

Edexcel IAL Chemistry A-level

Topic 15: Organic Chemistry: Carbonyls, Carboxylic Acids and Chirality

Detailed notes

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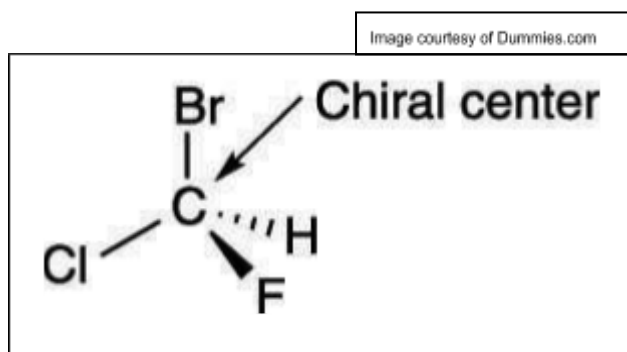


15A: Chirality

Chiral Centres

A chiral centre is a carbon atom with **four different groups** bonded around it, so there is **no line of symmetry** to the molecule.

Example:



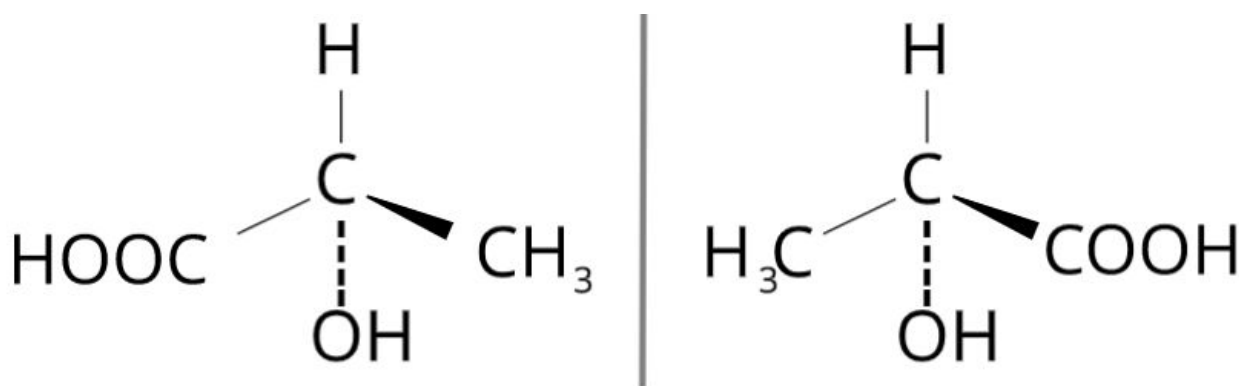
The chiral centre is commonly **indicated using *** next to the asymmetric carbon.

Optical Isomers

Optical isomerism is a type of **stereoisomerism** where molecules have the **same molecular formula** but a different **spatial arrangement** of atoms.

The presence of a chiral centre leads to **two possible isomers** that are **mirror images** of each other. These are called **optical isomers**.

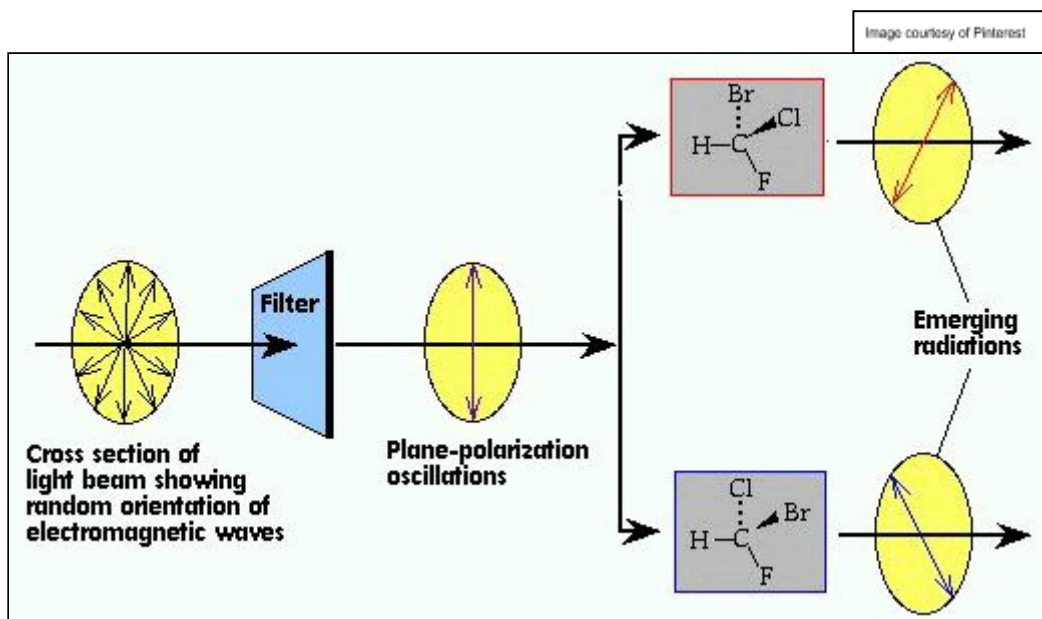
Example: Optical isomers of 2-hydroxypropanoic acid



The two different isomers are called **enantiomers** and are unique due to their effect on **plane polarised light**. Each enantiomer causes the rotation of plane polarised light by **90° in opposite directions**.



Example:



Racemic Mixtures

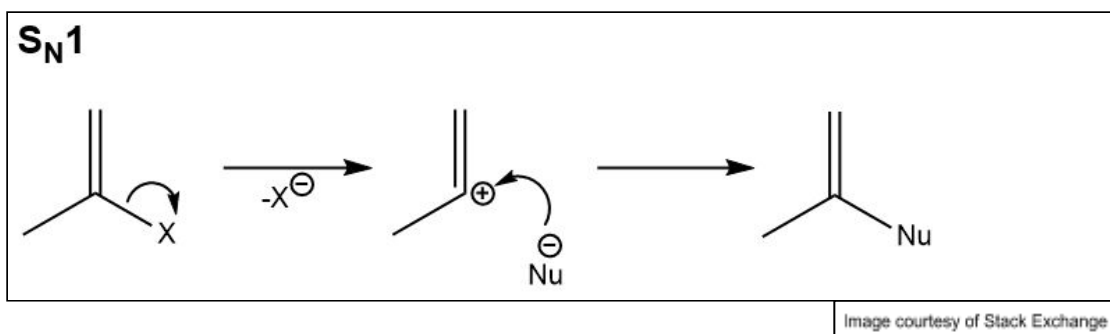
A **racemate** is formed when optical isomers are produced as a **pair of enantiomers** in a **1:1 ratio**. The optical rotational effect on polarised light caused by each enantiomer causes the overall effect to be **zero**, as the opposite directions of rotation cancel out. As a result, the mixture produced is **optically inactive** and is known as a racemic mixture.

The two isomers are able to be produced in equal quantities by a **nucleophilic addition reaction**.

Nucleophilic Substitution

S_N1 reactions proceed via a **planar carbocation intermediate**, meaning the incoming nucleophile can attack via **either face** of the compound. This means the product is a **racemic mixture**.

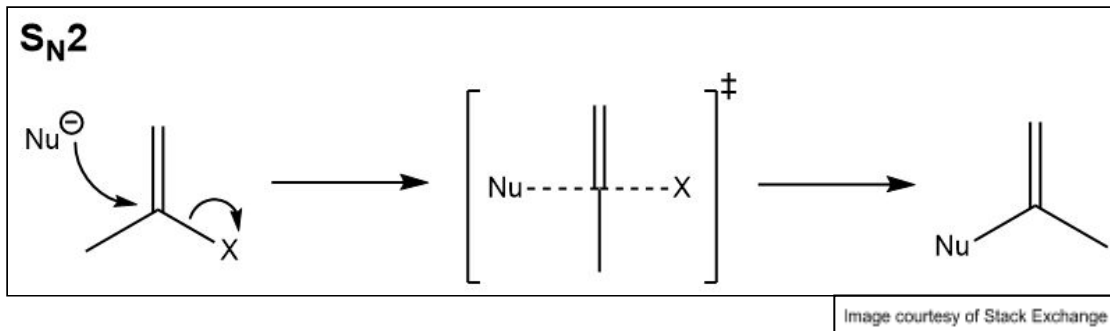
Mechanism



Conversely, S_N2 reaction mechanisms occur in a single step, since the nucleophile attacks while simultaneously the leaving group is removed. This means that there is only **one possible direction of attack** from the nucleophile. Therefore, S_N2 reactions produce a **single enantiomer**.



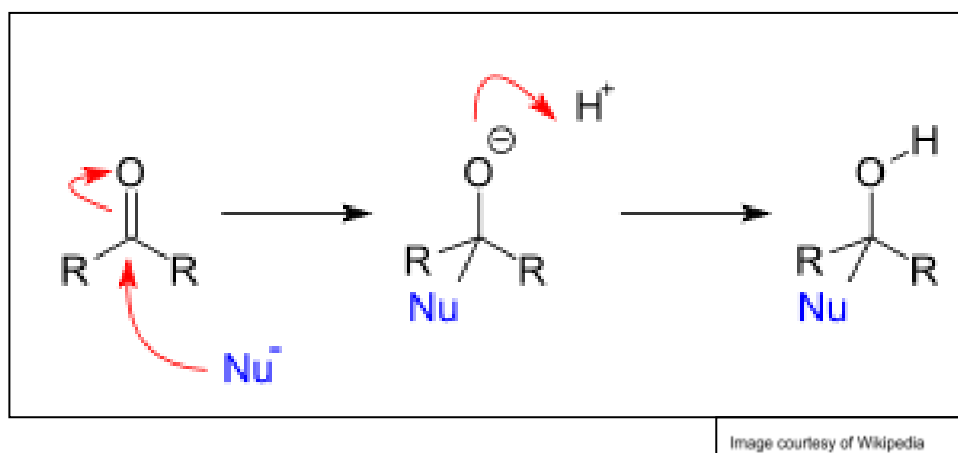
Mechanism



Nucleophilic Addition

In nucleophilic addition reactions, nucleophiles are able to attack a molecule with a **carbonyl group** from **above or below** the planar carbon-oxygen double bond. This means that the two possible products of the reaction are **mirror images**, and are therefore **optical isomers**. This mechanism, therefore, gives evidence for how optical activity arises in molecules.

Mechanism



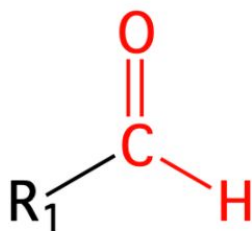
Topic 15B: Carbonyl Compounds

Carbonyl compounds are organic compounds containing a **carbonyl group**, $C=O$. This gives them the functional group **-CO**. The most common carbonyl compounds are **aldehydes and ketones**. The functional group allows these molecules to form hydrogen bonds with water. A hydrogen bond forms between a lone electron pair on the oxygen atom and a $\delta+$ region on a hydrogen atom. Aldehydes and ketones are **soluble in water** since they can form hydrogen bonds with water molecules.

However, because aldehydes and ketones themselves do not have a $\delta+$ hydrogen atom, they do **not** form hydrogen bonds between molecules. The only type of intermolecular force which exists between their molecules are **van der Waals forces**.

Aldehydes

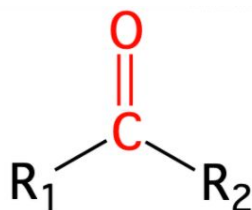
Aldehydes are produced from the initial oxidation and distillation of **primary alcohols**. Aldehydes have a carbonyl group on a carbon atom at the **end of the carbon chain** (only attached to **one other carbon atom**). This gives them the functional group **-CHO**.



Aldehydes can be **oxidised further**, in the presence of acidified potassium dichromate(VI), to produce **carboxylic acids**.

Ketones

Ketones are recognised by the **functional group -C=O**, a carbonyl group. They are produced from the oxidation of **secondary alcohols** with acidified potassium dichromate(VI). Ketones have a carbonyl group on a carbon atom that is attached to **two other carbon atoms**.



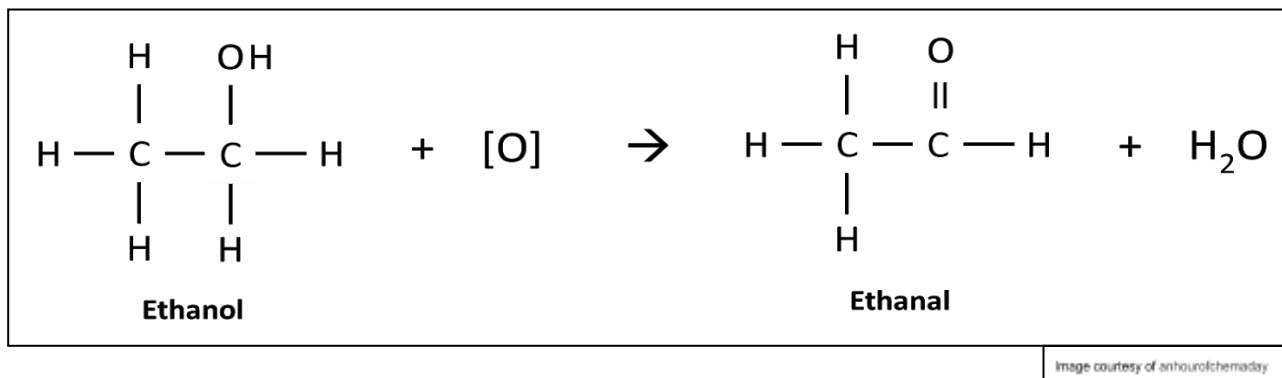
Reactions of Carbonyl Compounds

Oxidation

Primary and secondary alcohols can be **oxidised** to produce various products, but **tertiary** alcohols are **not easily oxidised**.

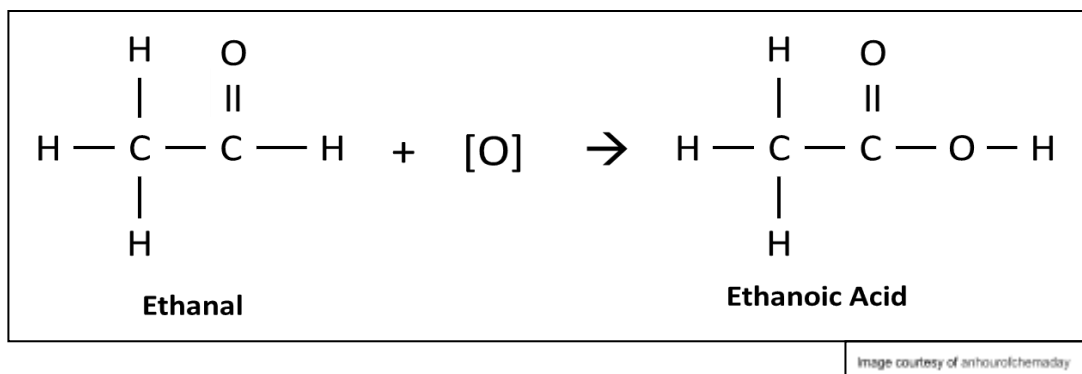
Primary alcohols can be heated in the presence of **acidified potassium dichromate(VI)** and distilled to produce **aldehydes**.

Example:



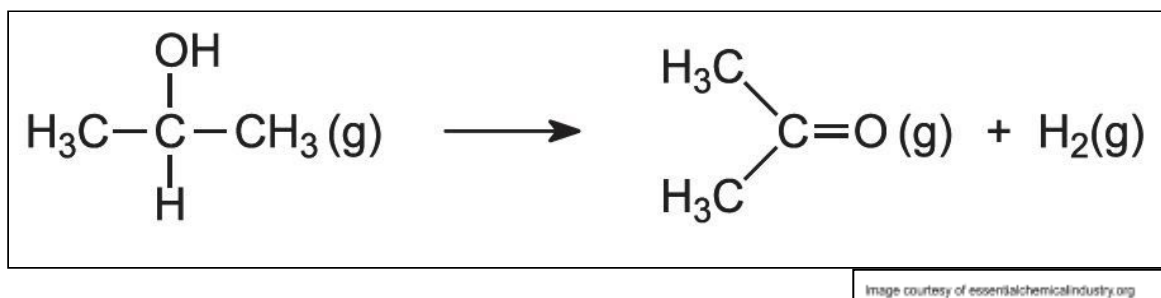
When heated under **reflux** conditions, primary alcohols will be **oxidised further** to produce **carboxylic acids**.

Example:



Secondary alcohols can be oxidised to **ketones** when heated in the presence of **acidified potassium dichromate(VI)**.

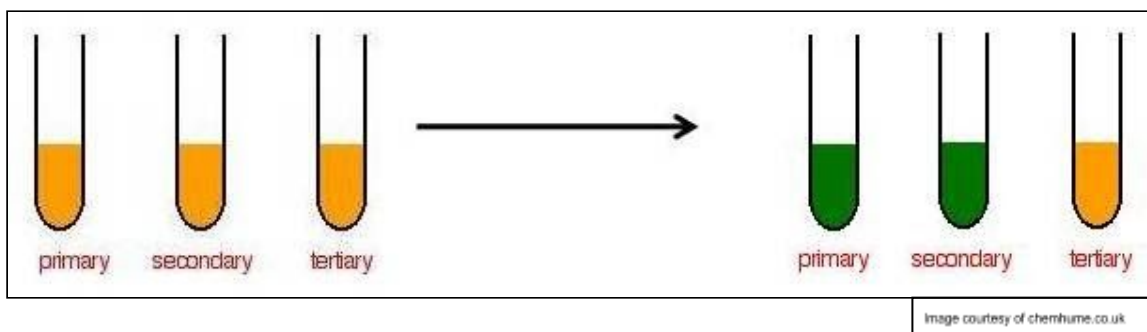
Example:



Potassium Dichromate(VI) ($K_2Cr_2O_7$)

Potassium dichromate(VI) is used as an **oxidising agent** in the oxidation of alcohols. As the alcohol is oxidised, potassium dichromate(VI) is **reduced**. This reduction is observed as a colour change from **orange to green**, which indicates the alcohol has undergone oxidation.

Example:



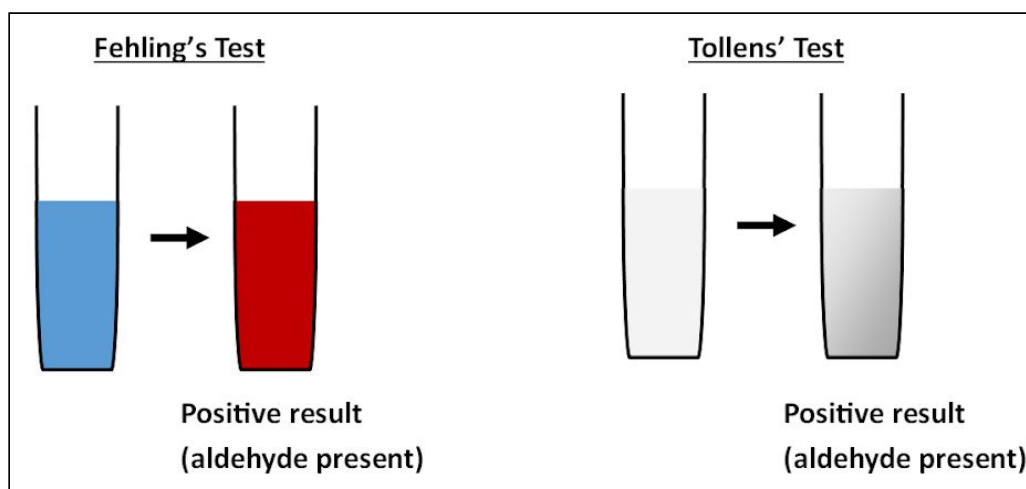
Test for Aldehydes and Ketones

Aldehydes are tested for using **Tollen's reagent** or **Fehling's solution** since they produce a positive result in both tests if present. Ketones will not give a positive result with either of these reagents. In these tests, the Fehling's solution/Tollen's reagent acts as an **oxidising agent**.

A few drops of **Fehling's solution** are added and the test tube is gently warmed. If an aldehyde is present a **red precipitate** will form. If a ketone is present the solution will remain **blue**.

Aldehydes can be tested in the same way using **Tollen's reagent**. If an aldehyde is present a layer of **silver** will form on the walls of the test tube. If a ketone is present the solution will remain colourless.

Example:



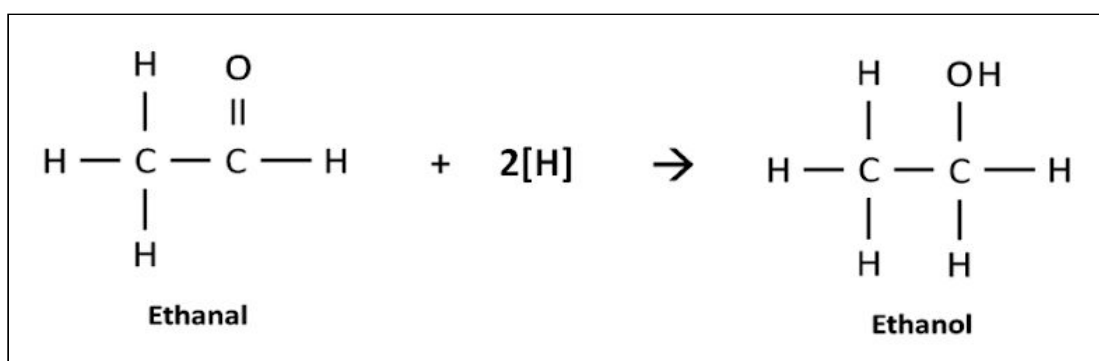
Reduction

All of the oxidation reactions involved in the production of carbonyl compounds from alcohols can be **reversed via reduction reactions**.

In these reactions, a **reducing agent** of lithium tetrahydridoaluminate(III) (lithium aluminium hydride, LiAlH_4) is used. The reaction is an example of **nucleophilic addition**. LiAlH_4 is a **very reactive** compound and will react violently with water and alcohols, so the reaction is carried out in a solvent of **dry ether**.

The reducing agent LiAlH_4 provides the **H^- nucleophile**. First a salt is formed, and then a dilute acid is added to release the alcohol from the salt. The reducing agent can be represented by **$[\text{H}]$** in the chemical equation.

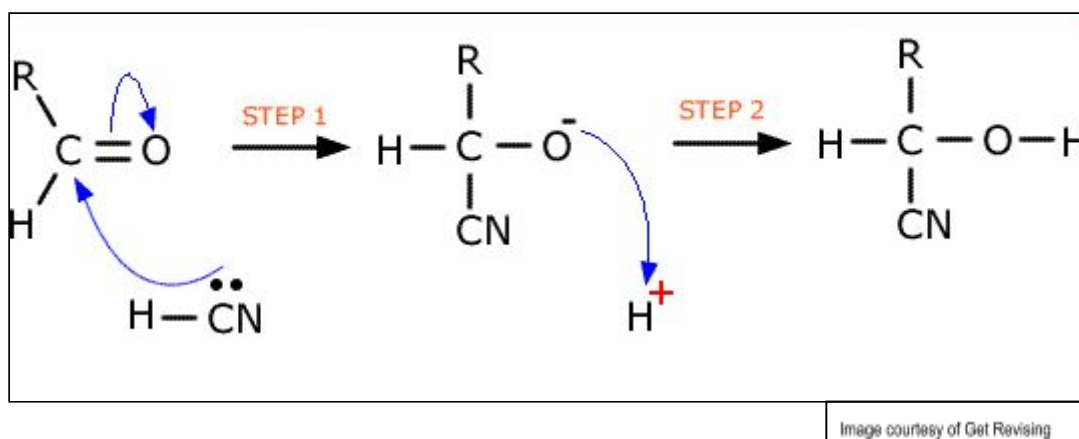
Example:



Hydroxynitriles

Nucleophilic addition reactions can also take place with the **$:\text{CN}^-$ nucleophile**. This is used in **chemical synthesis** as it causes the carbon chain to be **extended** by one carbon atom. The product of the reaction is a **hydroxynitrile**.

Mechanism



KCN (potassium cyanide) is often used as the reagent to provide the nucleophile instead of **HCN** (hydrogen cyanide). This is because HCN is **hard to store** and is a toxic gas which reacts to produce **dangerous byproducts**.

Hydroxynitriles commonly contain a **chiral carbon centre** meaning there exists optical isomers of the product. The :CN^- nucleophile can attack from either above or below the planar double bond, causing different **enantiomers** to be produced.

Iodoform Reaction

The **triiodomethane test** (iodoform test) is used to identify **CH_3CO^- groups**. This means it can be used to identify aldehydes and ketones.

Iodine solution is added to the unknown sample, followed by enough **sodium hydroxide solution** to remove the colour in the solution created by the iodine. A positive result is indicated by the formation of a **pale yellow precipitate**, known as triiodomethane (CHI_3).

Aldehydes and ketones will both give a **positive result**.

Identifying Carbonyl Compounds

2,4-dinitrophenylhydrazine (2,4-DNPH) Test

2,4-DNPH can be used as a qualitative test for the carbonyl functional group. When aldehydes and ketones are reacted with 2,4-DNPH a **yellow, orange or reddish-orange** precipitate will form; the exact colour depends on the identity of the compound. Alcohols and other molecules which don't contain carbonyl groups do not produce a precipitate.

Melting Points

Carbonyl compounds and their derivatives have **sharp melting points**, meaning they melt over a narrow range of temperatures. These compounds can have their melting points determined experimentally and their values compared to a **databook** to identify them.

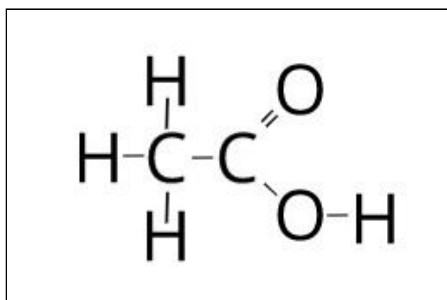
2,4-DNPH can be used to identify specific aldehydes/ketones by use of melting point data. The 2,4-DNP is added to the compound so that a precipitate forms. The solid is then purified by **recrystallisation**. The melting point of the pure crystals formed can then be compared with the melting points of **2,4-dinitrophenylhydrazones** of all the common aldehydes and ketones.



Topic 15C: Carboxylic Acids

Carboxylic acids are organic compounds identified by the **functional group -COOH**, which contains a **carbonyl group (C=O)** and an **-OH acid group**. When naming carboxylic acids, the suffix **-anoic acid** is used. For example, a carboxylic acid containing a chain of four carbon atoms would be called butanoic acid.

Example: The displayed structure of ethanoic acid.



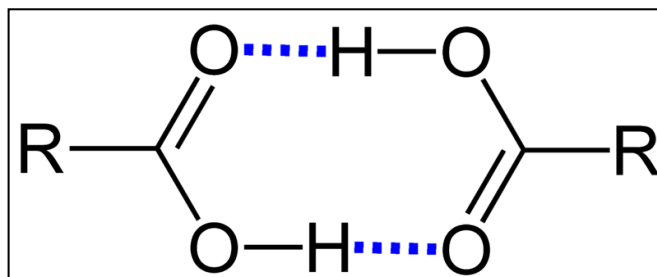
Carboxylic acids can be prepared by the **oxidation** of primary alcohols or aldehydes under **reflux**. Acidified potassium dichromate(VI) is commonly used as the oxidising agent. They can also be produced by the **hydrolysis** of **nitrile compounds**.

Properties

The **-COOH functional group** allows carboxylic acid molecules to form hydrogen bonds between each other. They can also form hydrogen bonds **with water**, meaning they are **soluble in water**. As chain length increases, their solubility decreases since CH_2 groups do not form hydrogen bonds with water - only van der Waals forces.

Since carboxylic acids can form **hydrogen bonds** between molecules, with both the C=O and O-H parts of the functional group, their boiling and melting points are even **higher** than those of alcohols, aldehydes and ketones.

Example: Hydrogen bonding between two carboxylic acid molecules.



Reactions of Carboxylic Acids

Reduction

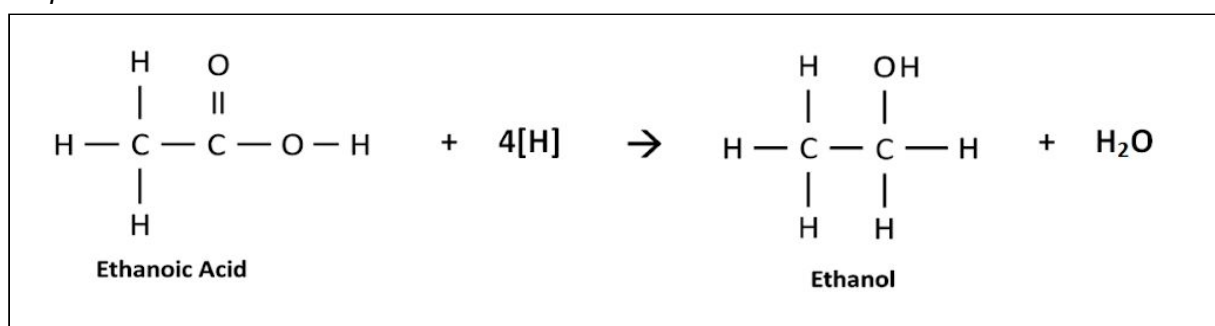


A **reducing agent** of lithium tetrahydridoaluminate(III) (lithium aluminium hydride, LiAlH_4) can be used to produce primary alcohols from carboxylic acids. This is an example of a **nucleophilic addition reaction**. LiAlH_4 is a **very reactive** compound and will react violently with water and alcohols, so the reaction is carried out in solvent of **dry ether**.

The reducing agent LiAlH_4 provides the **H^- nucleophile**. The reducing agent can be represented by **$[\text{H}]$** in the chemical equation.

Carboxylic acids are first reduced to aldehydes. However, aldehydes can not be isolated from this reaction as they are **more reactive** than carboxylic acids, so they are immediately reduced further to primary alcohols.

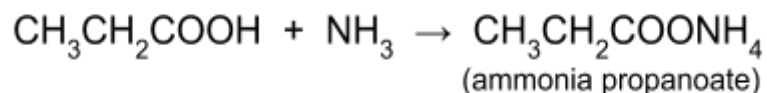
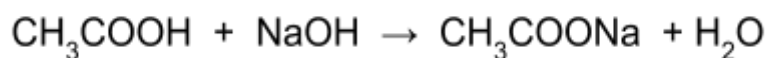
Example: Reduction of ethanoic acid to ethanol



Neutralisation with Bases

Carboxylic acids are **weak acids** and therefore react with bases in a **neutralisation** reaction to produce a **salt**.

Example:

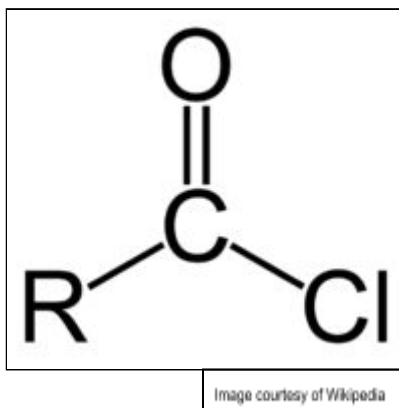


Acylation

Carboxylic acids have **derivative molecules** where the $-\text{OH}$ group is replaced by another group. **Acyl Chlorides** are one such derivative that reacts violently due to the **very polar $-\text{COCl}$ group**.

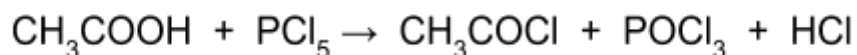
Example: Functional group of acyl chlorides





Acyl chlorides can be produced by the reaction between carboxylic acids and phosphorus(V) chloride (**phosphorus pentachloride, PCl_5**).

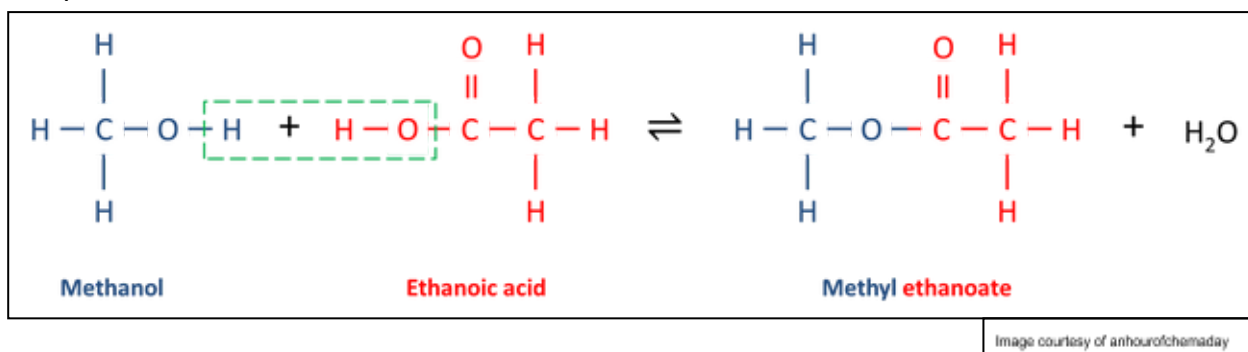
Example:



Esterification

Carboxylic acids can **react with alcohols** in the presence of a **strong acid catalyst** to form **esters**. **Concentrated sulfuric acid** is often used as the acid catalyst. This reaction is **esterification** and is carried out under **reflux**.

Example:



A method for remembering the reaction is: Remove the -OH from the acid and the hydrogen from the alcohol to make water. Then join the acid and alcohol together.

Esters are **sweet-smelling compounds** used in food flavourings and perfumes. They have **low boiling points** and make **good solvents** for polar molecules.

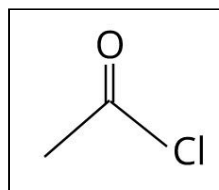
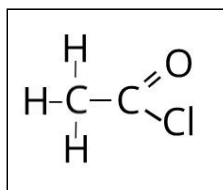


15D: Carboxylic acid derivatives

Acyl Chlorides and Esters

Acyl chlorides have the functional group **-COCl** and have the suffix **-oyl chloride**, with the stem of their name representing the longest chain of carbon atoms.

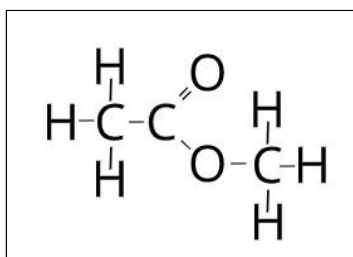
Example: The displayed structure and skeletal structure of ethanoyl chloride.



Esters have the functional group **-COO-**. They are named after the **alcohol and carboxylic acid** from which they are formed.

For example, the ester formed from methanol and propanoic acid is methyl propanoate and the ester formed from butanol and ethanoic acid is butyl ethanoate.

Example: The displayed structure of methyl ethanoate.



Reactions of Acyl Chlorides

The **-COCl** group makes acyl chlorides very reactive and so they react with a wide range of molecules to give a wide range of products:

- + Water** → **Carboxylic Acid**
- + Alcohol** → **Ester**
- + Ammonia** → **Amide**
- + Amines** → **N-substituted Amide**

Acyl chlorides react via **nucleophilic addition-elimination reactions**. In these reactions, the addition of a nucleophile leads to the elimination of a product under **aqueous conditions**.

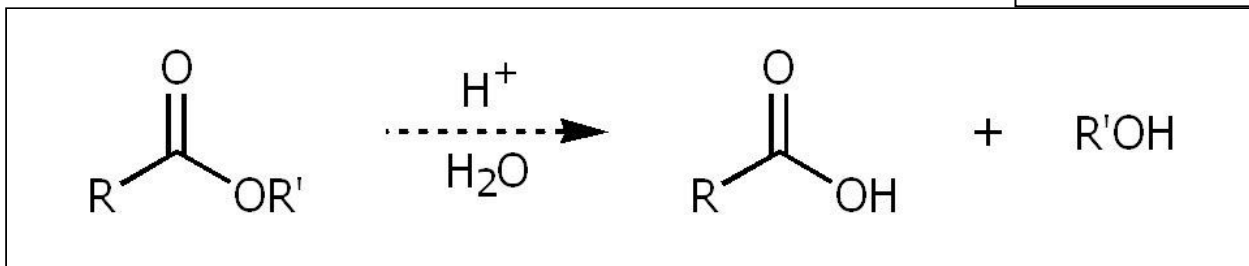


Hydrolysis of Esters

Ester hydrolysis is the **reverse reaction** to esterification, converting esters back into alcohols and carboxylic acids. This process is done by **adding water**, but can be carried out under **different conditions** to produce different products.

Acidic Conditions

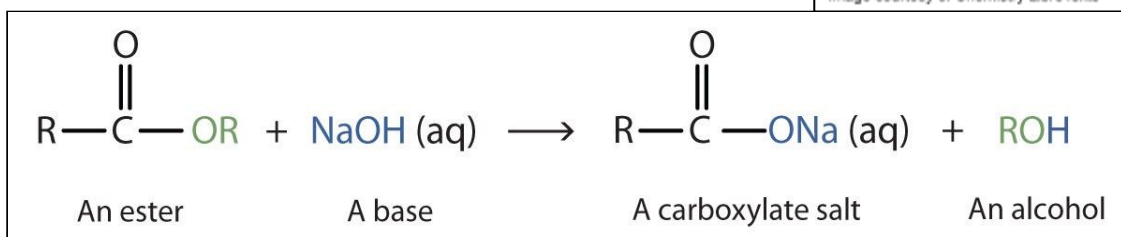
Image courtesy of SlidePlayer



*This produces a **simple reverse reaction** back to the alcohol and carboxylic acid.*

Alkaline Conditions

Image courtesy of Chemistry LibreTexts



*The carboxylic acid produced reacts further with the base to **form a salt**.*

The production of this salt is called **saponification**. Salts such as these are commonly used as **soaps** because they have **hydrophilic and hydrophobic** properties.

Condensation Polymers

Condensation polymers form when **a water molecule is removed** from the species of a reaction. Polyesters are formed in this way from a reaction between **dicarboxylic acids and a diol**, producing an **ester linkage**, -COO-.

Example:

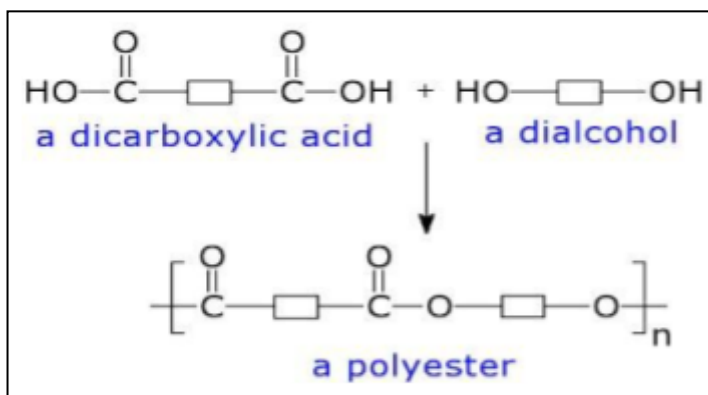
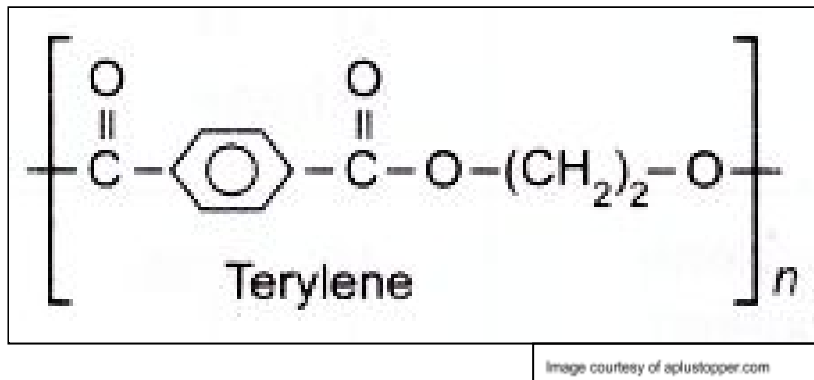


Image courtesy of QS Study



Terylene (PET) is a common polyester made from ethanediol and 1,4-benzenedicarboxylic acid.

Example:



Polyesters are useful as they can be broken down through **hydrolysis** due to the **polarity** within the polymer molecules. Therefore, they are **biodegradable** and can be broken down easily in nature by naturally occurring water or moisture. This means polyesters can be put into **landfill** to gradually break down.



15E: Spectroscopy and Chromatography

High Resolution Mass Spectrometry

High resolution mass spectrometry is a much **more sensitive** form of mass spectrometry (seen in Topic 10) which allows the Mr of a substance to be determined to **several decimal places**. Precise atomic masses are always given which can then be used to calculate the molecular formula of the compound being tested.

Once a molecular formula has been determined, you can predict **possible structures** of the compound. Knowledge of **general formulas** and **functional groups** aids this prediction.

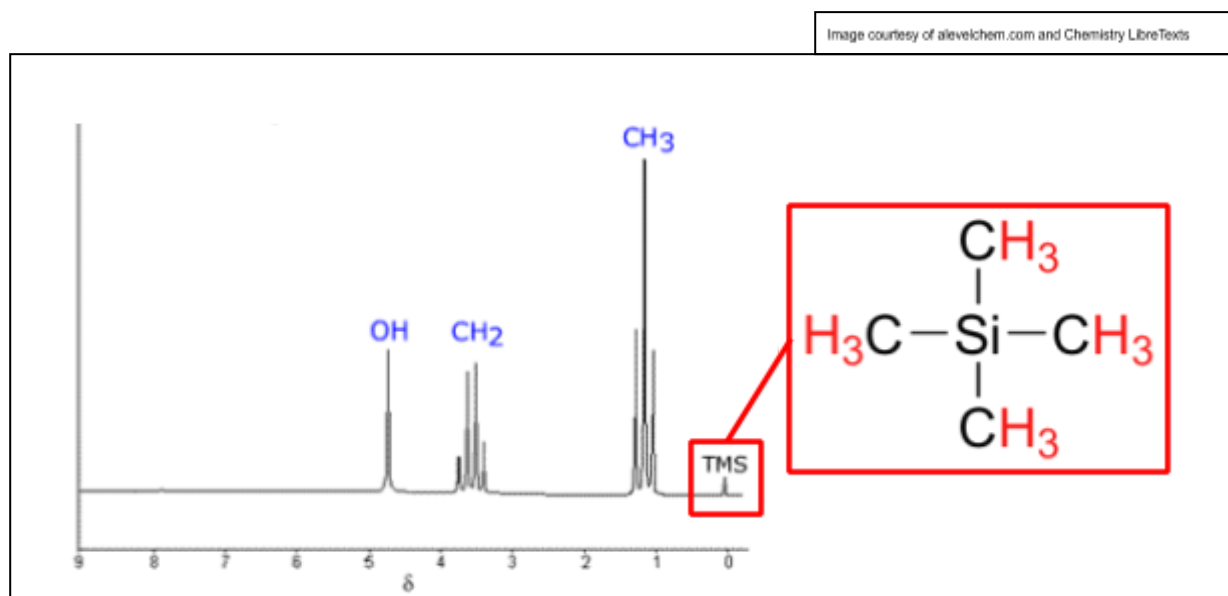
Nuclear Magnetic Resonance (NMR)

NMR

NMR is an **analytical technique** that allows the structure of a molecule to be determined by analysing the energy of each bond environment. Different bond environments within a molecule **absorb different amounts of energy** so they are displayed as **different peaks** on a spectra print out.

The bond environment peaks are measured against a standard molecule, **tetramethylsilane (Si(CH₃)₄)**, known as TMS. This is a standard molecule as it contains four **identical** carbon and hydrogen environments. It can be easily identified as it is seen as a peak at **δ=0 ppm** on the x-axis.

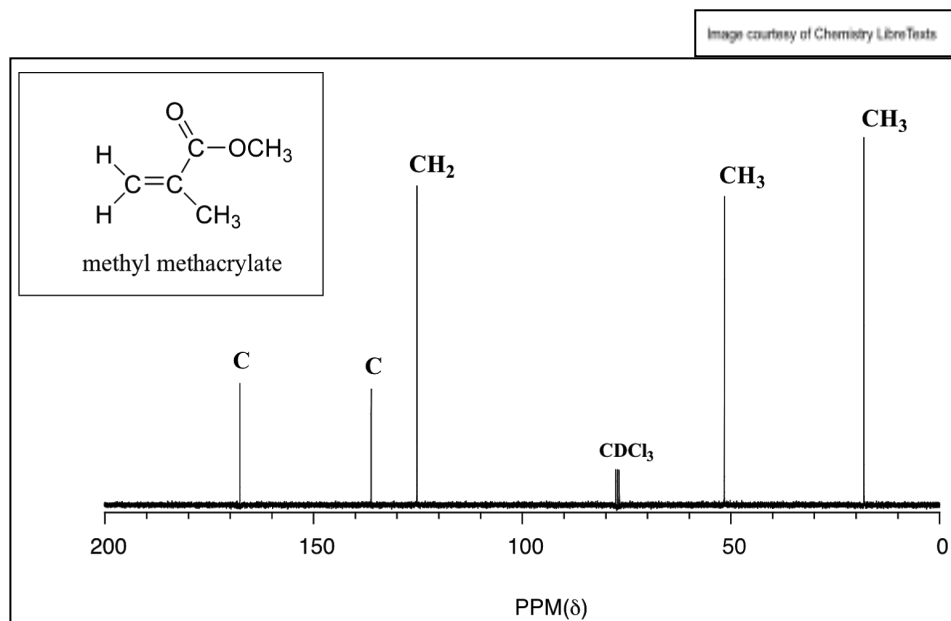
Example:



C¹³ NMR

C¹³ NMR spectroscopy analyses the different **carbon environments** in a molecule. The different environments are shown as peaks at different δ values.

Example:

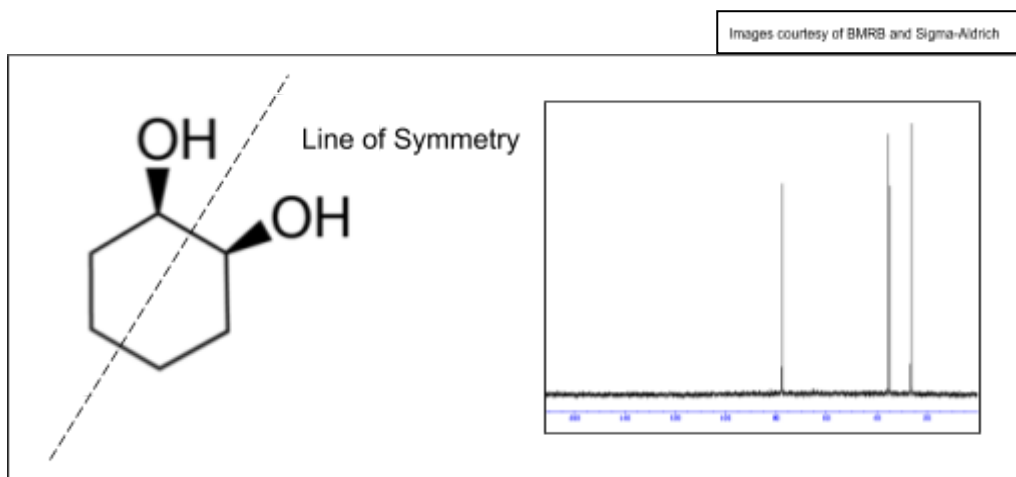


Carbon environments that are **near to oxygen atoms** have δ values that are **shifted to the right**. This is because oxygen is very **electronegative** and changes the bond environment and affects how it absorbs energy.

Molecule Symmetry

Molecules that have **symmetry** may display fewer δ peaks than the number of carbon atoms in the molecule. Therefore in these cases, it is important to look at the given molecular formula of the compound in order to decipher its displayed structure.

Example:



This molecule, 1,2-cyclohexanediol, contains six carbon atoms but the NMR spectrum only has three peaks due to the symmetry of the molecule.



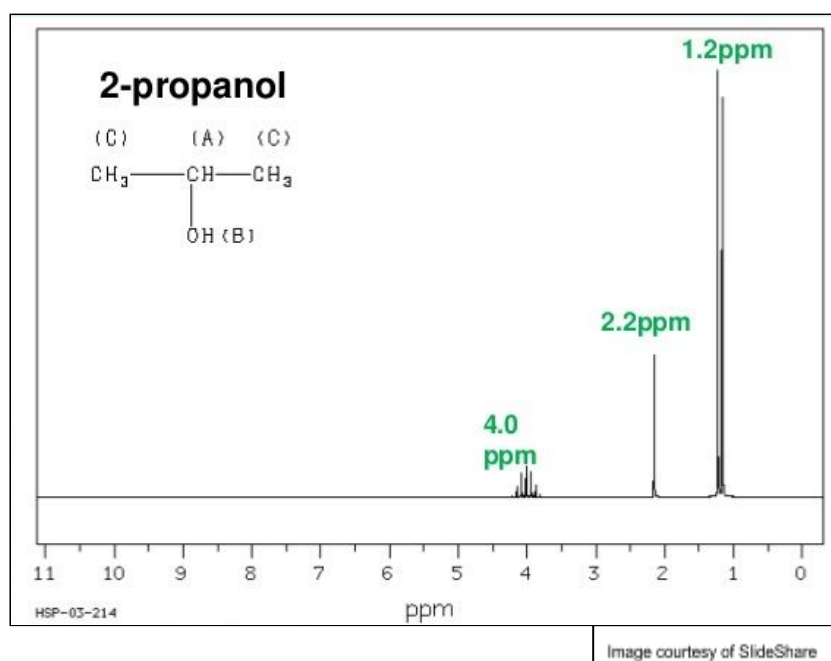
H¹ NMR (Proton NMR)

In H¹ NMR, the different **hydrogen environments** in a molecule are analysed and displayed as peaks on a spectra. These peaks are also measured against the TMS standard.

The samples being analysed must be dissolved in a **non-hydrogen-containing solvent** so that the solvent doesn't produce any δ peaks on the spectrum. CCl₄ is therefore a common solvent used along with **deuterated solvents** containing deuterium, an isotope of hydrogen.

H¹ NMR spectra are more complex than C¹³ spectra as the heights of the peaks show the **relative intensity** of each δ value. These relative intensities correspond to the number of hydrogens in that certain environment within a molecule, shown as a number above the peak.

Example:



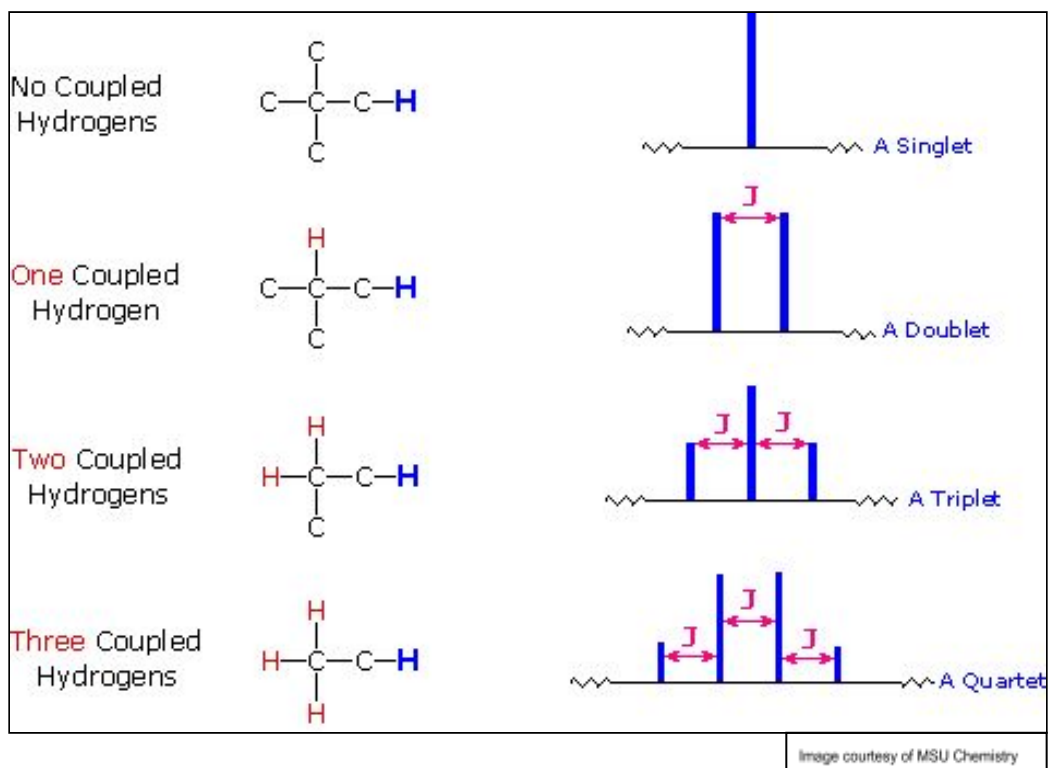
Splitting Patterns

The peaks of a H¹ NMR spectra also inform **where each environment is positioned** within the molecule. Peaks are split into a **small cluster**, with smaller peaks indicating how many hydrogens are on the **adjacent carbon atom** within the molecule. These smaller peaks are a **splitting pattern** and follow an '**n+1**' rule, where n is the number of hydrogen on the adjacent carbon:

- **Singlet** = 0 H on adjacent carbon
- **Doublet** = 1 H on adjacent carbon
- **Triplet** = 2 H on adjacent atom
- **Quartet** = 3 H on adjacent carbon

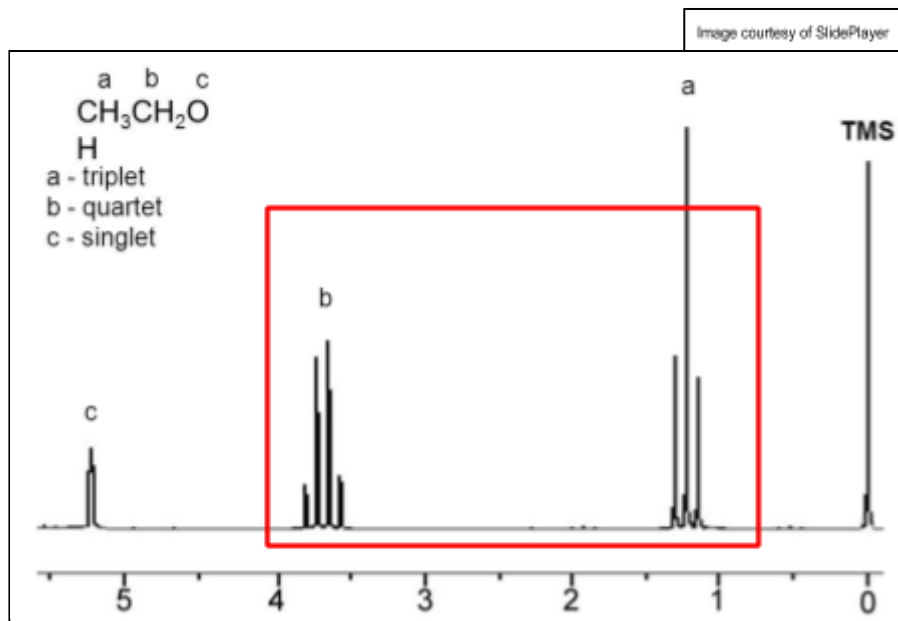
Example:





There are some common **combinations of peaks and splitting patterns** that make deciphering the structure of the molecule easier. A **triplet-quartet** splitting pattern is a common combination as it represents a **-CH₂-CH₃** fragment.

Example:



The boxed peaks are produced by the -CH₂-CH₃ fragment.

Multiple fragments can be worked out from these peaks and **pieced together** to determine the **full molecule structure**.



Chromatography Methods

Chromatography is an **analytical technique** used to separate and identify component molecules of a mixture. It involves a **mobile phase** and a **stationary phase**.

Mobile and Stationary Phases

The mobile phase is a substance that allows molecules to **move over or through** the stationary phase. It can be in the form of a **liquid or a gas** depending on the type of chromatography being carried out. Species that are more soluble in the mobile phase **move further and/or faster** within the mobile phase.

The stationary phase is a substance that has **affinity** to molecules in the mixture being analysed. The **greater the affinity** of a molecule to the stationary phase, the **shorter the distance and/or the slower** it moves within the mobile phase.

Rf Values

An Rf value is a value that is **unique** to each different component molecule in the mixture being analysed. This is because different molecules within the mixture will have **different affinities** for the mobile and stationary phase and so will move at different rates within the mobile phase. It is calculated by comparing the **distance moved by the component molecule to the distance moved by the mobile phase**.

Example:

$$R_f = \frac{\text{Distance moved by molecule}}{\text{Distance moved by solvent}}$$

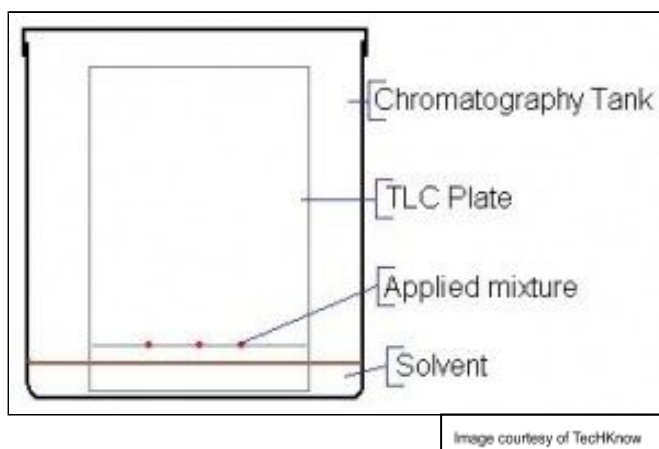
There are different types of chromatography that use different mobile and stationary phases. This will lead to **different Rf values** for the molecules present. A particular component molecule will have a different Rf value in different solvents.

Thin-Layer Chromatography

In TLC chromatography, a **metal plate** is coated with a **thin layer of silica** and the sample being analysed is dotted on the plate. The **solvent** is then allowed to move up the plate, separating the substances within the sample. The plate is then dried in a fume cupboard to reduce toxic fumes. The chemical traces can then be viewed using a **UV lamp** and the distances travelled can be measured. Alternatively, a **developing agent** can be added, such as **iodine**, to allow the traces to be seen by the naked eye.

Example:

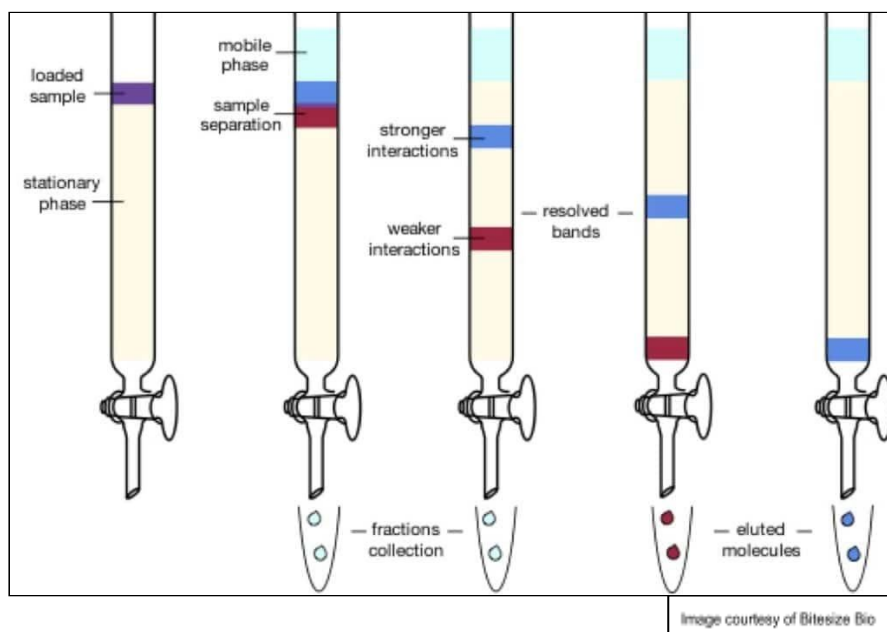




Column and HPL Chromatography

For column and HPL chromatography, a **vertical column** is packed with a **solid, powdered substance** which acts as the stationary phase. A **solvent** containing the mixture being analysed is then added and moves down the column as the mobile phase.

Example:



The varying affinities of the molecules present means that they **drain out of the column at different times**, allowing them to be collected as **separate samples**. The time taken for a substance to travel down the column is measured as the **retention time**. Similar to R_f values, retention times allow the individual molecules in the mixture to be identified.

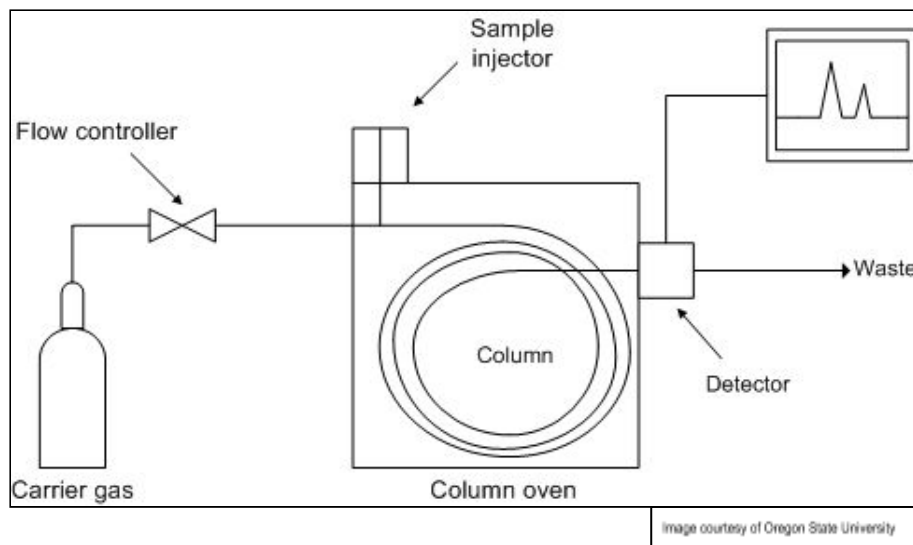
High Performance Liquid Chromatography (HPLC) is an improved form of column chromatography which uses **high pressures** to force the mobile phase through the column. It allows much **smaller** samples to be analysed in a much **shorter time**.



Gas Chromatography (GC)

In gas chromatography, a **thin tube** is packed with a **solid, powdered substance** which acts as the stationary phase. Instead of a solvent, a **high pressure gas** is passed through this tube and acts as the **mobile phase**. This method is used to separate mixtures of **volatile liquids** which are fed into the gas chromatography machine as vapours.

Example:



The analysis machine **records a retention time** for each component molecule in the mixture, allowing them to be identified.

Applications of Chromatography

Chromatography can be used to determine the identity of compounds within a mixture. This makes it useful for **drug testing** in sports and in **forensics**, where specific compounds may be screened for.

GC-MS is a **combination** of analytical techniques: **gas chromatography and mass spectrometry**. GC-MS allows for a more **advanced** level of molecular analysis. The molecules present are first separated using the gas chromatography technique. Then each molecule present is fed directly into a mass spectrometer so it can be **accurately identified**.

