Edexcel International A Level (IAL) Chemistry

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Organic Chemistry: Carboxylic Acids

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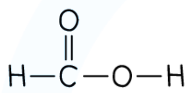
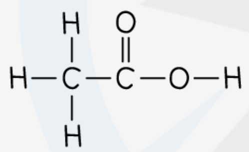
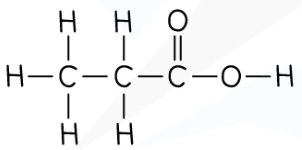
Carboxylic Acids – Physical Properties

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 alkanoic 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
	methanoic acid (also known as formic acid)	HCOOH
	ethanoic acid (also known as acetic acid)	CH_3COOH
	propanoic acid	CH_3CH_2COOH

Physical properties of carboxylic acids

- Carboxylic acids contain two polarised groups
  - **C=O** and **O-H**
- This means that the intermolecular forces that carboxylic acids experience are high and they will have relatively high melting points and boiling points
- The presence of the O-H bond means that they can exhibit hydrogen bonding

    - Not only does this contribute to the high melting and boiling points, it also contributes to the solubility in water and other polar solvents of the shorter chained carboxylic acids
- However, solubility falls as the length of the hydrocarbon chain in the carboxylic acid increases
- The hydrocarbon chains are forcing their way between water molecules and so breaking hydrogen bonds between those water molecules
    - Carboxylic acids with more than eight carbon atoms will be solids at room temperature and are very slightly soluble in cold water, but will be more soluble in hot water

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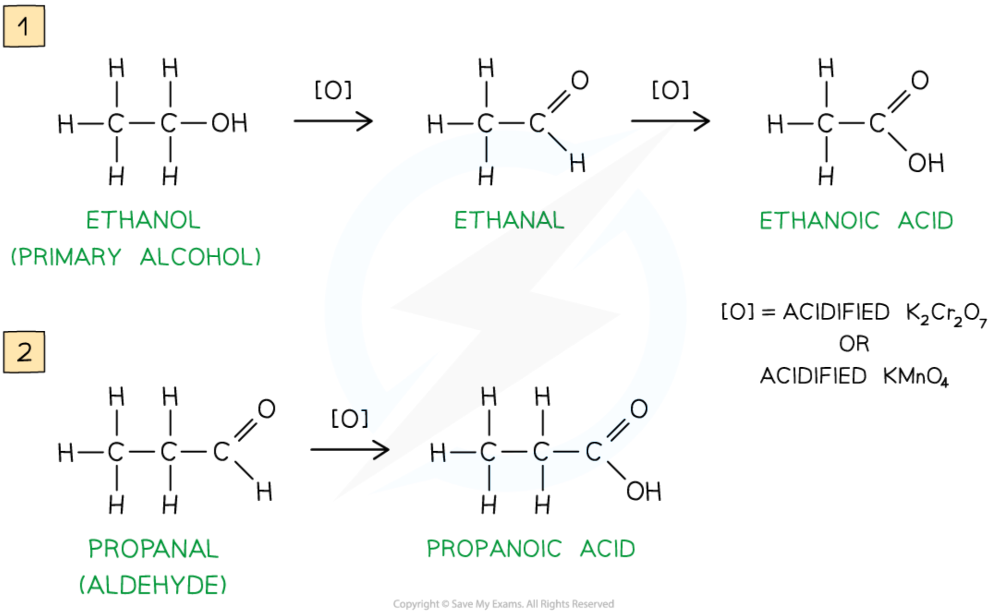
Carboxylic Acids – Preparation

- **Carboxylic acids** are compounds with a -COOH functional group
- They can be prepared by a series of different reactions

Oxidation of primary alcohols & aldehydes

- Carboxylic acids can be formed from the **oxidation** of **primary alcohols** and **aldehydes** by either **acidified $K_2Cr_2O_7$** or **acidified $KMnO_4$** and **reflux**
- The oxidising agents themselves get reduced causing the solutions to change colour
  - In $K_2Cr_2O_7$ the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
  - In KMnO4 the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions



Oxidation of primary alcohols (1) and aldehydes (2) gives carboxylic acids

Hydrolysis of nitriles

- Carboxylic acids can also be prepared from the **hydrolysis** of **nitriles** using 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

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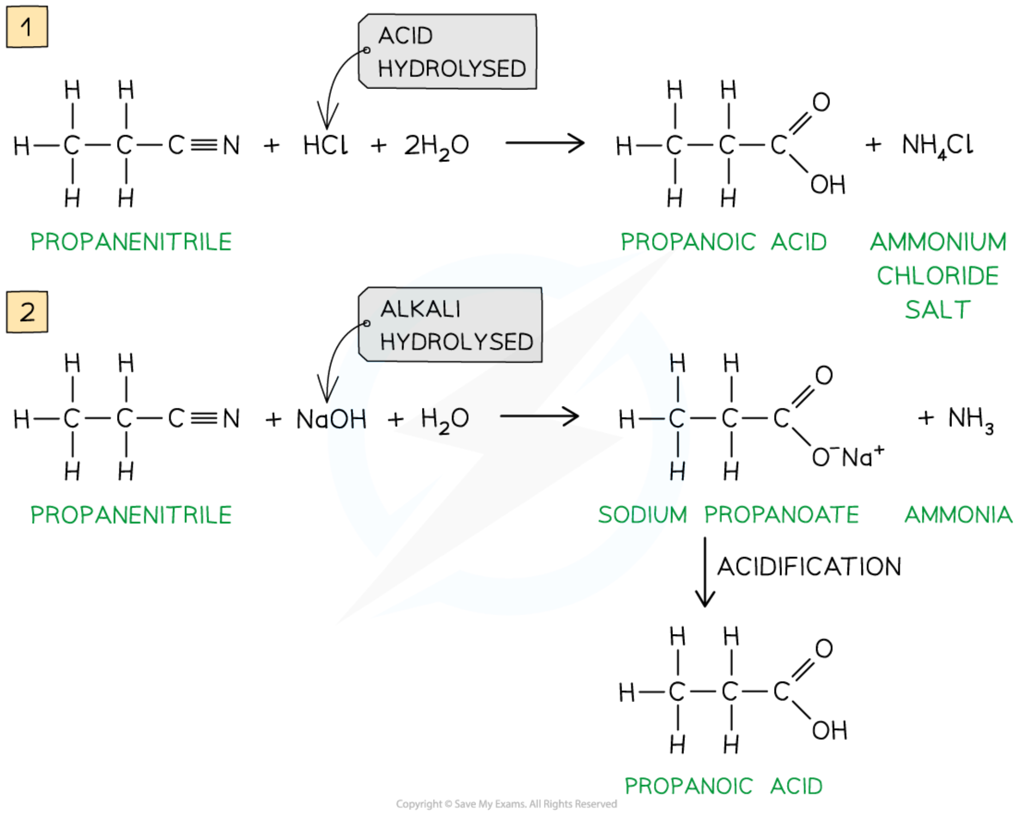
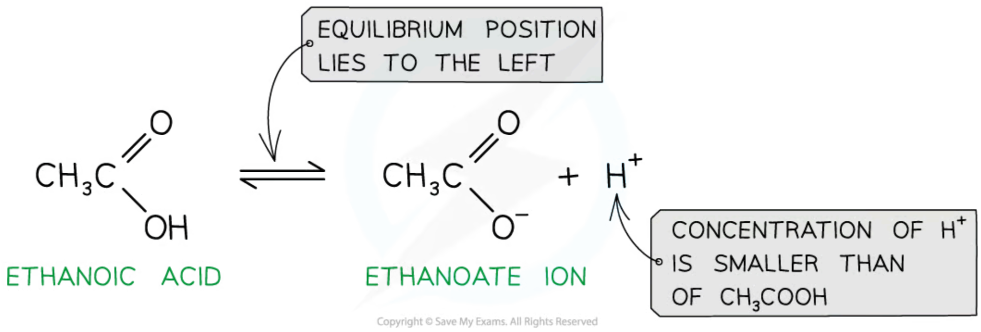
- The -CN group at the end of the hydrocarbon chain is converted to a -COOH group



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

Carboxylic Acids – Reactions

- In aqueous solution they are only slightly ionised, to give low concentrations of hydronium ions and alkanoate ions (often called carboxylate ions)
- This **partial ionisation** in solution means that carboxylic acids are **weak acids**
- This means that the position of the equilibrium lies to the left and that the concentration of H^+ is much smaller than the concentration of the carboxylic acid
- However, the concentration of hydrogen ions is sufficient to react with an aqueous solution of sodium carbonate or sodium hydrogen carbonate to produce carbon dioxide
- These reactions are a useful test for the possible presence of a carboxylic acid:
  - Sodium carbonate: $2RCOOH + Na_2CO_3 \rightarrow 2RCOO^-Na^+ + CO_2 + H_2O$
  - Ionic equation with carbonates: $2RCOOH + CO_3^{2-} \rightarrow 2RCOO^- + CO_2 + H_2O$
  - Sodium hydrogen carbonate: $RCOOH + NaHCO_3 \rightarrow RCOO^-Na^+ + CO_2 + H_2O$
  - Ionic equation with hydrogen carbonates: $RCOOH + HCO_3^- \rightarrow RCOO^- + CO_2 + H_2O$



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

Reaction with $LiAlH_4$

- Carboxylic acids can undergo reduction when they react with a reducing agent such as **lithium tetrahydridoaluminate,** $LiAlH_4$, suspended in dry ether at room temperature
- A carboxylic acid will be reduced to a primary alcohol, for example

$$\mathbf{CH_3CH_2COOH\ (l) + 4[H] \rightarrow CH_3CH_2CH_2OH\ (l) + H_2O\ (l)}$$

- Addition of water at the end will destroy any excess lithium tetrahydridoaluminate

Reaction with bases

- 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:

$$2CH_3COOH\ (aq) + MgO\ (s) \rightarrow (CH_3COO)_2Mg\ (aq) + H_2O\ (l)$$

- 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:

$$CH_3COOH\ (aq) + KOH\ (aq) \rightarrow CH_3COOK\ (aq) + H_2O\ (l)$$

- 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:

$$2CH_3COOH\ (aq) + K_2CO_3\ (s) \rightarrow 2CH_3COOK\ (aq) + H_2O\ (l) + CO_2\ (g)$$

Reaction with phosphorus(V) chloride

- Carboxylic acids react with solid phosphorus(V) chloride to form an acyl chloride
- For example, propanoic acid will react with phosphorus(V) chloride to form propanoyl chloride, phosphorus trichloride oxide and hydrogen chloride

$$CH_3CH_2COOH\ (l) + PCl_5\ (s) \rightarrow CH_3CH_2COCl\ (l) + POCl_3\ (l) + HCl\ (g)$$

- In this reaction, steamy fumes of HCl are produced
- The liquid products can be separated by fractional distillation

Reaction with alcohols

- When carboxylic acids react with alcohols an ester is formed
- **Esters** are compounds with an -COOR functional group and 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**
- The first part of the ester's name comes from the alcohol and the second part of the name comes from the carboxylic acid
    - E.g. Propanol and ethanoic acid will give the ester propyl ethanoate

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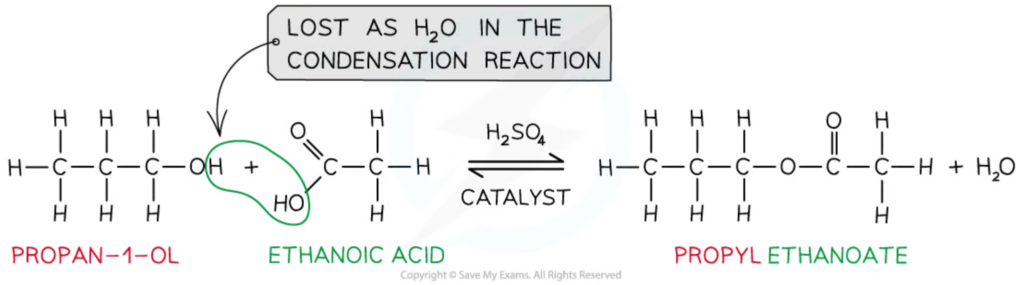

Esters are formed from the condensation reaction between carboxylic acids and alcohols

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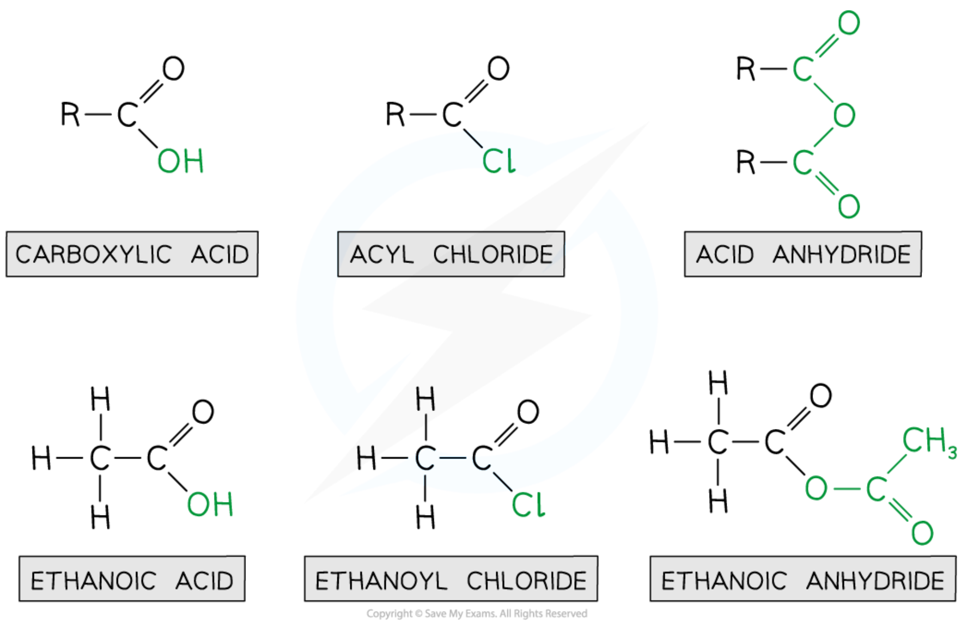
Acyl Chlorides & Esters

Acyl groups can be built into many molecules using acyl chlorides or acid anhydrides (known as acylating agents). Acyl chlorides are **derivatives of carboxylic acids** by substitution of the -OH group by a chlorine atom. They are named by identifying the parent hydrocarbon chain and adding the suffix -*oyl chloride*. They can also be named by removing the -oic acid from the carboxylic acid and adding -*oyl chloride*

- Acid anhydrides are also **derivatives of carboxylic acids** formed by substitution of the -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 -oic acid from the carboxylic acid and adding -*oic anyhydride*



Ethanoic acid derivatives

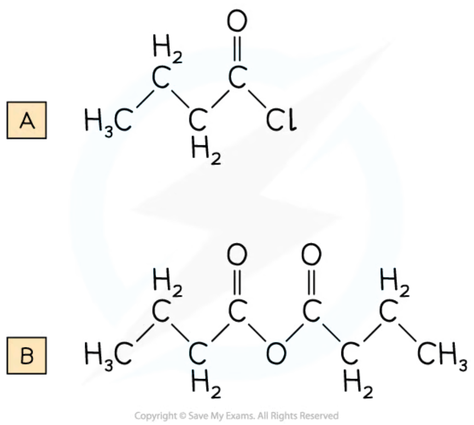
Worked Example

Draw the displayed formula for the following:

A. Butanoyl chloride

B. Butanoic anhydride

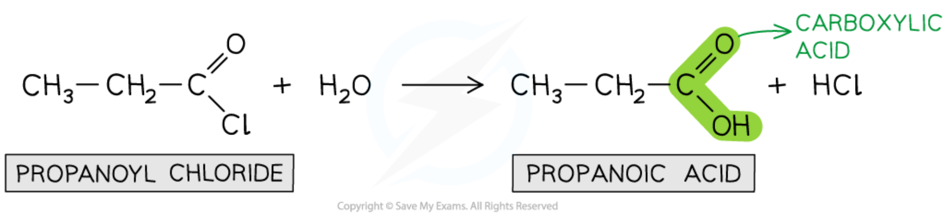
Answer:



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

Hydrolysis

- The **hydrolysis** of acyl chlorides results in the formation of a **carboxylic acid** and **HCl** molecule
- This is a **nucleophilic 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** to form esters
- The esterification of acyl chlorides is also a **nucleophilic addition-elimination** reaction

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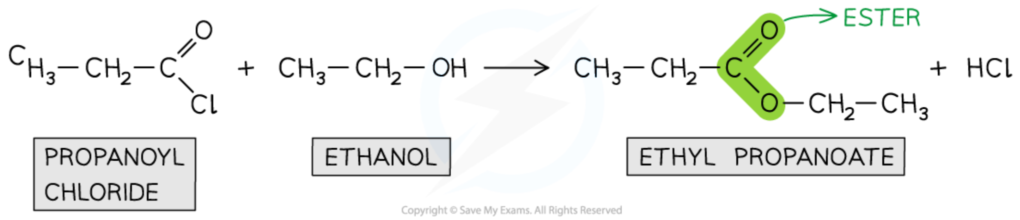
- The alcohol adds across the C=O bond
- A HCl molecule is eliminated



Acyl chlorides undergo esterification with alcohols to form esters

Formation of amides

- Acyl chlorides react with **ammonia** or **primary amines** to form **amides** in a **condensation reaction**.
- A **lone pair** on the nitrogen atom attacks the **carbonyl carbon** in the acyl chloride.
- The reaction proceeds via a nucleophilic **addition–elimination mechanism**:
  - The nucleophile adds to the C=O bond
  - A chloride ion (Cl^-) is eliminated
  - **Hydrogen chloride (HCl)** is formed

What happens to the HCl?

- The **HCl formed** does not remain unreacted.
- It is **immediately neutralised** by a **second molecule** of ammonia or amine present in excess.
- This forms an **ammonium salt** (e.g. NH_4Cl, CH_3NH_3Cl).

Why 2 molecules are needed

- The **1st molecule** of ammonia/amine forms the **amide**
- The **2nd molecule** of ammonia/amine neutralises the **HCl** and forms **ammonium salt**

Examples

- **Reaction with ammonia**
- **Product:** Primary amide (propanamide) and ammonium chloride

$$CH_3CH_2COCl + 2NH_3 \rightarrow CH_3CH_2CONH_2 + NH_4Cl$$

- **Reaction with methylamine**
- **Product:** Secondary (substituted) amide and methylammonium chloride

$$CH_3COCl + 2CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3NH_3Cl$$

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- **Reaction with ethylamine**
- **Product:** Secondary (substituted) amide and ethylammonium chloride

$$CH_3COCl + 2CH_3CH_2NH_2 \rightarrow CH_3CONHCH_2CH_3 + CH_3CH_2NH_3Cl$$

Summary for formation of amides

- All reactions form **HCl**, which is **not observed** as a separate product
- The **HCl is neutralised** by excess ammonia or amine
- The final products are an **amide** and an **ammonium salt**

Examiner Tips and Tricks

Acyl chlorides also react with secondary amines to form secondary amides. They do not react with tertiary amines.

- acyl chloride + primary amine → secondary amide + HCl
- acyl chloride + secondary amine → tertiary amide + HCl
- acyl chloride + tertiary amine → no reaction

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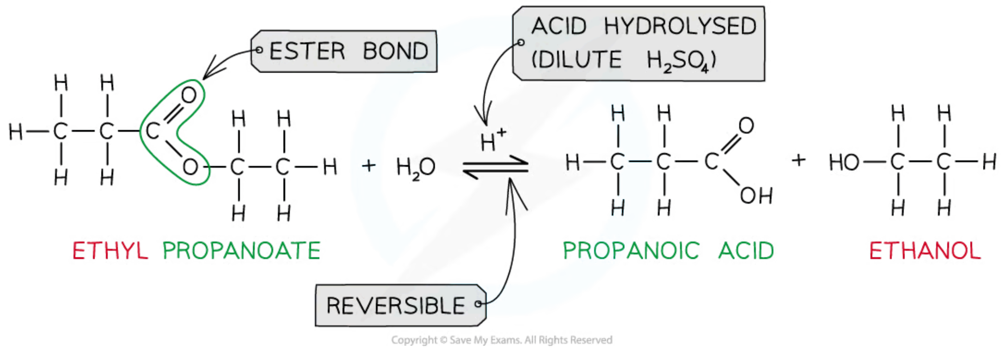
Acid & Alkaline Hydrolysis of Esters

Hydrolysis of Esters – Acid

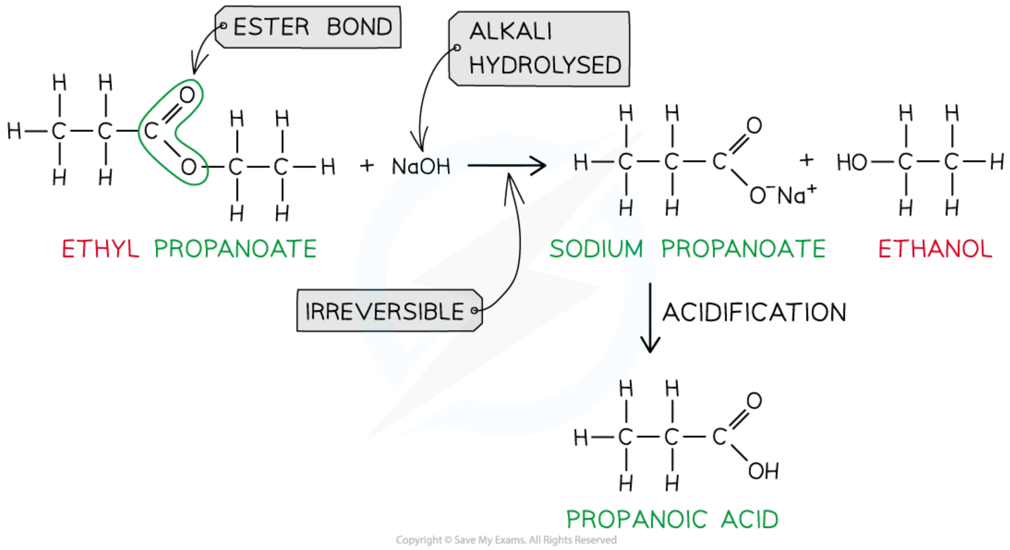
- The reverse of the esterification reaction is called **hydrolysis**
- Ester hydrolysis is a useful reaction for creating biodegradable plastics
- Esters can be **hydrolysed** to reform the carboxylic acid and alcohol or salts of carboxylic acids by using either **dilute acid** (e.g. sulfuric acid) or **alkali** (e.g. sodium hydroxide) and **heat**
- When an ester is **heated under reflux** with **acid** an equilibrium mixture is established, meaning that the hydrolysis reaction is not complete



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

Hydrolysis of Esters – Alkaline

- However, **heating** the ester **under reflux** with **dilute alkali** (e.g. sodium hydroxide) is an **irreversible** reaction as the ester is fully hydrolysed and the reaction goes to completion
- The ester directly reacts with the alkali (NaOH) to produce to form a **carboxylate salt** and **alcohol** in an irreversible step
- The **sodium carboxylate** salt requires further **acidification** to turn into a **carboxylic acid**
    - The sodium carboxylate ($-COO^-$) ion needs to get protonated by an acid (such as HC*l*) to form the carboxylic acid (-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_2SO_4)	Reflux, heat and dilute alkali (NaOH)
Carboxylic acid and alcohol produced	Carboxylate salt and alcohol produced

Worked Example

Name the products and write equations for the following hydrolysis reaction:

1. Ethyl ethanoate with hot dilute sulfuric acid solution
2. Methyl propanoate by hot sodium hydroxide solution

Answer:

Answer 1: Ethanoic acid and ethanol

$CH_3COOCH_2CH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH$

Answer 2: Sodium propanoate and methanol

$CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COONa + CH_3OH$

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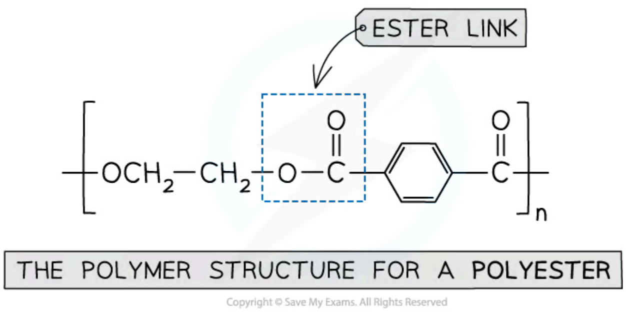
Forming Polyesters

- 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**

Polyester

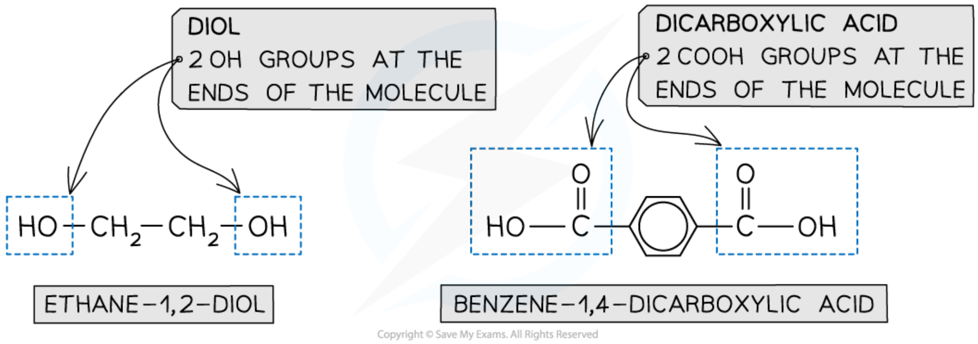
- Is formed by the reaction between **dicarboxylic acid monomers** and **diol monomers**
- Polyester is produced by linking these monomers with **ester bonds / links**



This polymer structure shows an ester functional group linking monomers together

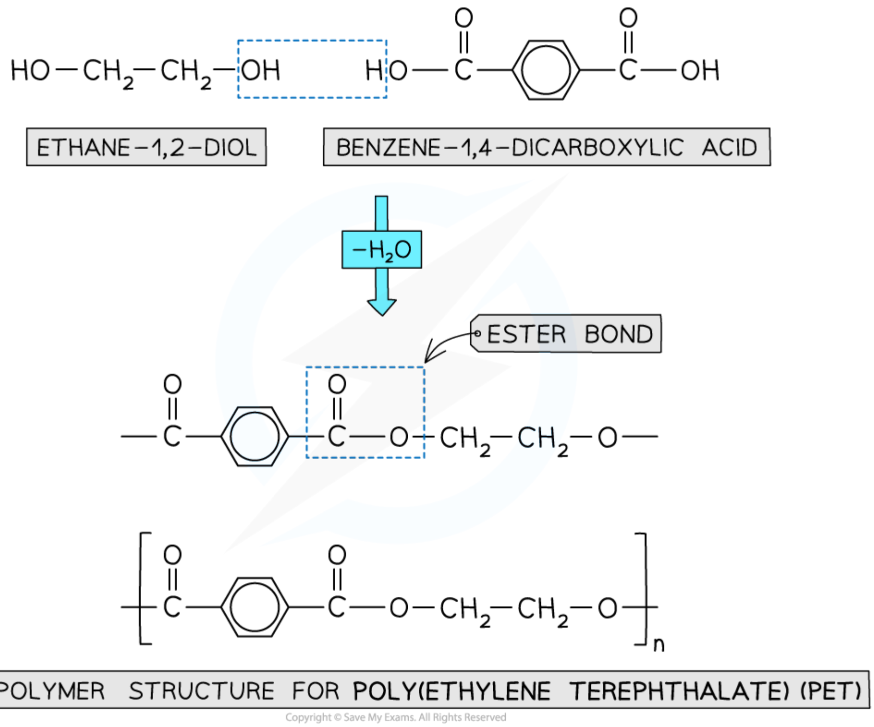
Formation of polyesters

- 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



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

- When the polyester is formed, the H atom on the diol and the -OH group of the -COOH are expelled as a water molecule (H_2O)
- 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

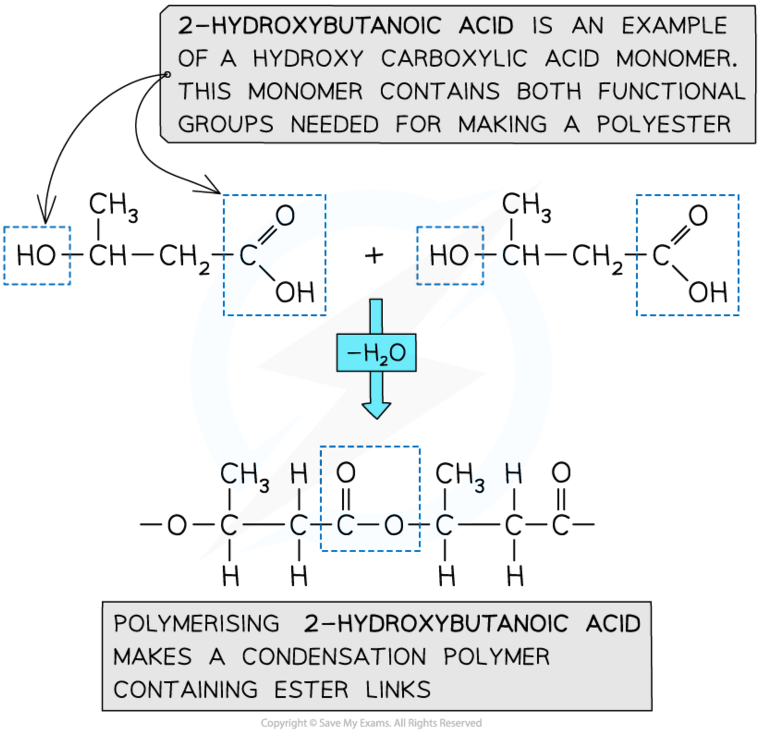


Expulsion of a water molecule in this condensation polymerisation forms the polyester called (ethylene terephthalate) (PET)

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

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