

# Edexcel Chemistry A-Level

## Topic 17: Organic Chemistry II Detailed Notes

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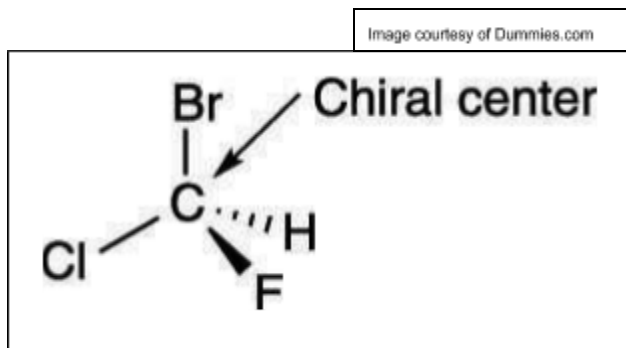


## Topic 17A: Chirality

### Chiral Centres

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

*Example:*



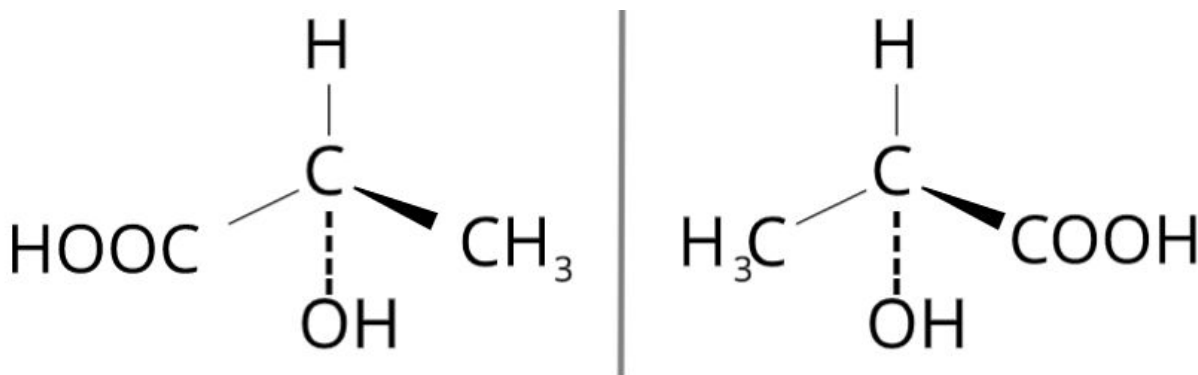
The chiral centre is commonly **indicated using \*** next to the asymmetric carbon.

### 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

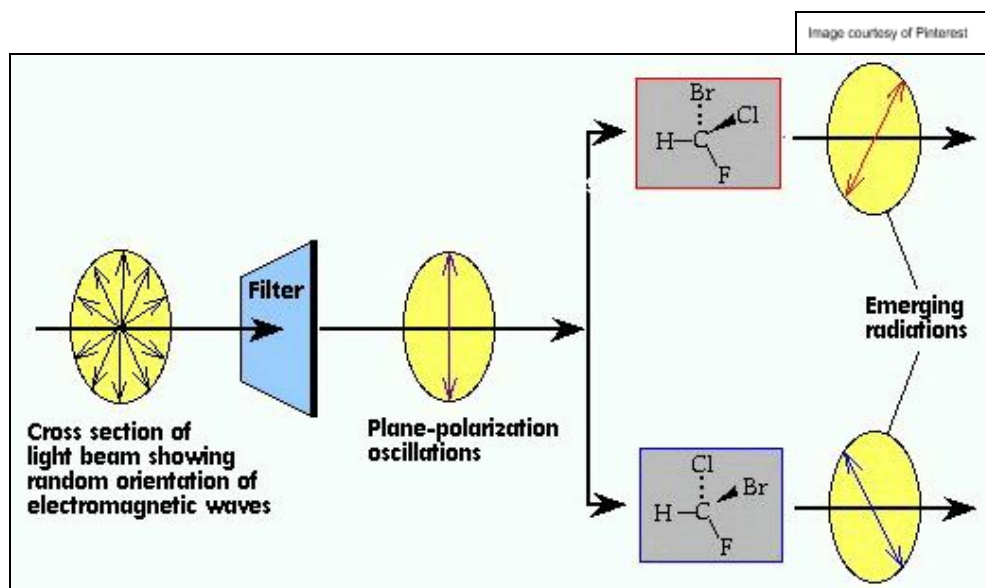


The two different isomers are called **enantiomers** and are unique due to their effect on **plane polarised light**. Each enantiomer causes the rotation of plane polarised light **in opposite directions**.





Example:



## Racemic Mixtures

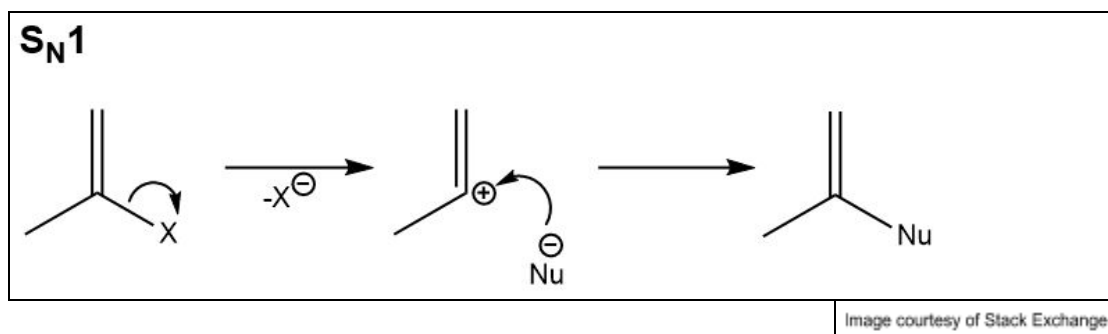
A **racemate** is formed when optical isomers are produced as a **pair of enantiomers** in a **1:1 ratio**. The optical rotational effect on polarised light caused by each enantiomer causes the overall effect to be **zero**, as the opposite directions of rotation cancel out. As a result, the mixture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

$\text{S}_{\text{N}}1$  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**.

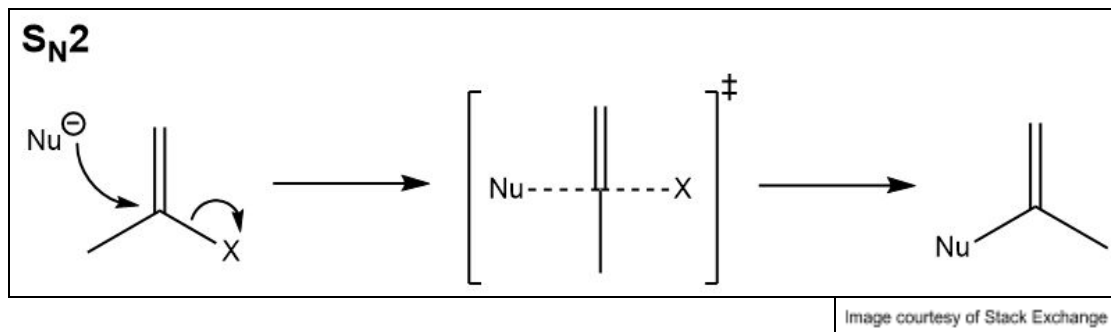
### Mechanism





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**.

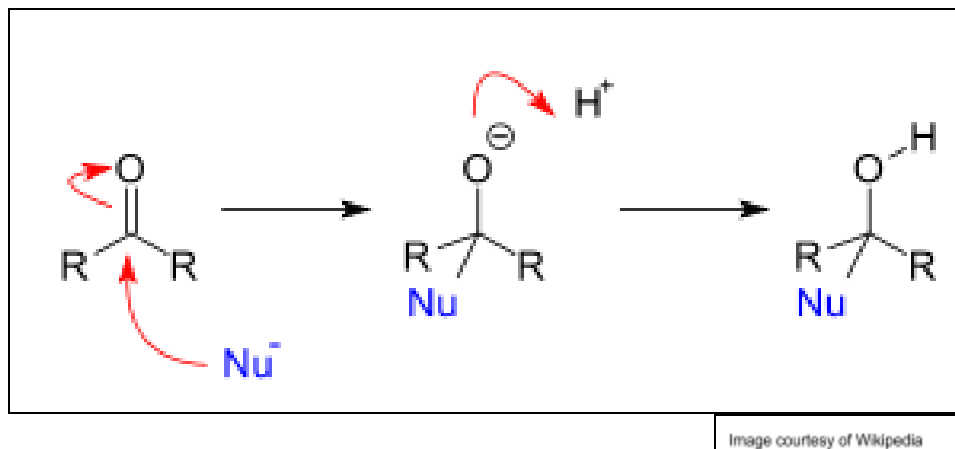
### Mechanism



### 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 17B: Carbonyl Compounds

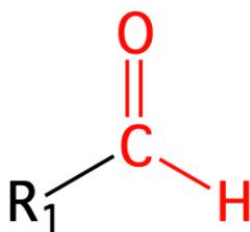
Carbonyl compounds are organic compounds containing a **carbonyl group**,  $C=O$ . This gives them the functional group **-CO**. The most common carbonyl compounds are **aldehydes and ketones**.

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, therefore, **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

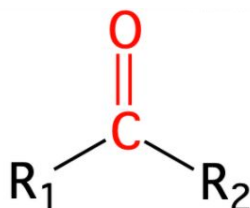
Aldehydes are produced from the initial oxidation and distillation of **primary alcohols**. Aldehydes have a carbonyl group on a carbon atom at the **end of the carbon chain** (only attached to **one other carbon atom**). This gives them the functional group **-CHO**.



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

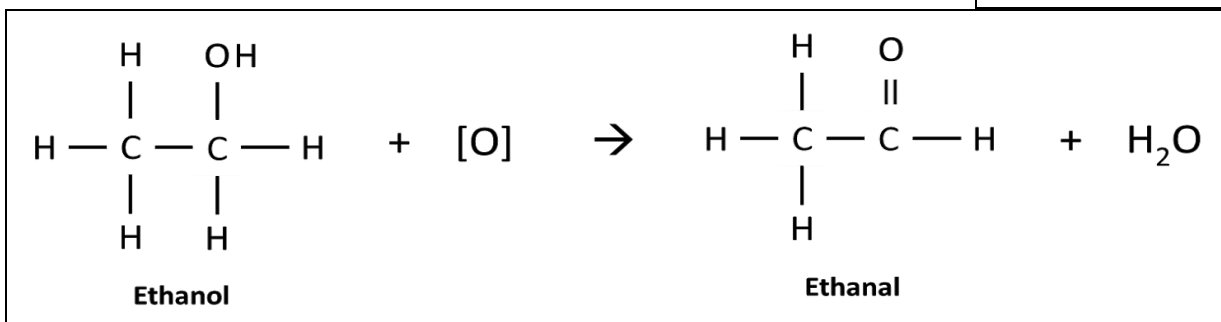
### Oxidation

**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:

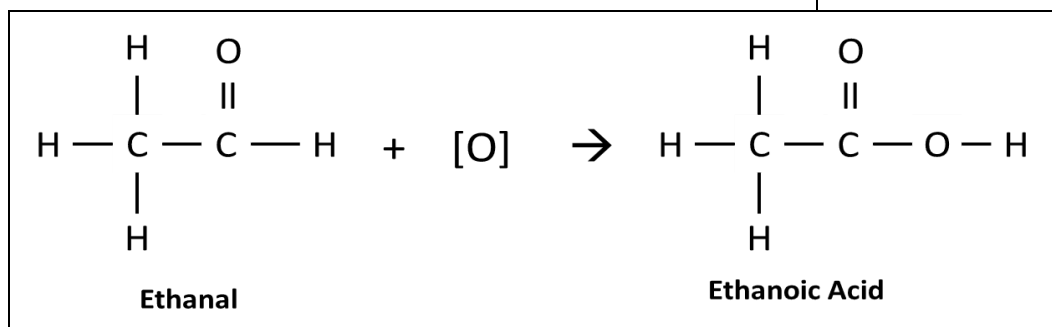
Image courtesy of anhoursofchemaday



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

Example:

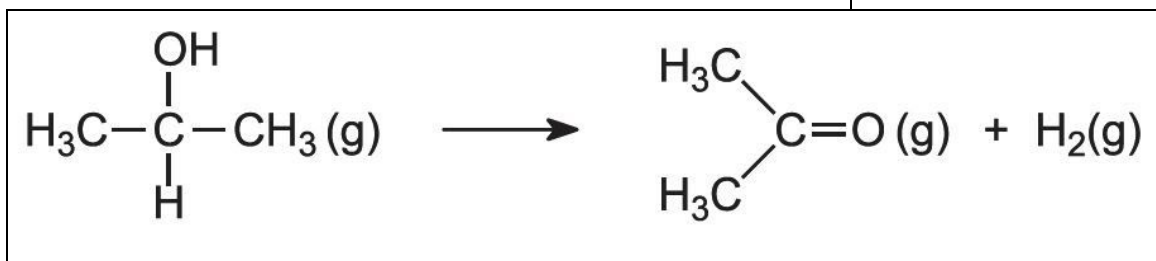
Image courtesy of anhoursofchemaday



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

Example:

Image courtesy of essentialchemicalindustry.org

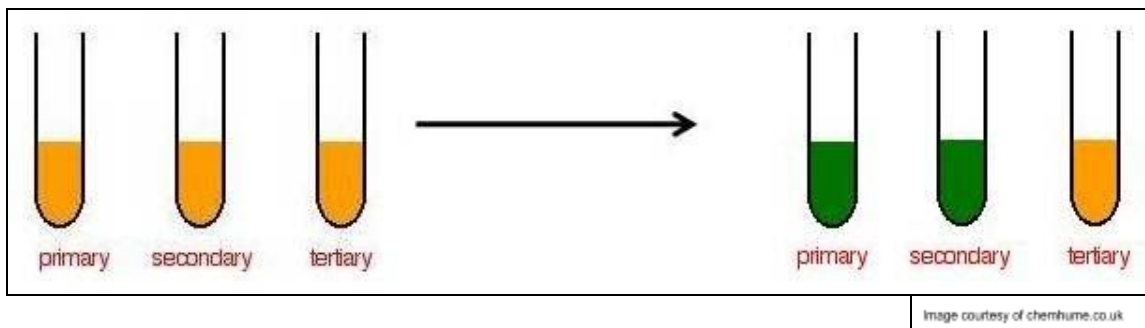




### Potassium Dichromate(VI) ( $K_2Cr_2O_7$ )

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:



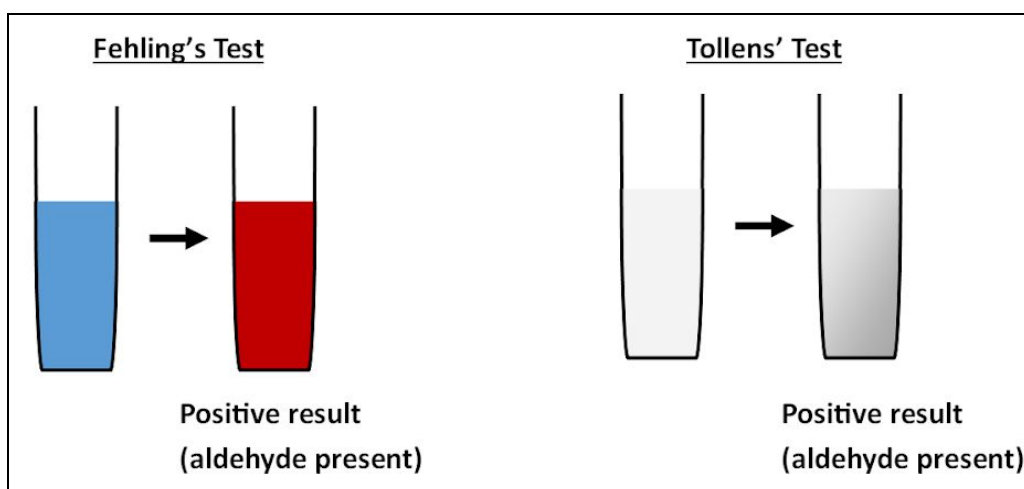
### Test for Aldehydes and Ketones

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:





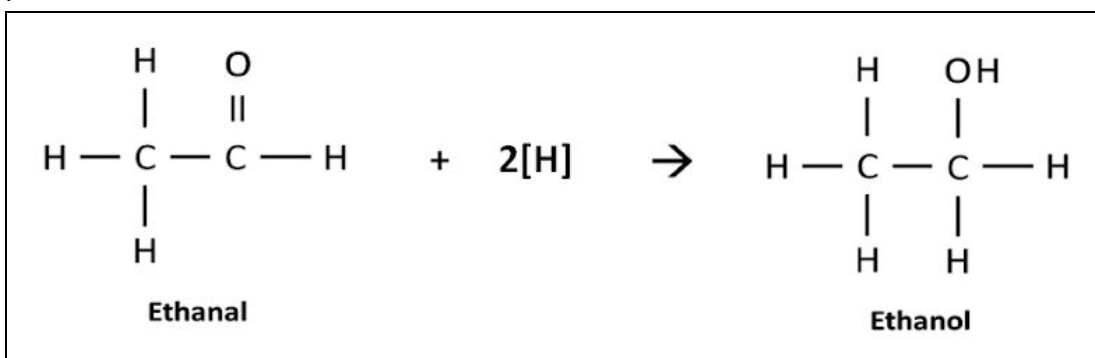
## Reduction

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,  $\text{LiAlH}_4$ ) is used. The reaction is an example of **nucleophilic addition**.  $\text{LiAlH}_4$  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  $\text{LiAlH}_4$  provides the  $\text{H}^-$  **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.

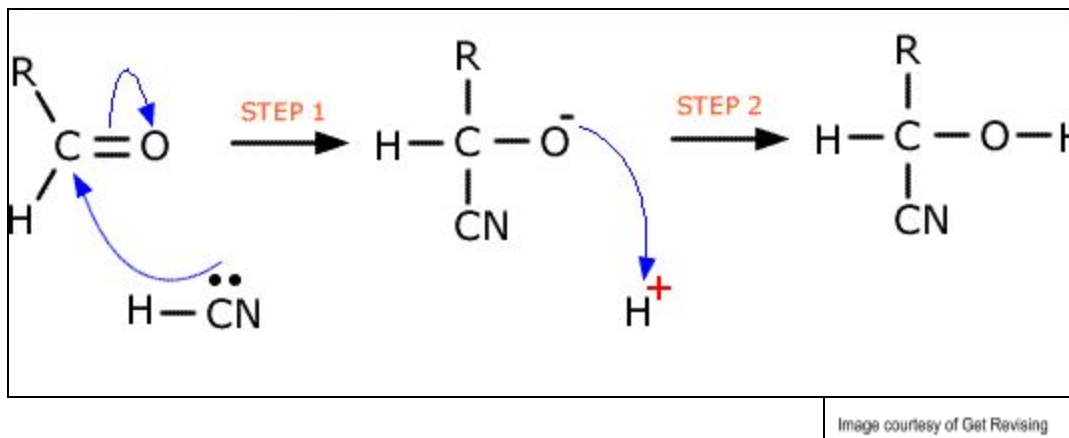
Example:



## 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 optical isomers of the product are produced. The  $\text{:CN}^-$  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  **$\text{CH}_3\text{CO}^-$  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 ( $\text{CHI}_3$ ).

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-DNPH 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.

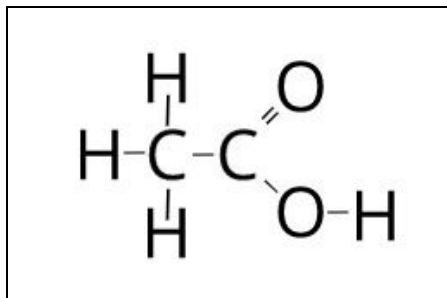




## Topic 17C: Carboxylic Acids

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



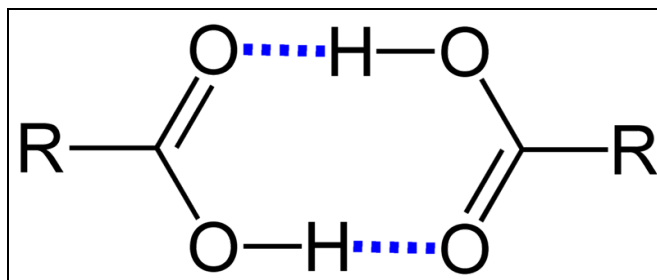
Carboxylic acids can be prepared by the **oxidation** of primary alcohols or aldehydes under **reflux**. Acidified potassium dichromate(VI) is commonly used as the oxidising agent. They can also be produced by the **hydrolysis** of **nitrile compounds**.

### 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  $\text{CH}_2$  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  $\text{C}=\text{O}$  and  $\text{O}-\text{H}$  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

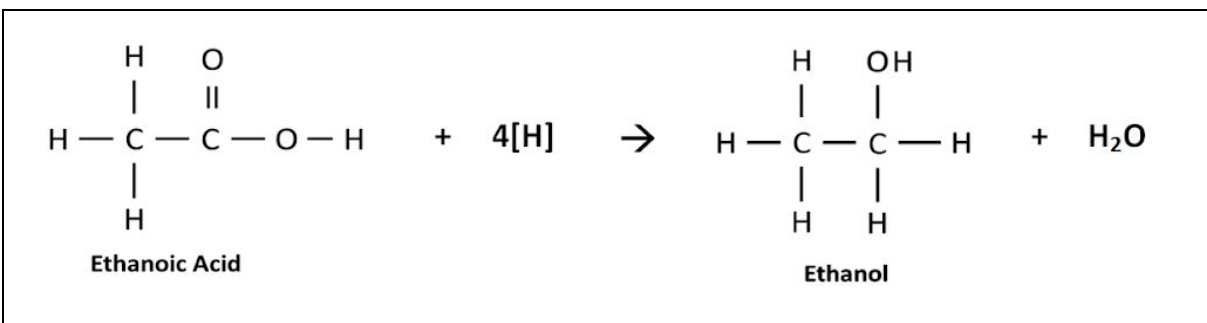
### Reduction

A **reducing agent** of lithium tetrahydridoaluminate(III) (lithium aluminium hydride,  $\text{LiAlH}_4$ ) can be used to produce primary alcohols from carboxylic acids. This is an example of a **nucleophilic addition reaction**.  $\text{LiAlH}_4$  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  $\text{LiAlH}_4$  provides the  **$\text{H}^-$  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.

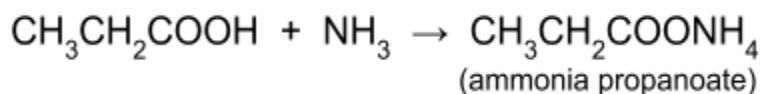
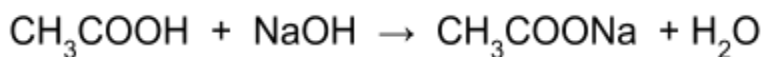
*Example:* Reduction of ethanoic acid to ethanol



### Neutralisation with Bases

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

*Example:*

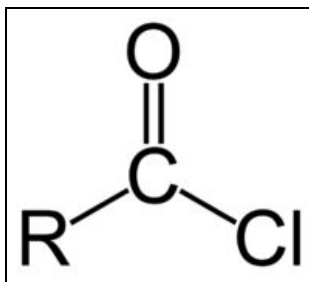




## Acylation

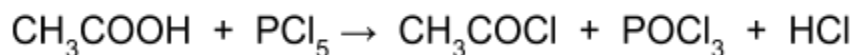
Carboxylic acids have **derivative molecules** where the -OH group is replaced by another group. **Acyl Chlorides** are one such derivative that reacts violently due to the **very polar -COCl group**.

*Example:* Functional group of acyl chlorides



Acyl chlorides can be produced by the reaction between carboxylic acids and phosphorus(V) chloride (**phosphorus pentachloride,  $\text{PCl}_5$** ).

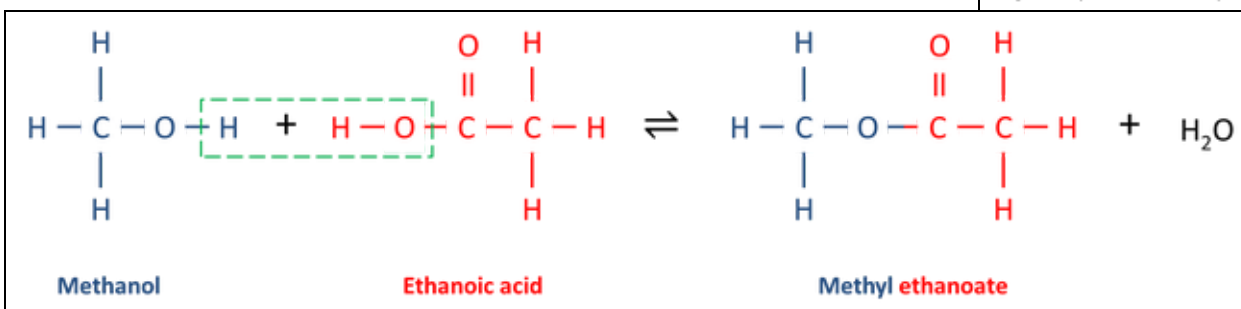
*Example:*



## 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.



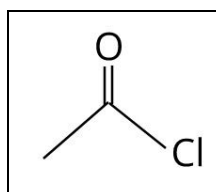
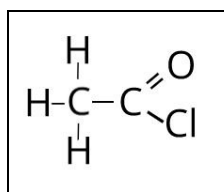


## Carboxylic acid derivatives

### 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.

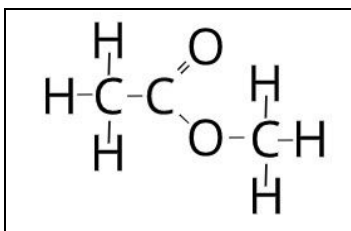
*Example:* The displayed structure and skeletal structure of ethanoyl chloride.



**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 (also known as methyl acetate).



### 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**.



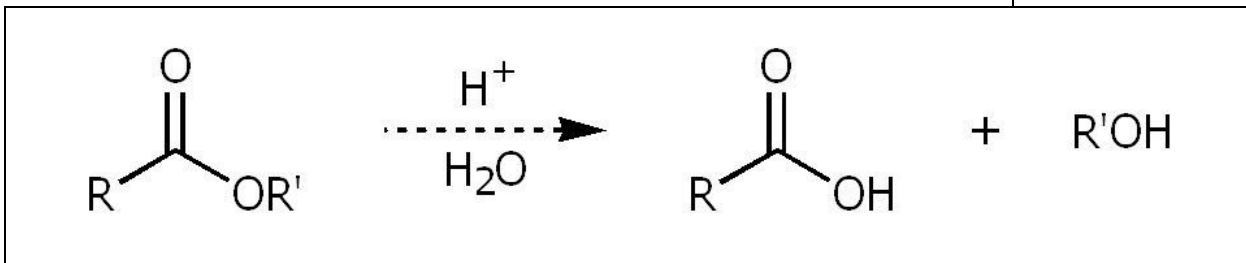


## Hydrolysis of Esters

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

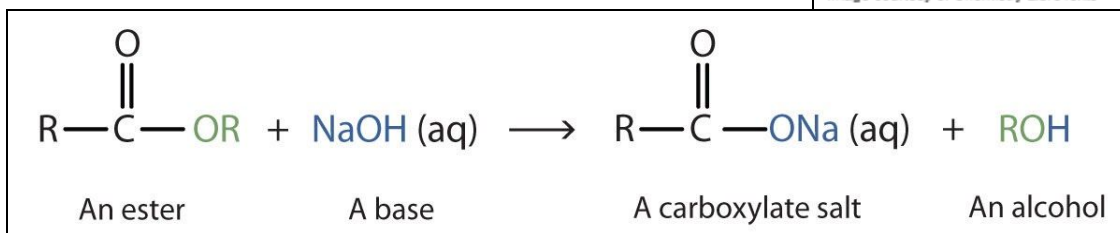
Image courtesy of SlidePlayer



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

## Condensation Polymers

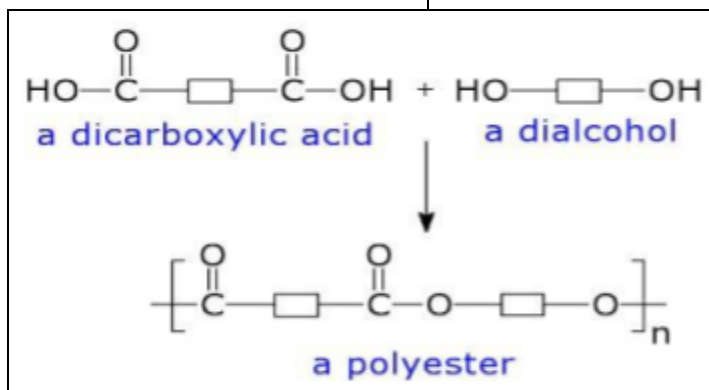
Condensation polymers form when **a water molecule is removed** from the species of a reaction. Polyesters are formed in this way from a reaction between a **dicarboxylic acid and a diol**, producing an **ester linkage**, -COO-.





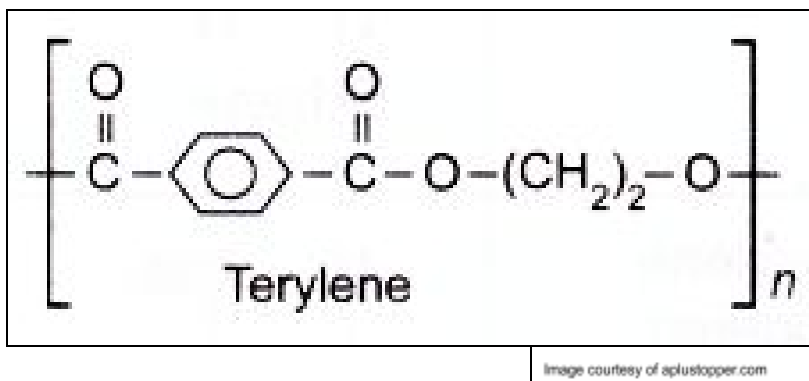
Example:

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** where they will gradually break down.

