ^1H NMR
- For example propanone
 - There are 2 molecular environments
 - 2 signals will be present on its ^{13}C NMR spectrum



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There are 2 molecular environments in propanone



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The ^{13}C NMR of propanone showing 2 signals for the 2 molecular environments



Exam Tip

Counting the number of ^{13}C resonances should be the first step in analysing a spectrum. For example, it is possible to differentiate the three isomers of dihydroxybenzene quickly by considering the symmetry of the molecules and therefore the number of resonances expected in their spectra.

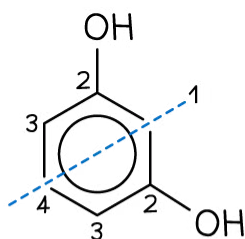


Worked Example

How many chemical environments and therefore number of peaks / resonances would be in a ^{13}C spectra of 1,3-dihydroxybenzene?

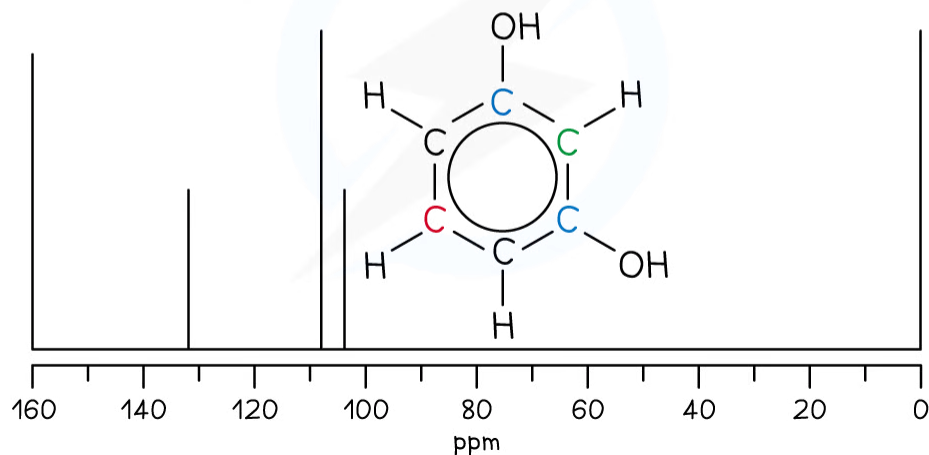
Answer:

4 chemical environments and therefore four peaks / resonances on the spectra



1,3-DIHYDROXYBENZENE
(4 CHEMICAL ENVIRONMENTS)

1,3-DIHYDROXYBENZENE



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6.9.5 Proton NMR

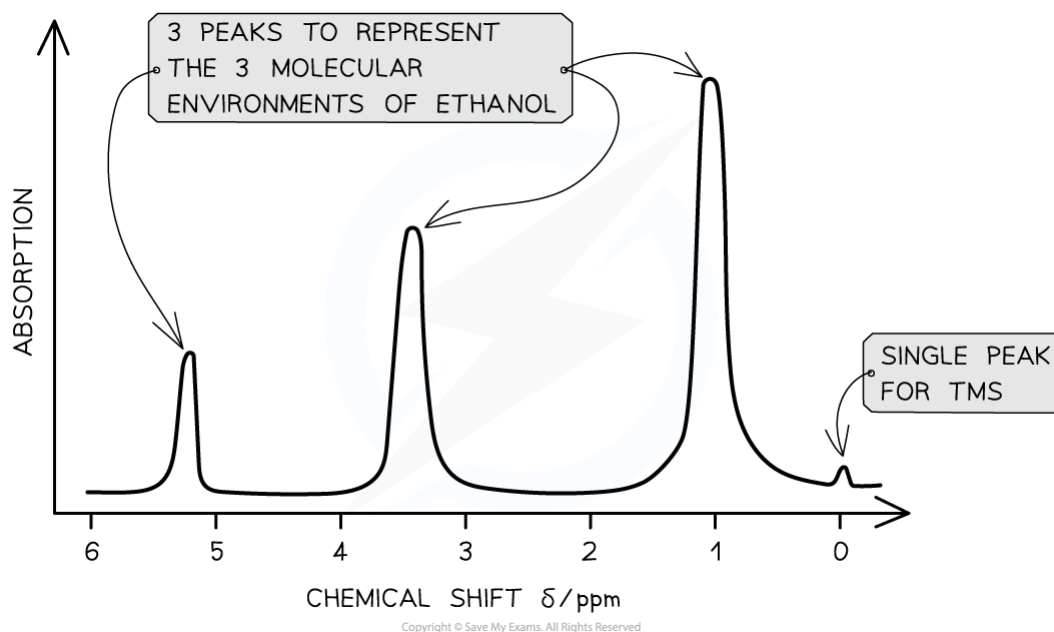
YOUR NOTES



Low & High Resolution Proton NMR

Features of a ^1H NMR spectrum

- An NMR spectrum shows the intensity of each peak against its chemical shift
- The area under each peak gives information about the number of protons in a particular environment
- The area under each peak shows the intensity / absorption from protons
- A single sharp peak is seen to the far right of the spectrum
 - This is the reference peak from TMS
 - By definition the chemical shift is at 0 ppm



A low resolution ^1H NMR for ethanol showing the key features of a spectrum

Molecular environments

- ^1H nuclei that have different neighbouring atoms (said to have different **chemical environments**) absorb at slightly different field strengths
- The different environments are said to cause a **chemical shift** away from TMS
 - Ethanol has the structural formula $\text{CH}_3\text{CH}_2\text{OH}$
 - There are 3 chemical environments: $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{OH}$
- The hydrogen atoms in these environments will appear at 3 different chemical shifts
- Different types of protons are given their own range of chemical shifts



Worked Example

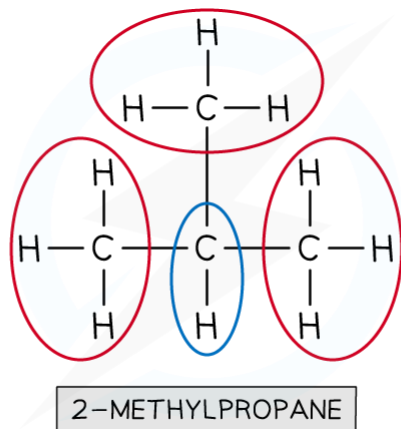
How many different ^1H chemical environments occur in 2-methylpropane?



Answer:

Two different ^1H chemical environments occur in 2-methylpropane

- The three methyl groups are in the same ^1H environment
- The lone hydrogen is in its own ^1H environment



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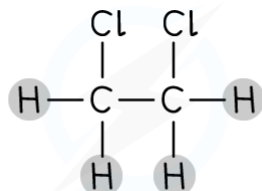
Chemical shift values for ^1H molecular environments table



| Environment of proton | Chemical shift range δ /ppm |
|--------------------------------|------------------------------------|
| ROH | 0.5–5.5 |
| RCH ₃ | 0.7–1.2 |
| RNH ₂ | 1.0–4.5 |
| R ₂ CH ₂ | 1.2–1.4 |
| R ₃ CH | 1.4–1.6 |
| RCOCH– | 2.1–2.6 |
| ROCH– | 3.1–3.9 |
| RCH ₂ Cl or Br | 3.1–4.2 |
| RCOOCH– | 3.7–4.1 |
| RC=CH– | 4.5–6.0 |
| RCHO | 9.0–10.0 |
| RCOOH | 10.0–12.0 |

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- ♦ Protons in the same chemical environment are chemically equivalent
 - 1,2-dichloroethane, Cl-CH₂-CH₂-Cl has one chemical environment as these four hydrogens are all exactly equivalent
- ♦ Each individual peak on a ¹H NMR spectrum relates to protons in the same environment
 - Therefore, 1,2-dichloroethane would produce one single peak on the NMR spectrum as the protons are in the same environment



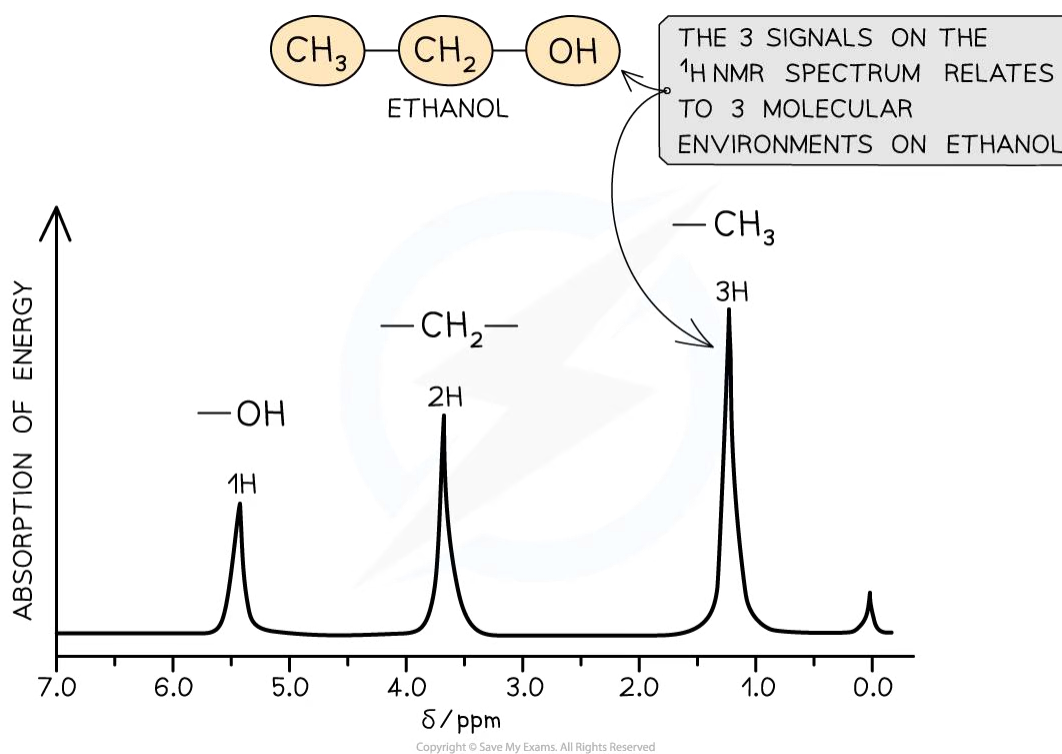
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Low resolution ¹H NMR

- ♦ Peaks on a low resolution NMR spectrum refer to molecular environments of an organic compound



- Ethanol has the molecular formula $\text{CH}_3\text{CH}_2\text{OH}$
- This molecule has 3 separate proton environments: $-\text{CH}_3$, $-\text{CH}_2$, $-\text{OH}$
- So 3 peaks would be seen on its spectrum at 1.2 ppm ($-\text{CH}_3$), 3.7 ppm ($-\text{CH}_2$) and 5.4 ppm ($-\text{OH}$)
- The strengths of the absorptions are proportional to the number of equivalent ^1H atoms and are proportional to the area underneath each absorption peak
- Hence, the areas of absorptions of $-\text{CH}_3$, $-\text{CH}_2$, $-\text{OH}$ are in the ratio of 3:2:1 respectively



A low resolution NMR spectrum of ethanol showing 3 peaks for the 3 molecular environments

High resolution ^1H NMR

- More structural details can be deduced using high resolution NMR
- The peaks observed on a high resolution NMR may sometimes have smaller peaks clustered together
- The splitting pattern of each peak is determined by the number of protons in neighbouring environments

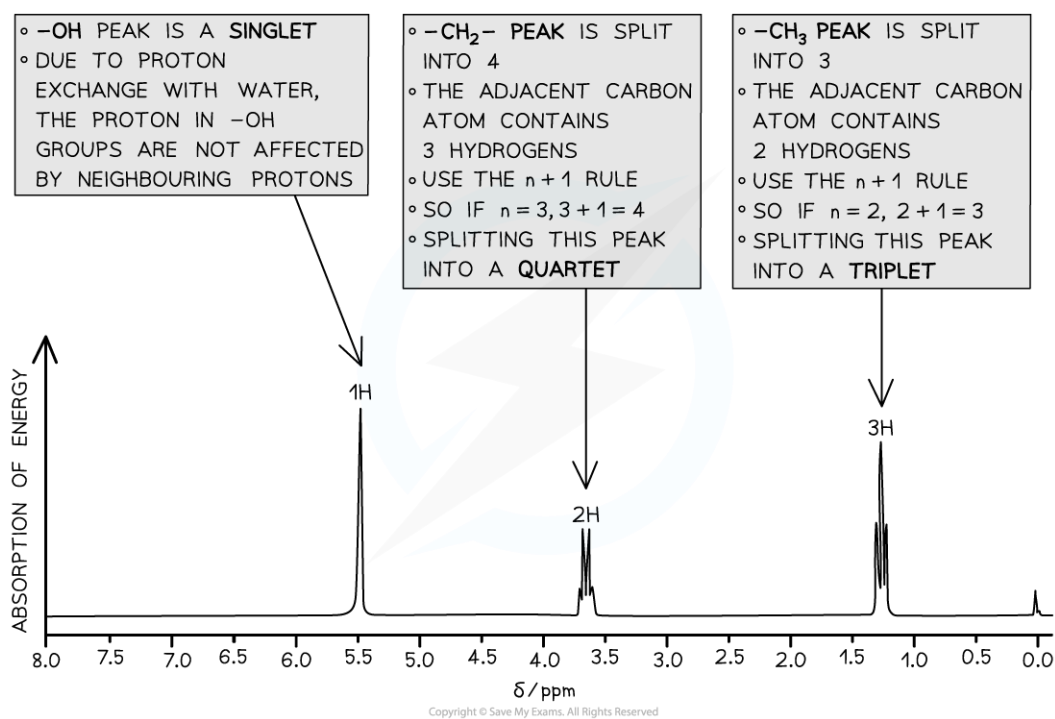
Spin-Spin Splitting Patterns

YOUR NOTES



Spin-Spin Splitting

- A high resolution ^1H NMR spectrum can show you the structure of the molecule but also the peaks can be split into sub-peaks or splitting patterns
- These are caused by a proton's spin interacting with the spin states of nearby protons that are in different environments
 - This can provide information about the number of protons bonded to adjacent carbon atoms
 - The splitting of a main peak into sub-peaks is called spin-spin splitting or spin-spin coupling



High resolution ^1H NMR spectrum of ethanol showing the splitting patterns of each of the 3 peaks. Using the $n+1$, it is possible to interpret the splitting pattern



Exam Tip



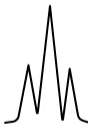

- It is very rare that the spin-spin splitting of equivalent protons is covered in teaching because it is so rarely asked in exams
- Equivalent protons do **not** cause spin-spin splitting
 - The simplest example of this is benzene
 - In benzene, all of the protons are equivalent
 - This means that they are seen as one singlet in the high resolution ^1H NMR spectrum of benzene

The $n+1$ rule



- The number of sub-peaks is one greater than the number of adjacent protons causing the splitting
 - For a proton with n protons attached to an adjacent carbon atom, the number of sub-peaks in a splitting pattern = $n+1$
- When analysing spin-spin splitting, it shows you the number of hydrogen atoms on the adjacent carbon atom
- These are the splitting patterns that you need to be able to recognise from a ^1H spectra:

^1H NMR peak splitting patterns table

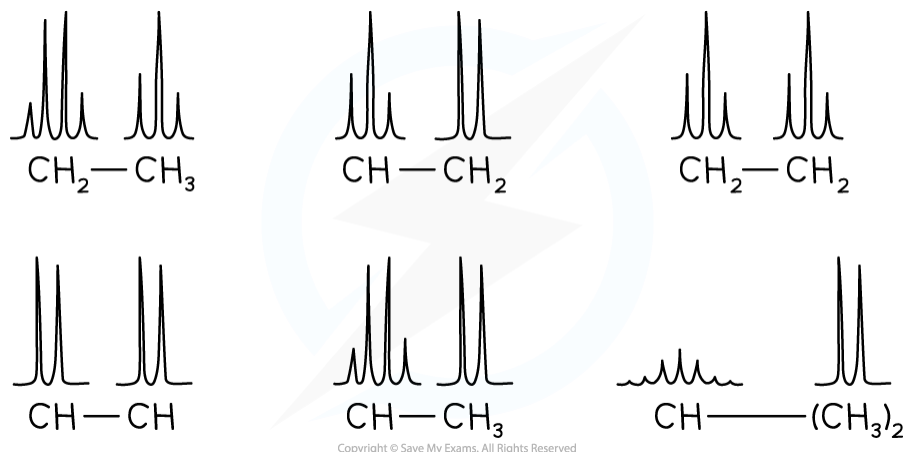
| Number of adjacent protons (n) | Splitting pattern using the $n+1$ rule the peak will split into... | Relative intensities in splitting pattern | Shape |
|------------------------------------|--|---|---|
| 0 | 1, singlet | 1 |  |
| 1 | 2, doublet | 1:1 |  |
| 2 | 3, triplet | 1:2:1 |  |
| 3 | 4, quartet | 1:3:3:1 |  |

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- Splitting patterns must occur in pairs, because each protons splits the signal of the other
- There are some common splitting pairs you will see in a spectrum however you don't need to learn these but can be worked out using the $n+1$ rule
 - You will quickly come to recognise the triplet / quartet combination for a CH_3CH_2 because it is so common

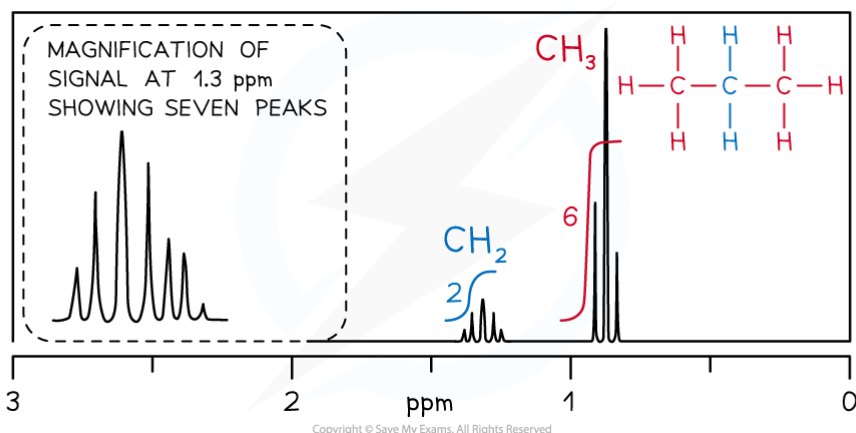
Common pair of splitting patterns

- A quartet and a triplet in the same spectrum usually indicate an ethyl group, CH_3CH_2-
- The signal from the CH_3 protons is split as a triplet by having two neighbours
- The signal from the CH_2 protons is split as a quartet by having three neighbours
- Here are some more common pairs of splitting patterns



Common pairs of splitting patterns

^1H NMR spectrum of propane



- The CH_2 signal in propane (blue) is observed as a heptet because it has six neighbouring equivalent H atoms ($n+1$ rule), three either side in two equivalent CH_3 groups
- The CH_3 groups (red) produce identical triplets by coupling with the CH_2 group

? Worked Example

For the compound $(\text{CH}_3)_2\text{CHOH}$ predict the following:

- the number of peaks
- the type of proton and chemical shift (using the Data sheet)
- the relative peak areas
- the splitting pattern

Answers:

- 3 peaks

- ii) $(\text{CH}_3)_2\text{CHOH}$ at 0.7 – 1.2 ppm, $(\text{CH}_3)_2\text{CHOH}$ at 3.1 – 3.9 ppm, $(\text{CH}_3)_2\text{CHOH}$ at 0.5 – 5.5 ppm
- iii) Ratio 6 : 1 : 1
- iv) $(\text{CH}_3)_2\text{CHOH}$ split into a doublet ($1+1=2$), $(\text{CH}_3)_2\text{CHOH}$ split into a heptet ($6+1=7$)

YOUR NOTES



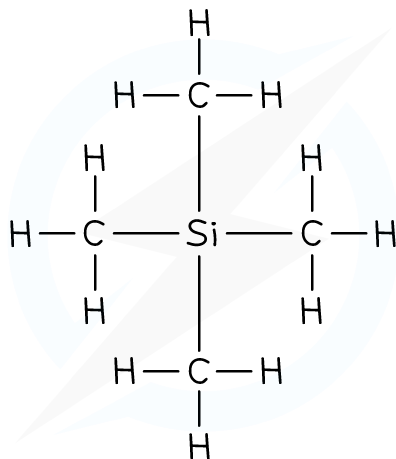
Tetramethylsilane as a Standard

YOUR NOTES



Tetramethylsilane

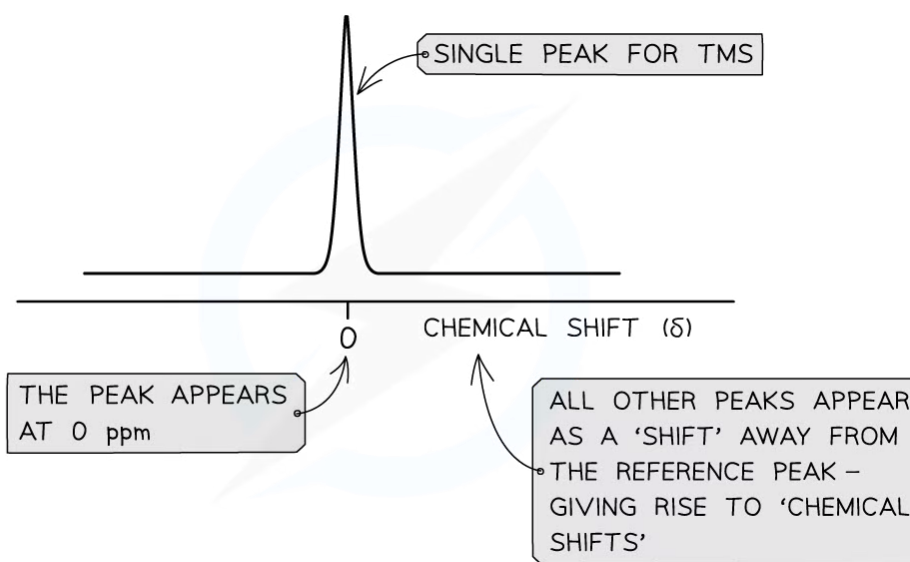
- The horizontal scale on an NMR spectrum represents **chemical shift (δ)**
- Chemical shift is measured in parts per million (ppm) of the radio frequency needed for resonance compared to a reference chemical called tetramethylsilane, abbreviated to **TMS**



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The displayed formula of tetramethylsilane

- TMS is used universally as the reference compound for NMR as its methyl groups are particularly well shielded and so it produces a strong, single peak at the far right of an NMR spectrum
- The signal from the hydrogen atoms in TMS is defined as having a chemical shift of 0 ppm



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The NMR reference peak for TMS



Hydroxyl and amino protons

- Organic compounds often contain protons from part of a functional group rather than being bonded to a carbon, examples include:
 - Alcohols, ROH
 - Carboxylic acids, RCOOH
 - Phenols, ArOH
 - Amines, RNH₂
 - Amides, RCONH₂
 - Amino acids, H₂NCHRCOOH
- These hydroxyl, OH, protons and amino, NH, protons can be involved in hydrogen bonding which causes their peaks to be broader than normal and they can appear at almost any chemical shift
 - The broadening of the peak means that they are not usually involved in spin-spin coupling and therefore appear as singlets

Deuterated solvents

- Deuterated solvents such as D₂O (heavy water) and CDCl₃ can be used to identify OH and NH protons
- This is achieved by:
 - Performing a standard proton NMR on the sample compound
 - A small amount of the deuterated solvent is added to the sample compound and mixed
 - A second proton NMR is then performed
- Deuterium atoms from the solvent replace the OH and NH protons in the sample, e.g for ethanol



- This means that the second proton NMR will still have the peaks for the CH₃ and CH₂ protons of ethanol but will not have the OH peak as that proton has been **exchanged**

6.9.6 Combined Techniques

Deducing Organic Structures

- ♦ Organic chemists use a variety of techniques to determine an organic structure
 - In real laboratory practice, certain pieces of information might already be known as target molecules are often tested once they are produced to check that the reaction has gone as planned
- ♦ The typical sequence using the common analytical techniques would be:
 1. Elemental analysis – to determine the empirical formula
 2. Mass spectrometry – to determine the molecular mass, and consequently the molecular formula, as well as fragments of the molecule
 3. Infrared spectrometry – to primarily identify functional groups but also identify types of bond, e.g. C-C, C=C
 4. NMR spectrometry – to determine the number of carbon / hydrogen atoms and their environments
- ♦ Each technique provides valuable information that can be used to propose a structure, although some techniques provide more information than others
 - Elemental analysis is sometimes skipped as the combination of mass spectrometry and NMR can suggest the molecular formula without the need for elemental analysis

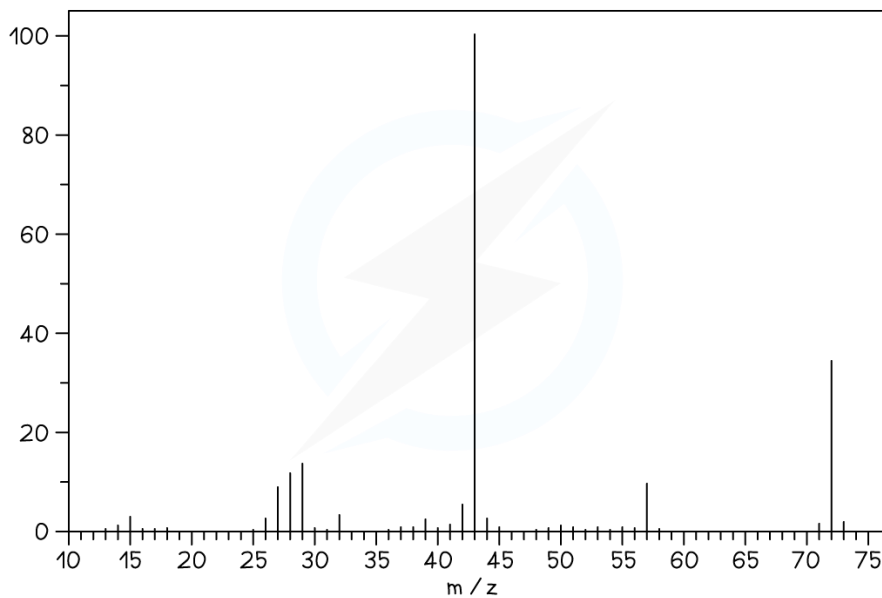
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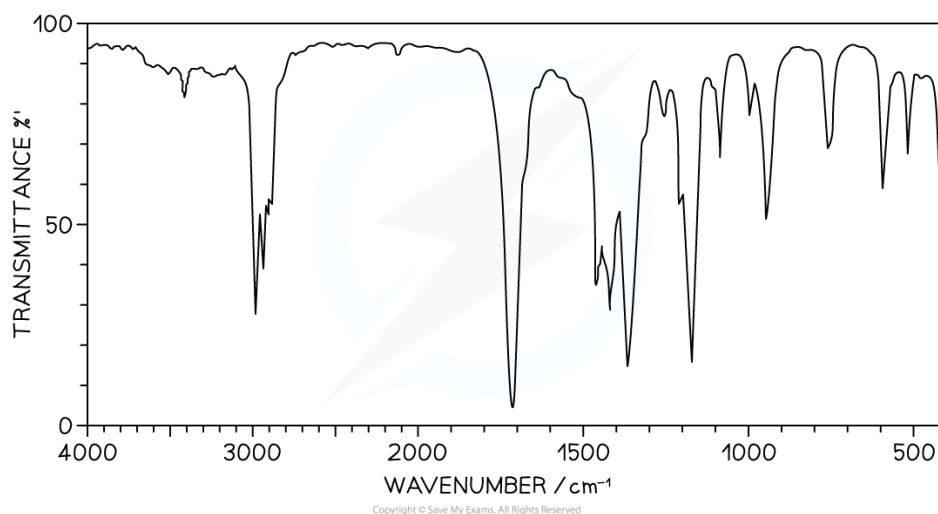


Worked Example

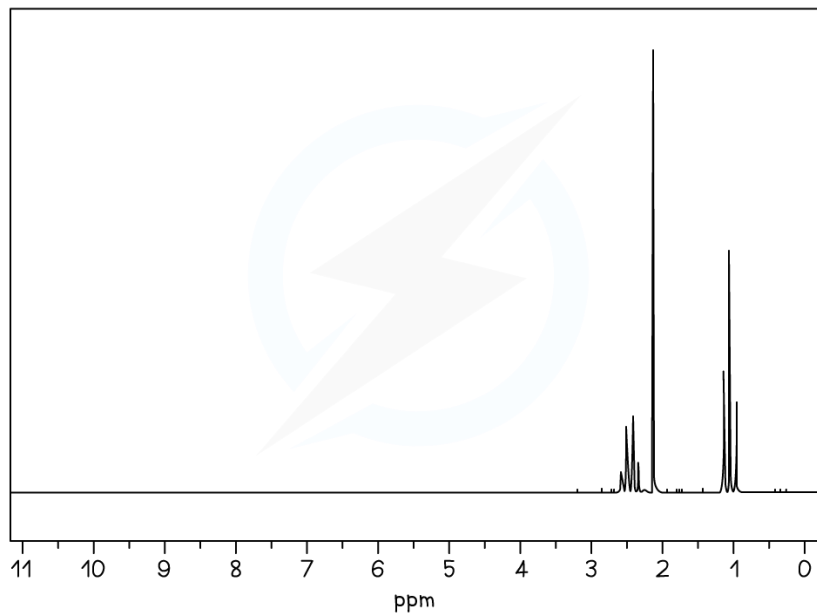
An unknown compound, X, of molecular formula, C_4H_8O , has the following MS, IR and 1H NMR spectra.



MS of X



IR spectrum of X



¹H NMR spectrum of X

Deduce the structure of X using the information given and any other additional information in the Data booklet. For each spectrum assign as much spectroscopic information as possible.

Answer

Mass Spectrum

- The molecular ion peak is at $m/z = 72$, which corresponds to the relative molecular mass of C_4H_8O
- $$M_r = (12 \times 4) + (8 \times 1) + (16) = 72$$
- The large peak at $m/z = 43$ could correspond to $CH_3CH_2CH_2^+$ or CH_3CO^+ indicating the loss of CH_4O or C_2H_5 from X, that is $(M_r - 43)$
 - The peak at $m/z = 29$ could correspond to $CH_3CH_2^+$ indicating the loss of C_2H_3O from X, that is $(M_r - 29)$

IR Spectrum

- There is a strong absorption in the range $1700-1750\text{ cm}^{-1}$ which corresponds to $C=O$, based on Section 26 of the Data book
- This suggests an aldehyde or ketone is present (it cannot be an ester or carboxylic acid as only one oxygen is in the formula)

¹H NMR Spectrum

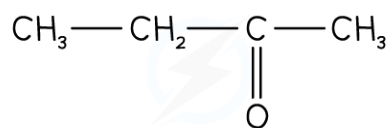
- The ¹H NMR spectrum shows three proton environments
- The peak around chemical shift 1.0 ppm could correspond to a proton on the end of a chain, $-CH_3$

- The peaks around chemical shift 2.2 – 2.7 ppm could correspond to a proton next to a carbonyl group $\text{RCH}_2\text{CO}-$
- The peak splitting is a quartet, singlet and triplet
- A quartet and triplet in the same spectrum usually corresponds to an ethyl group, CH_3CH_2 , following the $n+1$ rule
- The singlet indicates an isolated proton environment

YOUR NOTES



Putting the information together the structure of X is



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The structure of X is butanone