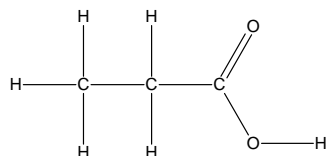


## Carboxylic Acids

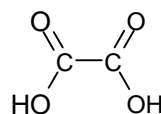
### Carboxylic acids

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



Propanoic acid

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

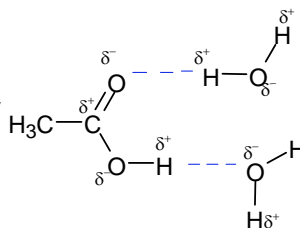


Ethanedioic acid

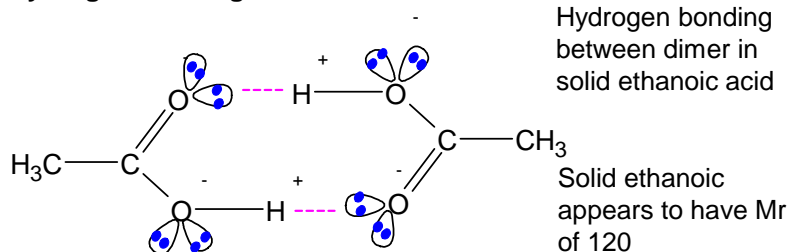
Note the **e** in this name

### Solubility in Water

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



### Hydrogen bonding in solid ethanoic acid

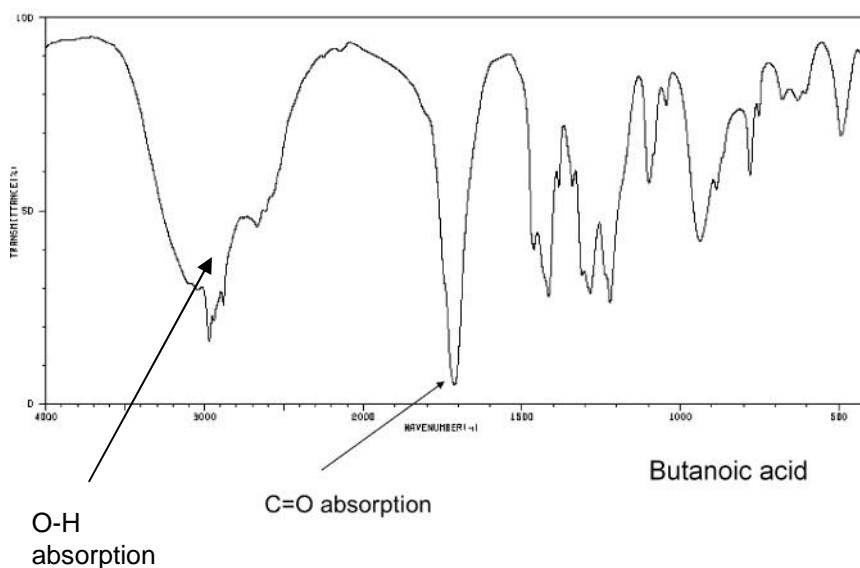


Hydrogen bonding between dimer in solid ethanoic acid

Solid ethanoic appears to have Mr of 120

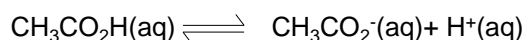
## IR Spectrum for Carboxylic acids

Carboxylic acids have distinct IR spectra with a broad -O-H absorption around (2500-3000) and a sharp -C=O absorption (around 1680-1750)



## Acidity

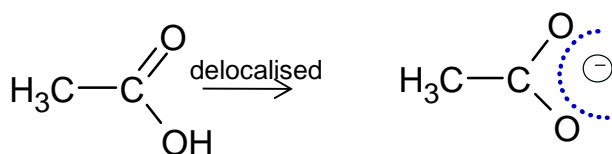
The carboxylic acids are only weak acids in water and only slightly dissociate, but they are strong enough to displace carbon dioxide from carbonates.



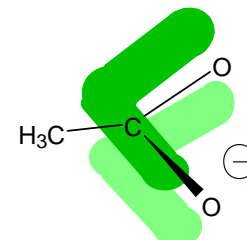
## Delocalisation

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

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

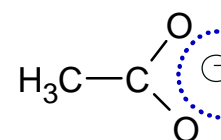
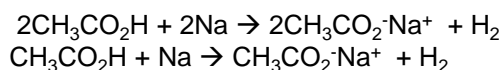


The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form.

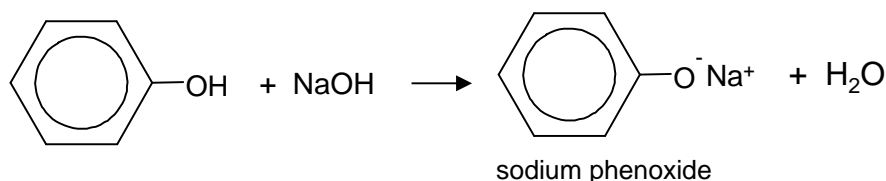
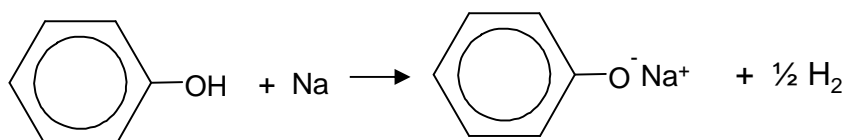


## Relative acidities of carboxylic acids, phenols and alcohols

Carboxylic acids are acidic enough to react with sodium, sodium hydroxide, and sodium carbonate. As mentioned earlier the carboxylic acid salts are stabilised by delocalisation, which makes the formation of the salts more likely. Delocalisation spreads out the negative charge which makes it more stable

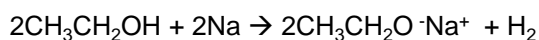


Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Phenols will react with sodium metal and sodium hydroxide, but are not strong enough an acid to react with sodium carbonate. In phenol the lone pair of electrons on the oxygen is delocalised with the electron charge cloud of the arene ring. The delocalised bonding stabilises the formation of the phenoxide ion. The delocalisation is less effective than that in a carboxylate ion

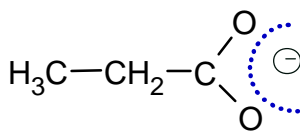
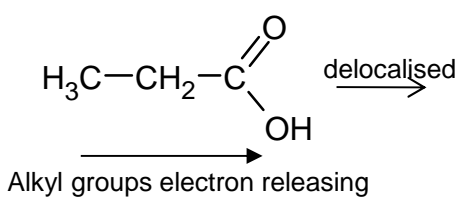


Alcohols have almost no acidity. They do not react with sodium hydroxide or sodium carbonate. They can react with sodium metal.

There is no delocalisation within an alcohol so the formation of a stable ethoxide ion from ethanol is not possible except with the reaction with sodium. The negative charge stays on the oxygen atom which makes it very unstable

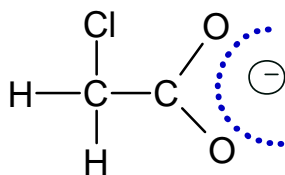
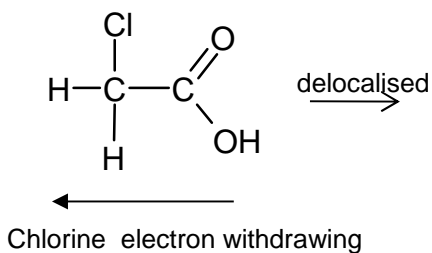


## Strength of carboxylic acids



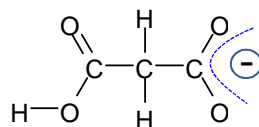
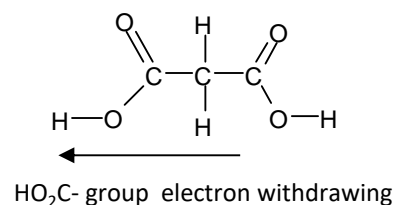
Increasing chain length pushes electron density on to the  $\text{COO}^-$  ion, making it more negative and less stable. This makes the acid less strong.

Propanoic acid less acidic than ethanoic acid



Electronegative chlorine atoms withdraw electron density from the  $\text{COO}^-$  ion, making it less negative and more stable. This makes the acid more strong.

chloroethanoic acid more acidic than ethanoic acid



In a dibasic acid the second  $\text{HO}_2\text{C}$ - group withdraws electron density from the  $\text{COO}^-$  ion, making it less negative and more stable and weakens the O-H bond. This makes the acid more strong.

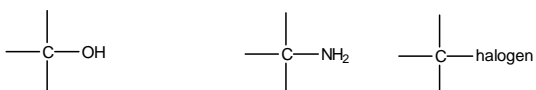
## Revisiting Functional group level

This idea was met in my chapter on alcohols. Although it is only tested explicitly on Pre-U courses it is a good scaffolding exercise to see how the functional groups relate to each other, and is particularly useful for carboxylic acid and related compounds.

The functional group level of a carbon atom can be worked out by counting the number of bonds to electronegative atoms on the carbon.

- No such bonds is called the Hydrocarbon level
- one bond is called the Alcohol level
- two bonds is the Carbonyl level
- three bonds the Carboxylic Acid level
- four bonds the Carbon Dioxide level

### Alcohol level



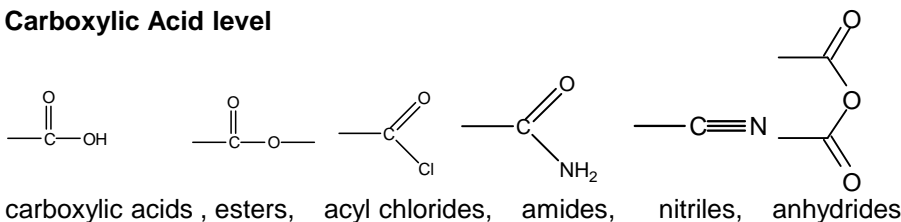
common examples within the Alcohol level include alcohols, amines, halogenoalkanes

### Carbonyl level



examples in the Carbonyl level: aldehydes, ketones

### Carboxylic Acid level



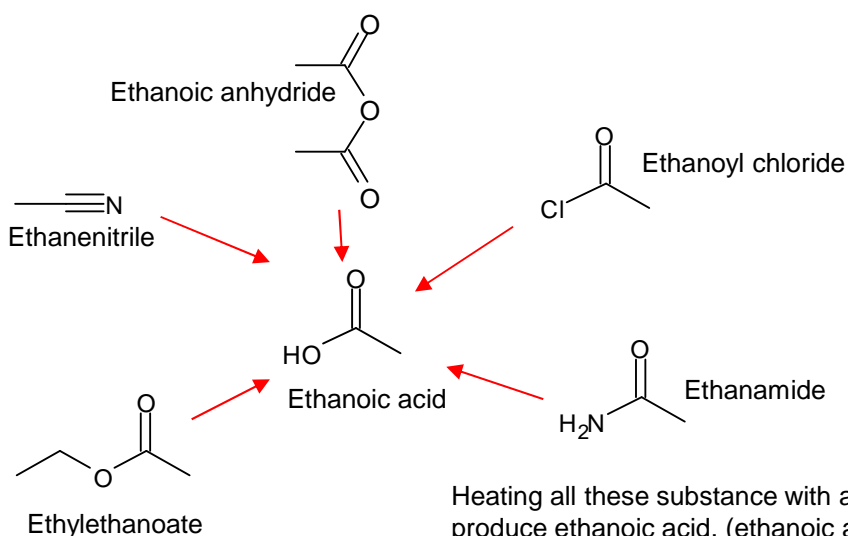
Examples in the Carboxylic Acid level: carboxylic acids, esters, acyl chlorides, amides, nitriles;

carboxylic acids, esters, acyl chlorides, amides, nitriles, anhydrides

The functional groups in the carboxylic acid level are often called carboxylic acid derivatives. The carbon in the functional group has the same oxidation state in all these compounds. Conversions between functional groups within this level are therefore not redox reactions.

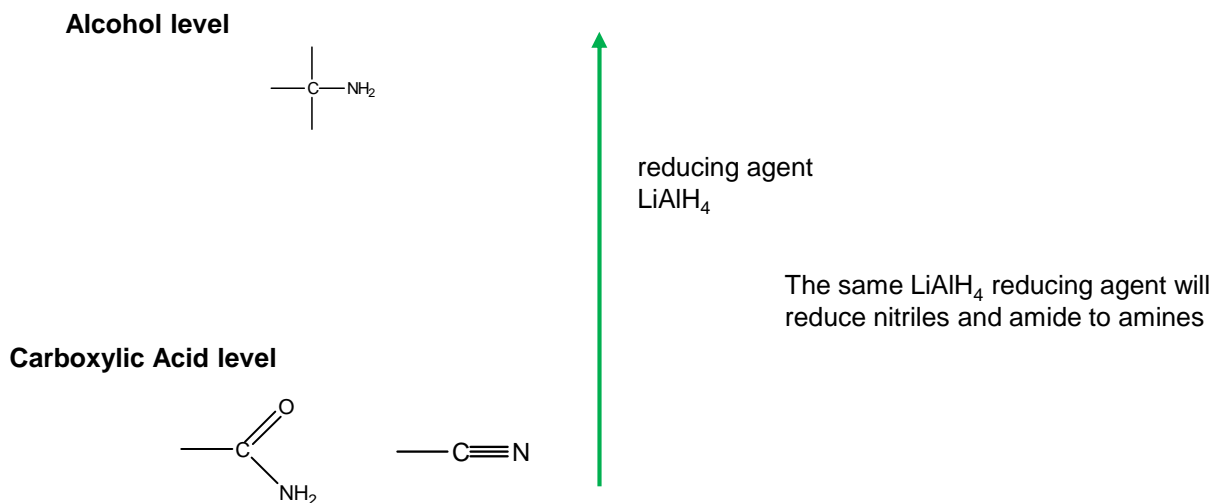
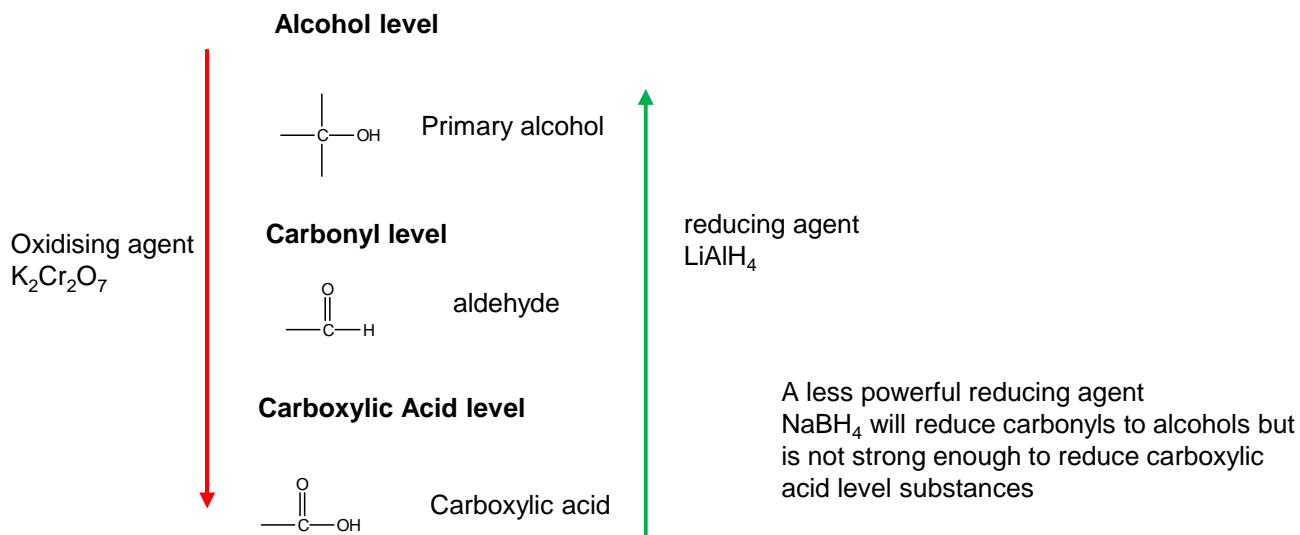
One reaction they all have in common is the **hydrolysis reaction**.

All functional groups within a carboxylic acid level will on reaction with acid produce a carboxylic acid.



Heating all these substance with a dilute acid will produce ethanoic acid. (ethanoic anhydride and ethanoyl chloride will undergo the reaction in milder conditions with just water)

Moving a carbon atom up a level is oxidation and requires an oxidizing agent. Moving a carbon atom down a level is reduction and requires a reducing agent



## Methods of preparing carboxylic acids

As the previous pages show there are many ways carboxylic acids can be produced either by oxidation or hydrolysis. There follows some more detail on some of the more useful reactions of this type.

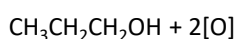
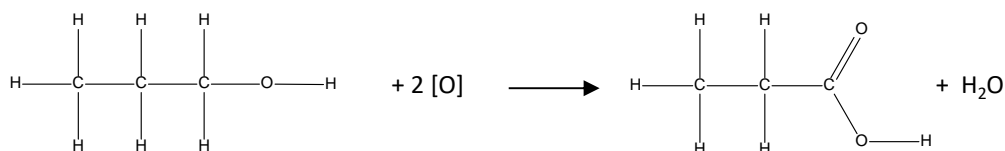
### Full Oxidation of Primary Alcohols

**Reaction:** primary alcohol  $\rightarrow$  carboxylic acid

**Reagent:** potassium dichromate(VI) solution and dilute sulfuric acid

**Conditions:** use an excess of dichromate, and **heat under reflux**: (distil off product after the reaction has finished)

Observation: the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) reduces to the green  $\text{Cr}^{3+}$  ion



propan-1-ol

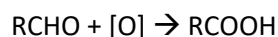
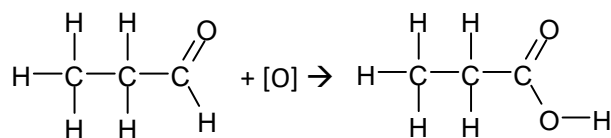
Propanoic acid

### Oxidation of Aldehydes

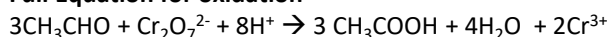
**Reaction:** aldehyde  $\rightarrow$  carboxylic acid

**Reagent:** potassium dichromate (VI) solution and dilute sulfuric acid.

**Conditions:** heat under reflux



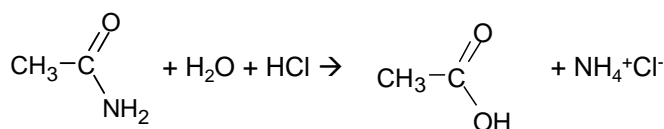
#### Full Equation for oxidation



### Amide hydrolysis

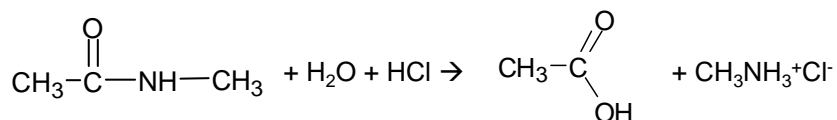
Primary amides can be hydrolysed by aqueous acids.

With HCl an amide will be hydrolysed and split up into a carboxylic acid and an ammonium salt.



Secondary amides can be hydrolysed by aqueous acids.

With HCl an amide will be hydrolysed and split up into a carboxylic acid and an amine salt.

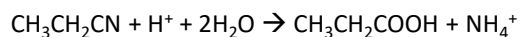


### Hydrolysis of Nitriles

**Reaction:** Nitrile  $\rightarrow$  carboxylic acid

**Reagent:** dilute hydrochloric/ sulfuric acid.

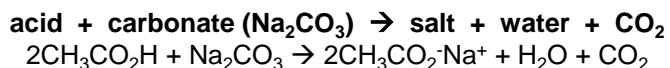
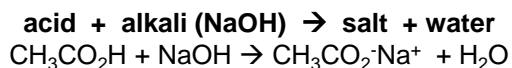
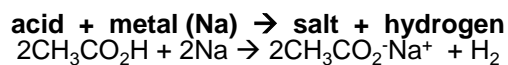
**Conditions:** heat under reflux



## The Reactions of Carboxylic Acids

### Salt formation reactions of carboxylic acids

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



The effervescence caused by production of  $\text{CO}_2$  with carboxylic acids with solid  $\text{Na}_2\text{CO}_3$  or aqueous  $\text{NaHCO}_3$  can be used as a functional group test for carboxylic acids

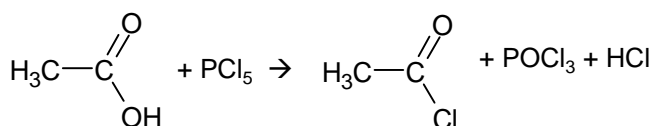
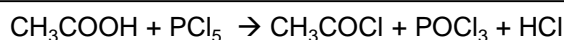
### Reaction of carboxylic acid with phosphorous (V) chloride

**Reaction:** carboxylic acid  $\rightarrow$  acyl chloride

**Reagent:**  $\text{PCl}_5$  phosphorous(V)chloride

**Conditions:** room temp

This reaction with  $\text{PCl}_5$  (phosphorous(V)chloride) can be used as a test for carboxylic acids. You would observe misty fumes of  $\text{HCl}$  produced.



### Reduction of carboxylic acids to alcohols

Lithium tetrahydridoaluminat ( $\text{LiAlH}_4$ ) is a strong reducing agent

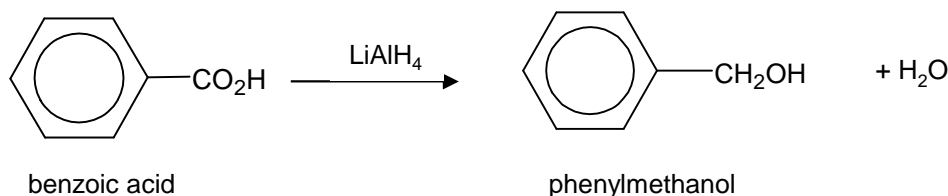
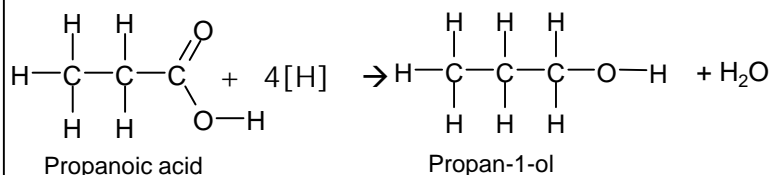
**Reagents:**  $\text{LiAlH}_4$  In dry ether

**Conditions:** Room temperature and pressure

**Type of reaction:** Reduction

**Role of reagent:** Reducing agent

Carboxylic acids will be reduced to primary alcohols



The  $\text{LiAlH}_4$  acts as a nucleophile since  $\text{H}^-$  ions are present.

$\text{LiAlH}_4$  can also be used to reduce carbonyls to alcohols

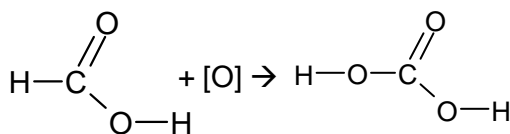
It is not possible to partially reduce a carboxylic acid to an aldehyde.

## Oxidation of carboxylic acids

Most carboxylic acids cannot be oxidised but there are a couple of very specific examples

### Oxidation of methanoic acid

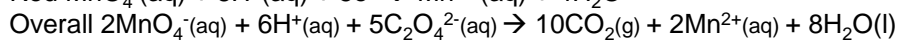
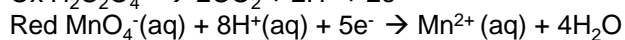
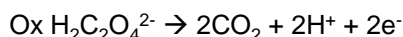
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group



It forms carbonic acid ( $\text{H}_2\text{CO}_3$ ) which can decompose to give  $\text{CO}_2$

### Oxidation of ethanedioic acid

Ethanedioic acid can be oxidised by potassium manganate (VII). The ethanedioic acid is oxidised to carbon dioxide gas. This reaction can be done as a quantitative titration.

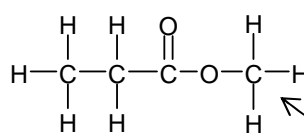


The reaction between  $\text{MnO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to  $60^\circ\text{C}$  to speed up the initial reaction.



## Esterification

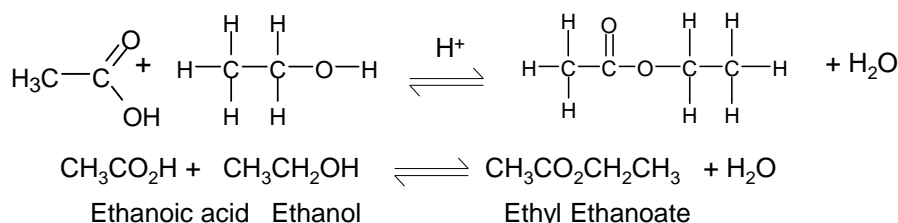
Carboxylic acids react with alcohols, in the presence of a strong acid catalyst, to form esters and water.



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

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

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

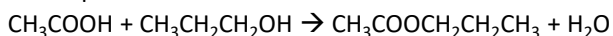


The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst ( $\text{H}_2\text{SO}_4$ ) is needed.

### Detailed Method for Preparing and Purifying an Ester

Propyl ethanoate can be made in the laboratory from propan-1-ol and ethanoic acid.

The equation for the reaction is



#### Procedure

1. Propan-1-ol (50 cm<sup>3</sup>) and ethanoic acid (50 cm<sup>3</sup>) are mixed thoroughly in a 250 cm<sup>3</sup> round-bottomed flask.

2. **Concentrated sulfuric acid** (10 cm<sup>3</sup>) is added **drop by drop to the mixture**, keeping the contents of the flask well-shaken and **cooled** in an ice-water bath.

3. When the acid has all been added, a **reflux condenser** is fitted to the flask and the mixture gently boiled over an **electric heating mantle** for about **30 minutes**.

4. The mixture is cooled, and the apparatus rearranged for distillation. The crude ester (about 60 cm<sup>3</sup>) is distilled off.

5. The distillate is placed in a separating funnel and shaken with about half its volume of **30% sodium carbonate** solution, with the **pressure being released at intervals**. The **lower aqueous layer is then discarded**.

6. The crude ester is shaken in a separating funnel with about half its volume of 50% calcium chloride solution, which removes unreacted alcohol. The lower layer is discarded.

7. The ester is run into a clean, dry flask containing **some anhydrous calcium chloride** and swirled.

8. The ester is filtered into a clean, dry flask, with a **few anti-bumping granules**, and distilled. The fraction boiling between 100°C and 103°C is collected.

**Sulfuric acid** is a catalyst

Adding conc  $\text{H}_2\text{SO}_4$  is an exothermic reaction- to prevent uncontrolled boiling over add **drop by drop** and **cool**

In **reflux** the reactant vapours of volatile compound are condensed and returned to the reaction mixture. The reaction is slow so it is heated for **30 minutes**. **The electric heating mantle** allows for controlled heating and stops flammable vapour lighting

**Sodium carbonate** reacts with unreacted acid and remaining catalyst still present after distillation. The reaction produces  $\text{CO}_2$  so the **pressure** of gas needs to be **released**.

The upper layer is organic because it has a lower density than water

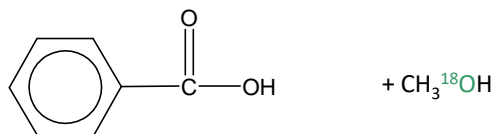
**Calcium chloride** is a drying agent. The liquid will appear clear when dry.

**Anti-bumping granules** are added to prevent vigorous, uneven boiling by making small bubbles form instead of large bubbles

## Mechanism for Esterification

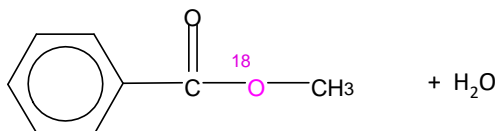
There are two possibilities for the mechanism. Does the single bonded oxygen come from the alcohol or the carboxylic acid?

Experiments were done where a radioactive isotope of oxygen  $O^{18}$  was inserted in an alcohol that was used to make an ester.

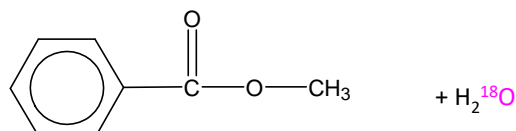


There are two possible results and esters

### Result 1



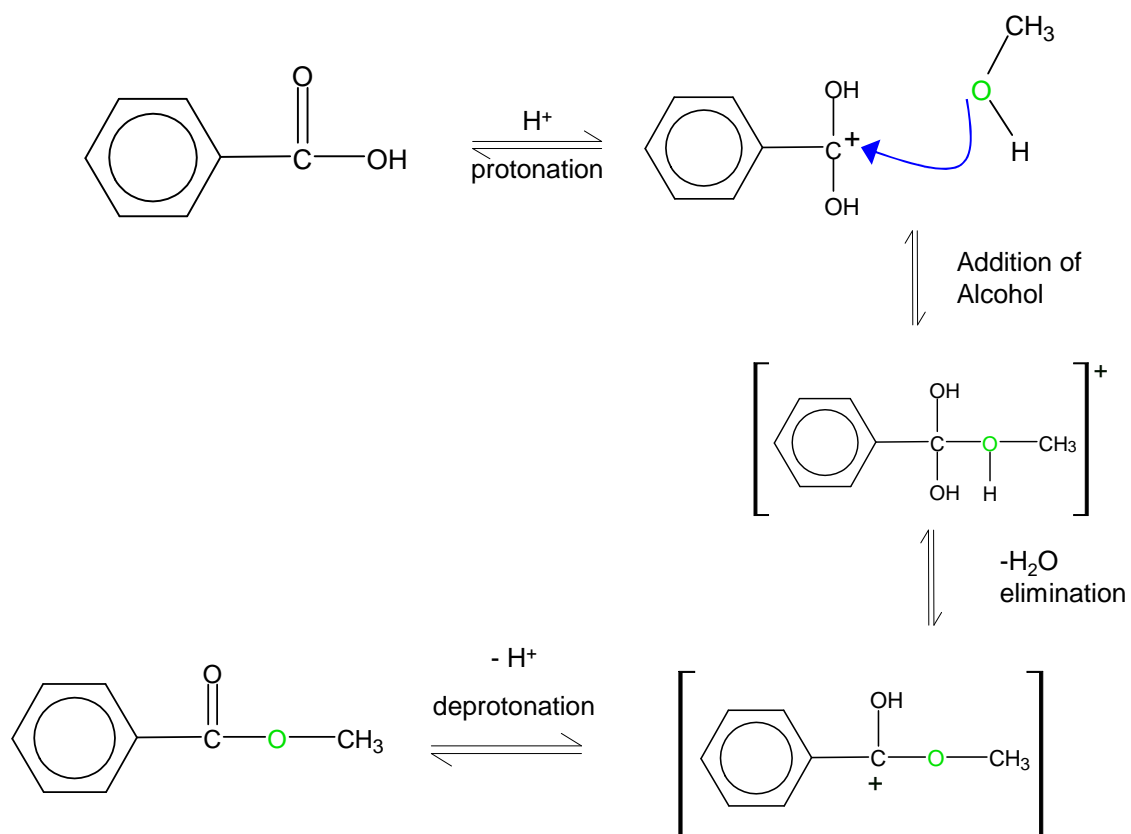
### Result 2



A mass spectrometer showed that the oxygen was found in the ester and not in the water. Result 1 occurs. These bonds must therefore be broken.



### Acid catalysed Addition - Elimination



## Uses of Esters

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

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

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

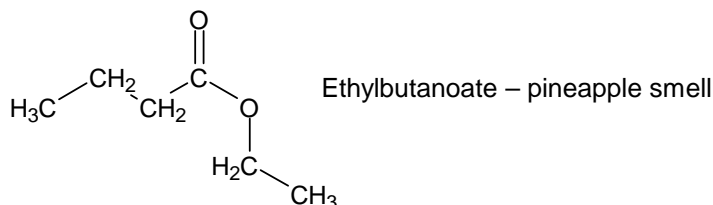
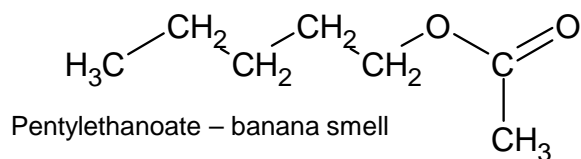
Ethyl ethanoate is used as a solvent in glues and printing inks

Esters can be used as **plasticisers** for polymers

To make PVC 'mock leather' material up to 50% by weight plasticiser must be added.

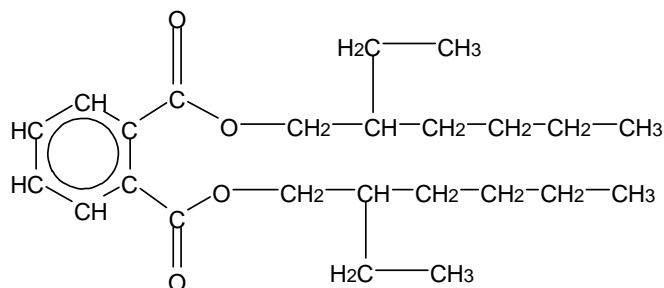
The plasticiser may evaporate over time making the plastic more brittle as it ages.

Esters can have pleasant smells



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

Often pure polymers have limited flexibility because the polymer chains cannot move over each other. Incorporating some plasticiser into the polymer allows the chains to move more easily and the polymer can become more flexible.



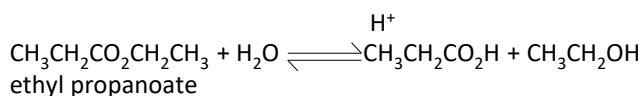
A common ester plasticiser

## Hydrolysis of esters

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

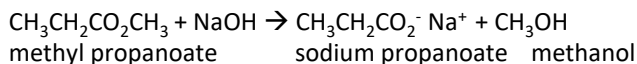
i) with acid  
reagents: dilute acid (HCl)  
conditions: heat under reflux

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



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

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



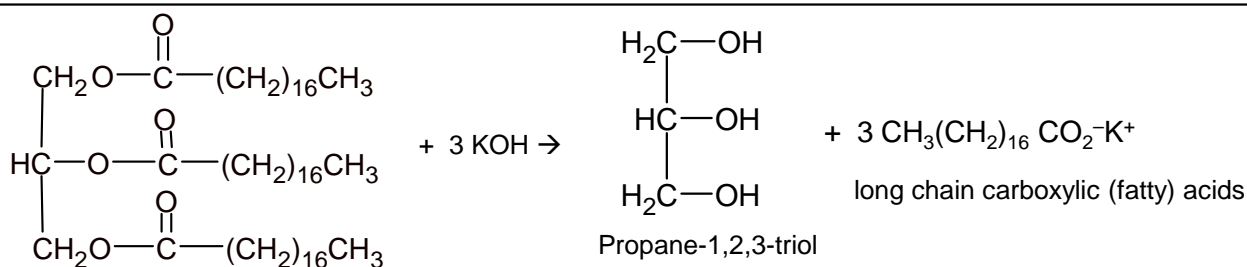
This reaction goes to completion.

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

## Fats and soaps

Fats and oils are ESTERS of glycerol and long chain carboxylic acids (fatty acids)

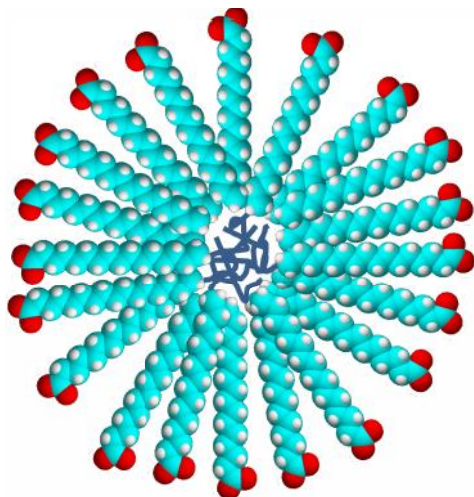
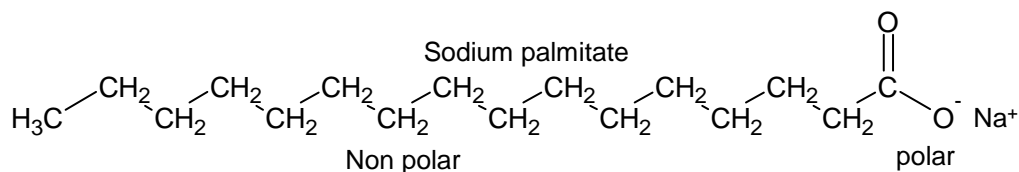
Vegetable oils and animal fats can be hydrolysed to give soap, glycerol and long chain carboxylic (fatty) acids



**Glycerol (propane-1,2,3-triol)** forms hydrogen bonds very easily and is readily soluble in water. It is used in cosmetics, food and in glues.

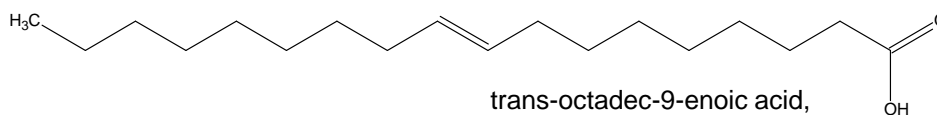
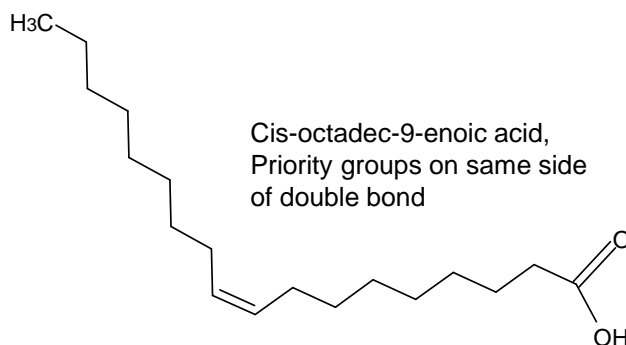
### Soap

Long chain carboxylic (fatty) acids, produced by the hydrolysis of fats, act as soaps. The polar  $\text{CO}_2^-$  end is hydrophilic and mixes with water.



The long non-polar hydrocarbon chain is hydrophobic and mixes with grease. The soap molecules surround a droplet of oil with the hydrophobic ends pointing towards the oil and the hydrophilic ends towards the water. The droplet is then washed away.

unsaturated fatty acids

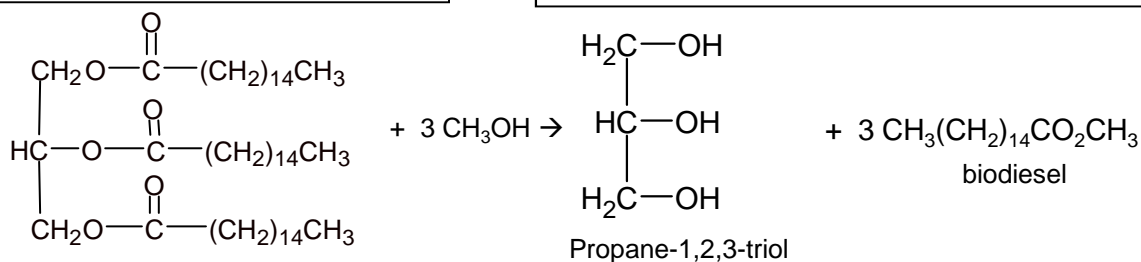


*trans* fatty acids are thought to possibly cause an increase in 'bad' cholesterol and the resultant increased risk of coronary heart disease and strokes.

### Biodiesel

Biodiesel is a mixture of methyl esters of long chain carboxylic acids

Vegetable oils can be converted into biodiesel by reaction with methanol in the presence of a (strong alkali) catalyst



It can be argued that the biodiesel produced from this method is classed as carbon-neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

This does not take into account any energy needed to irrigate plants, extract the oil, heat the reaction with methanol mixture or process the fuel. If the energy for this process comes from fossil fuels then the biofuel produced is not carbon neutral.

It also does not take into account the effect on land available for food production.