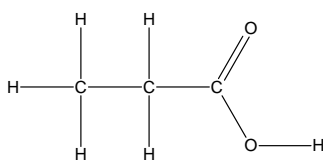# 3.9 Carboxylic Acids and Derivatives
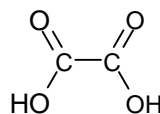
Naming carboxylic acids
These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end.

Propanoic acid

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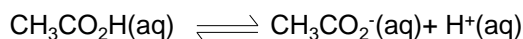

Ethanedioic acid

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.
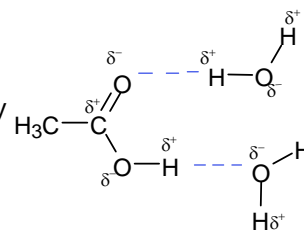

Acidity
The carboxylic acid are only weak acids in water and only slightly dissociate, but they are strong enough to displace carbon dioxide from carbonates.
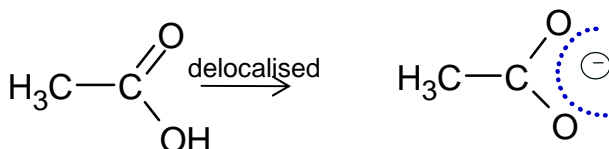
$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

Delocalisation

The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.
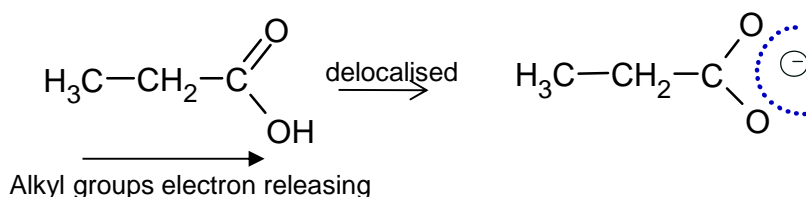
The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.

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

delocalised
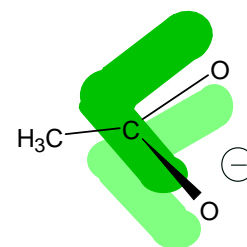
Strength of carboxylic acids

delocalised

Alkyl groups electron releasing

Increasing chain length pushes electron density on to the COO⁻ ion, making it more negative and less stable. This make the acid less strong.

Propanoic acid is less acidic than ethanoic acid

delocalised

Chlorine electron withdrawing
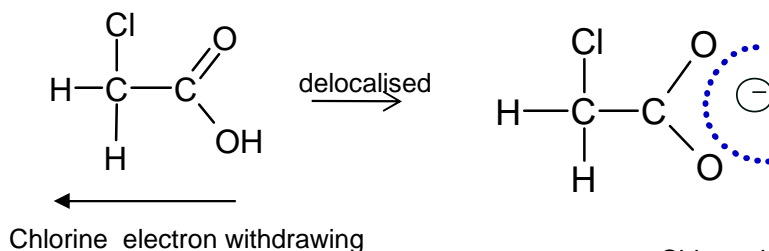
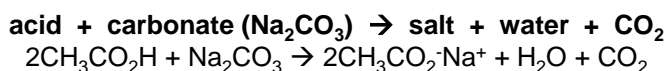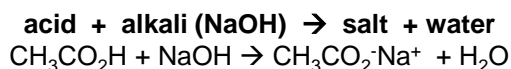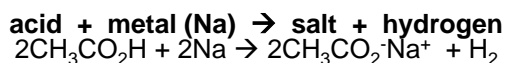Electronegative chlorine atoms withdraw electron density from the COO⁻ ion, making it less negative and more stable. This make the acid more strong.

Chloroethanoic acid is more acidic than ethanoic acid

Salt formation reactions of carboxylic acids

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

acid + metal (Na) → salt + hydrogen
$2CH_3CO_2H + 2Na → 2CH_3CO_2^-Na^+ + H_2$

acid + alkali (NaOH) → salt + water
$CH_3CO_2H + NaOH → CH_3CO_2^-Na^+ + H_2O$

acid + carbonate (Na$_2$CO$_3$) → salt + water + CO$_2$
$2CH_3CO_2H + Na_2CO_3 → 2CH_3CO_2^-Na^+ + H_2O + CO_2$

The effervescence caused by production of CO_2 with carboxylic acids with solid Na_2CO_3 or aqueous $NaHCO_3$ can be used as a functional group test for carboxylic acids

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.
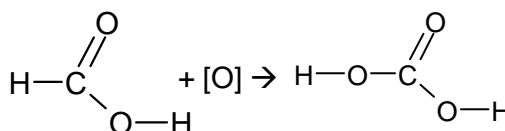
It forms carbonic acid (H_2CO_3) which can decompose to give CO_2

Esterification

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

carboxylic acid + alcohol $\overset{H^+}{\rightleftharpoons}$ ester + water
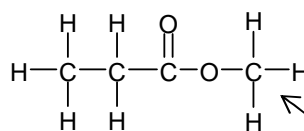
Esters have two parts to their names, eg **methyl** propanoate.

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.

$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$
ethanoic acid   ethanol   ethyl ethanoate
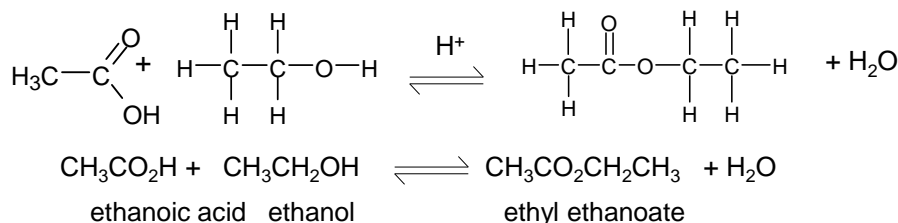
The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst (H_2SO_4) is needed.

Uses of esters

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

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.

Esters can have pleasant smells

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.

Although polar, they do not form hydrogen bonds (reason: there is no hydrogen bonded to a highly electronegative atom).
They have a lower b.p. 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.

2

Hydrolysis of esters | Esters can be hydrolysed and split up by either heating with acid or with sodium hydroxide.
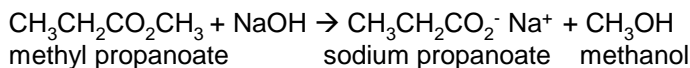
i) with acid
reagents: dilute acid (HCl)
conditions: heat under reflux

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

$$CH_3CH_2CO_2CH_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CH_2CO_2H + CH_3CH_2OH$$
ethyl propanoate
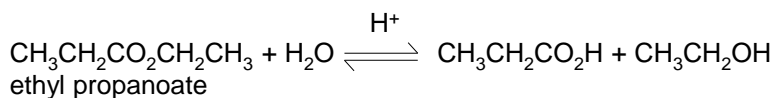
This reaction is reversible and does not give a good yield of the products.

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

$$CH_3CH_2CO_2CH_3 + NaOH \rightarrow CH_3CH_2CO_2^- \ Na^+ + CH_3OH$$
methyl propanoate   sodium propanoate   methanol

This reaction goes to completion. Using excess sodium hydroxide will ensure the ester is completely hydrolysed.

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.

Addition of a strong acid such as hydrochloric acid to the carboxylic acid salt will convert the salt to the carboxylic acid form. $CH_3CH_2CO_2^- \ Na^+ + HCl \rightarrow CH_3CH_2CO_2H + NaCl$

## Practical method for formation of ester and hydrolysis of esters.

Both formation of esters and hydrolysis of esters can be done by heating under reflux. Questions often cover this area.
See practical guide AQA required practical 5 –full oxidation of alcohols using reflux for practical set up and reasons for steps.
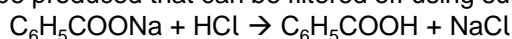Most esters are liquids, so esters produced by reflux can be purified by the steps outlined in practical guide AQA required practical 10 purification of an organic liquid.

Hydrolysis of ethyl benzoate

The liquid ethyl benzoate can be hydrolysed by sodium hydroxide by heating under reflux for 30 minutes.

ethyl benzoate   sodium benzoate
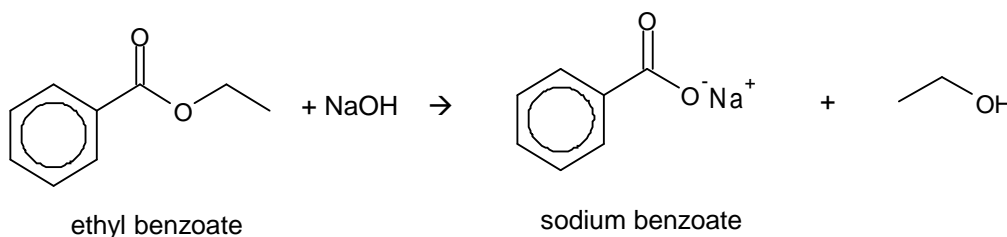
After the reaction is complete allow the mixture to cool to room temperature and add hydrochloric acid. A precipitate of benzoic acid will be produced that can be filtered off using suction filtration.
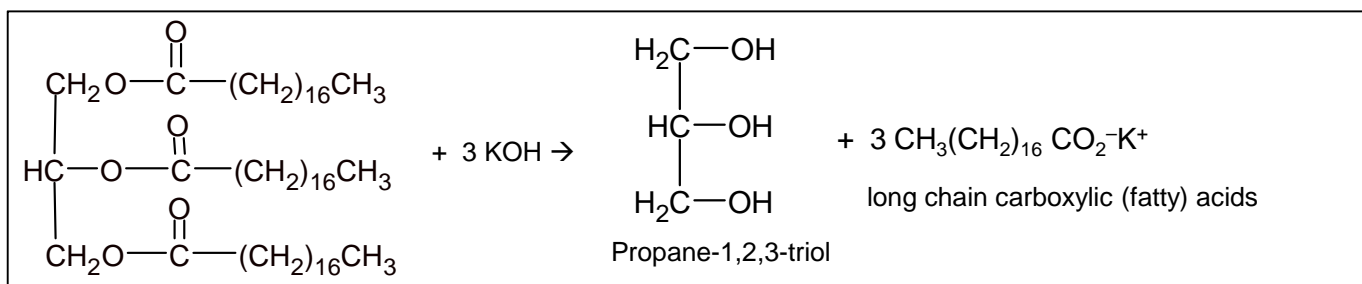$$C_6H_5COONa + HCl \rightarrow C_6H_5COOH + NaCl$$
The benzoic acid can then be purified with the steps outlined in practical guide AQA required practical 10 purification of an organic solid.

Sodium benzoate is soluble in water because it is ionic. Benzoic acid, however, is insoluble. This is because even though the polar COOH group can form hydrogen bonds, the benzene ring is non-polar. In organic compounds there are often polar parts and non-polar parts. The solubility in water of a compound will controlled by whether the polar or non polar part is of greater importance.

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

$$CH_2O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{16}CH_3$$

$$HC - O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{16}CH_3 \quad + \; 3 \; KOH \rightarrow$$

$$CH_2O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{16}CH_3$$

$$H_2C - OH$$
$$HC - OH$$
$$H_2C - OH$$

$+ \; 3 \; CH_3(CH_2)_{16} \, CO_2^- K^+$

long chain carboxylic (fatty) acids

Propane-1,2,3-triol

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.
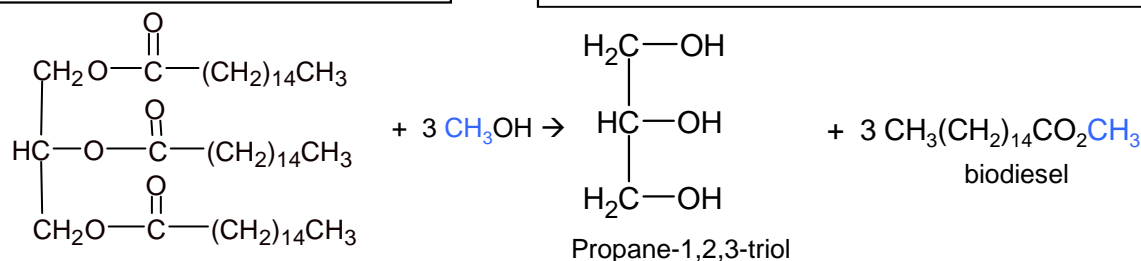
Soap
Long chain carboxylic (fatty) acids, produced by the hydrolysis of fats, act as soaps. The polar CO_2^- end is hydrophilic and mixes with water. The long non-polar hydrocarbon chain is hydrophobic and mixes with grease. So this allows the grease and water to mix and be washed away.
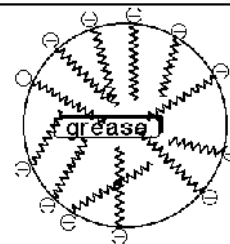
Biodiesel

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

$$CH_2O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{14}CH_3$$

$$HC - O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{14}CH_3 \quad + \; 3 \; CH_3OH \rightarrow$$

$$CH_2O - \overset{\displaystyle O}{\overset{\|}{C}} - (CH_2)_{14}CH_3$$

$$H_2C - OH$$
$$HC - OH$$
$$H_2C - OH$$

$+ \; 3 \; CH_3(CH_2)_{14}CO_2CH_3$

biodiesel

Propane-1,2,3-triol

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 these processes 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.

Carboxylic acid derivatives: Acyl chlorides and Acid anhydrides
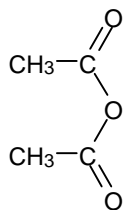
Acyl chlorides
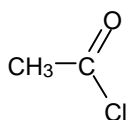
ethanoyl chloride

Acyl chlorides are much more reactive than carboxylic acids

The Cl and –OCOCH$_3$ groups are classed as good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides and acid anhydrides much more reactive than carboxylic acids and esters

Acid anhydrides

ethanoic anhydride.

Acid anhydrides have a similar reactivity to acyl chlorides and therefore bring about the same changes in functional groups.

The main difference is the by-products. Acyl chlorides mostly give off HCl. Acid anhydrides give off RCOOH

Reaction with water

Change in functional group: **acyl chloride → carboxylic acid**
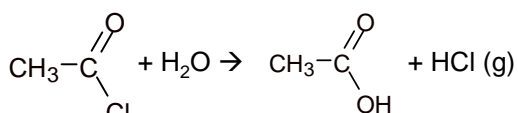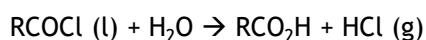
Reagent: **water**

Conditions: **room temp.**
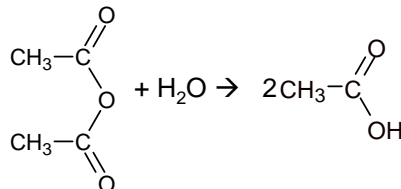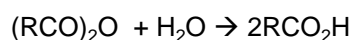
$$RCOCl\ (l) + H_2O \rightarrow RCO_2H + HCl\ (g)$$

Observation: Steamy white fumes of HCl are given off
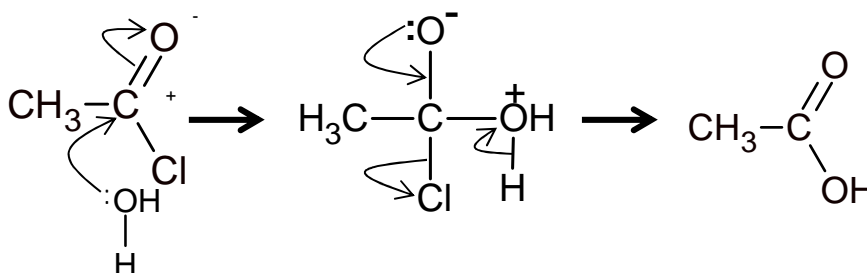
Change in functional group: **acid anhydride → carboxylic acid**

Reagent: **water**

Conditions: **room temp.**

$$(RCO)_2O\ + H_2O \rightarrow 2RCO_2H$$

Nucleophilic Addition Elimination Mechanism

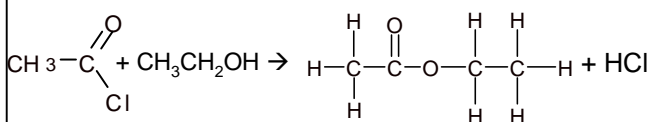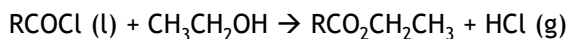## Reaction with alcohol

Change in functional group: **acyl chloride → ester**
Reagent: **alcohol**
Conditions: **room temp.**

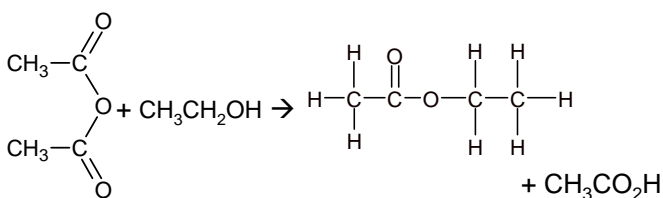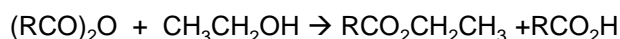$$RCOCl\ (l) + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + HCl\ (g)$$

Observation: Steamy white fumes of HCl are given off

Change in functional group: **acid anhydride → ester**
Reagent: **alcohol**
Conditions: **room temp.**

$$(RCO)_2O\ + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + RCO_2H$$

This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction.
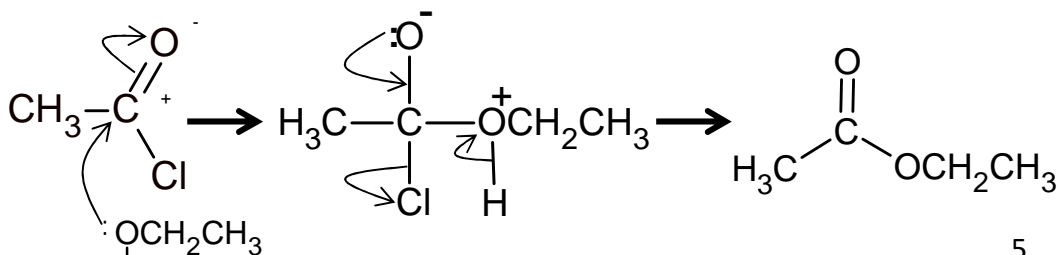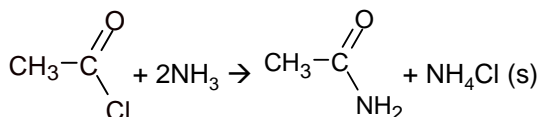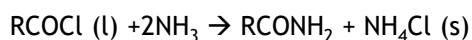
Nucleophilic Addition Elimination Mechanism

Reaction with ammonia

Change in functional group: **acyl chloride → primary amide**
Reagent: **ammonia**
Conditions: **room temp.**
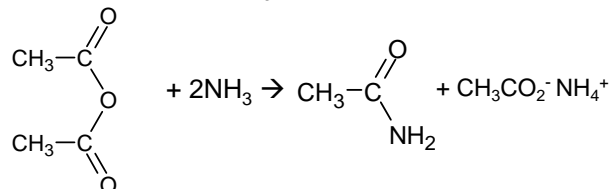
$RCOCl$ (l) $+2NH_3$ → $RCONH_2$ + NH_4Cl (s)

Observation: white smoke of NH_4Cl is given off

Change in functional group: **acid anhydride → primary amide**
Reagent: **ammonia**
Conditions: **room temp.**

$(RCO)_2O$ + $2NH_3$ → $RCONH_2$ + $RCO_2^-NH_4^+$

Nucleophilic Addition Elimination Mechanism
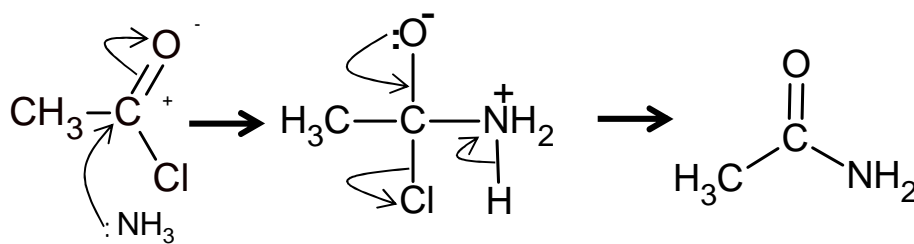
Reaction with primary amines

Change in functional group: **acyl chloride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

$RCOCl$ $+2CH_3NH_2$ → $RCONHCH_3$ + $CH_3NH_3^+Cl^-$

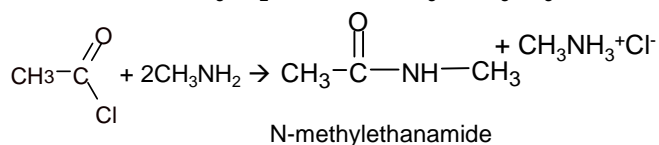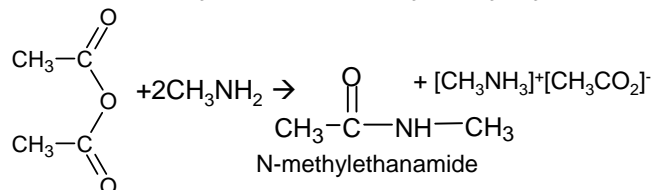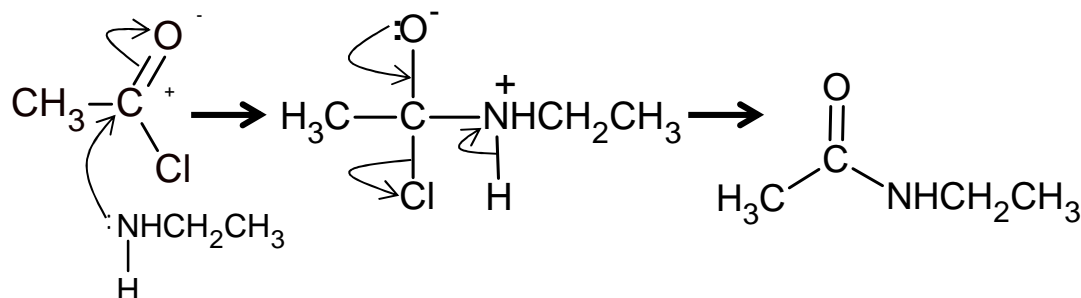N-methylethanamide

Change in functional group: **acid anhydride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

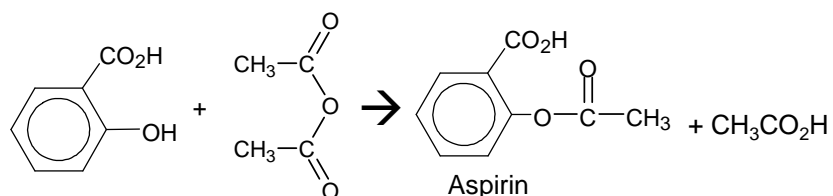$(RCO)_2O$ $+2CH_3NH_2$ → $RCONHCH_3$ + $[CH_3NH_3]^+[RCO_2]^-$

N-methylethanamide

Nucleophilic Addition Elimination Mechanism

Practical: Making Aspirin

Aspirin is made from 2-hydroxybenzoic acid which contains a phenol group. In the reaction the phenol group is turned into an ester by reacting it with the reactive ethanoic anhydride.

Ethanoic anhydride is used instead of acid chlorides because it is cheaper, less corrosive, less vulnerable to hydrolysis, and less dangerous to use.

## Purifying an organic solid: Recrystallisation

Used for purifying aspirin

Step	Reason
1. Dissolve the impure compound in a **minimum volume** of **hot** (near boiling) **solvent**.	An appropriate solvent is one which will dissolve both compound and impurities when hot **and** one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain a saturated solution and to enable crystallisation on cooling
2. **Hot filter** solution through (fluted) filter paper quickly.	This step will remove any insoluble impurities and heat will prevent crystals reforming during filtration
3. **Cool** the filtered solution by inserting beaker **in ice**	Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so solution is not saturated. Ice will increase the yield of crystals
4**. Suction filtrate** with a Buchner flask and funnel to separate out crystals	The water pump connected to the Buchner flask reduces the pressure and speeds up the filtration.
5 Wash the crystals with distilled water	To remove soluble impurities
6. Dry the crystals between absorbent paper	

Loss of yield in this process
- Crystals lost when filtering or washing
- Some product stays in solution after recrystallisation
- other side reactions occurring

The crystals formed through recrystallisation may appear as larger, needle-like crystals, that are lighter in colour than the impure crystals.
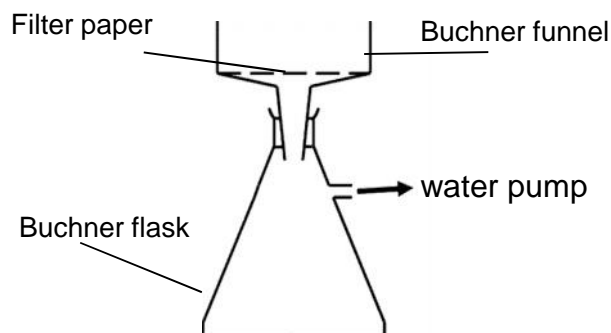
Measuring melting point

One way of testing for the degree of purity is to determine the melting "point", or melting range, of the sample.

If the sample is very pure then the melting point will be a sharp one, at the same value as quoted in data books.

If **impurities** are present (and this can include solvent from the recrystallisation process) the **melting point will be lowered** and the sample will **melt over a range** of several degrees Celsius

Melting point can be measured in an electronic melting point machine or by using a practical set up where the capillary tube is strapped to a thermometer immersed in some heating oil.

In both cases a small amount of the salt is put into a capillary tube. The tube is heated up and is **heated slowly near the melting point**

Comparing an experimentally determined melting point value with one quoted in a data source will verify the degree of purity.

Sometimes an error may occur if the temperature on the thermometer is not the same as the temperature in the actual sample tube.

Thermometer with capillary tube strapped to it containing sample

Heating oil- needs to have boiling point higher than samples melting point and low flammability

Heat