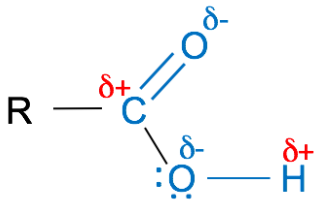
3.9 Carboxylic acids and esters

Introduction to carboxylic acids

- Carboxylic acids have the general formula:

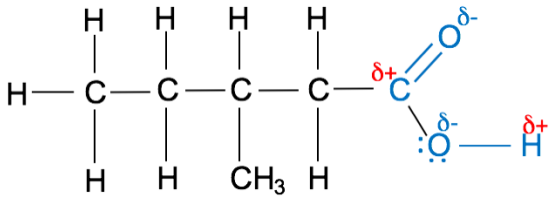


Has carbonyl group C = O

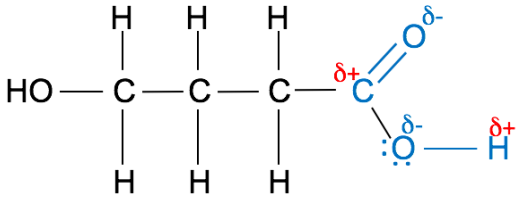
and hydroxyl group C – OH

Naming:

- All carboxylic acids end in 'oic acid'
- The COOH group is the priority group so counting starts from this carbon:



3 methyl pentanoic acid



4 hydroxy butanoic acid

Naming carboxylic acids

- Give the IUPAC name of the following:

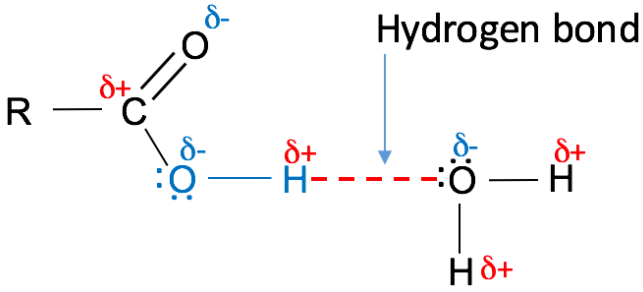
Structure	IUPAC name
$CH_3CH_2CH_2CH_2CH_2COOH$	
$(CH_3)_2CHCH_2COOH$	
$CH_3CH_2CH(CH_3)CH_2COOH$	

- Draw the structure of the following:

Carboxylic acid	Structural formula	Skeletal formula
Methanoic acid		
Ethanoic acid		
2,3 dimethyl hexanoic acid		

Solubility

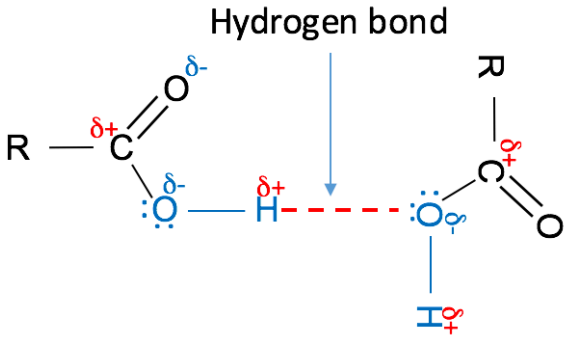
- Solubility – C_1 - C_4 carboxylic acids mix readily:



- C_5 → solubility reduces due to length of insoluble R chain.

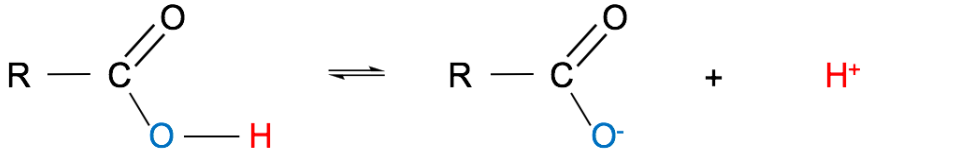
Melting points

- All carboxylic acids hydrogen bond
- With increased R chain, VDW also increases:



Acidic nature of carboxylic acids:

- Carboxylic acids are weak acids as they partially dissociate in water.
- They react as acids to form salts called carboxylates.



Carboxylic acid | Carboxylate ion | Hydrogen ion

- Carboxylic acids are acidic enough to react with metals, alkalis and carbonates.
- Like inorganic acids they behave in the same way:

Metal	+	Acid	→	Salt	+	Hydrogen
Na	+	HCl	→	NaCl	+	½H_2
Na	+	HOOCR	→	NaOOCR	+	½H_2

Usually written:

RCOOH	+	Na	→	RCOONa	+	½H_2

Metal hydroxide	+	Acid	→	Salt	+	Water
NaOH	+	HCl	→	NaCl	+	H_2O
NaOH	+	HOOCR	→	NaOOCR	+	H_2O

Usually written:

RCOOH	+	NaOH	→	RCOONa	+	H_2O

Metal Carbonate	+	Acid	→	Salt	+	Water	+	Carbon dioxide
Na_2CO_3	+	2HCl	→	2NaCl	+	H_2O	+	CO_2
Na_2CO_3	+	2HOOCR	→	2NaOOCR	+	H_2O	+	CO_2

Usually written:

2RCOOH	+	Na_2CO_3	→	2RCOONa	+	H_2O	+	CO_2

Top tip: Remember the test for a carboxylic acid is fizzing with $NaHCO_3$:

$NaHCO_3$	+	HCl	→	NaCl	+	H_2O	+	CO_2
$NaHCO_3$	+	HOOCR	→	NaOOCR	+	H_2O	+	CO_2

Usually written:

RCOOH	+	$NaHCO_3$	→	RCOONa	+	H_2O	+	CO_2

Examples:

$2CH_3CO_2H$ + Mg → $(CH_3CO_2)_2Mg$ + H_2
Magnesium ethanoate

CH_3CO_2H + NaOH → CH_3CO_2Na + H_2O
Sodium ethanoate

$2CH_3CO_2H$ + Na_2CO_3 → $2CH_3CO_2Na$ + H_2O + CO_2
Sodium ethanoate

Questions:

1) For the reactions beneath, finish off the word equations, then write balanced equations underneath:
   a. Ethanoic acid + sodium →

   b. Propanoic acid + magnesium →

   c. Butanoic acid + lithium hydroxide →

   d. Ethanoic acid + sodium carbonate →

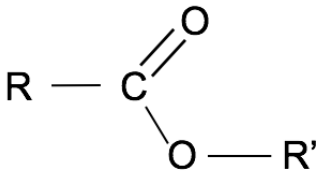
   e. Propanoic acid + lithium hydrogen carbonate →

2) The solubility of the carboxylic acids decreases as the alkyl group increases. Explain this trend:

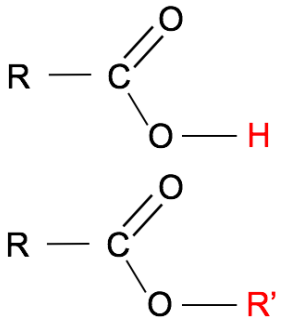
3) Ethanoic acid has a boiling point of 118^{o}C and cyclohexane of 81^{o}C. Both have an Mr = 60. Explain the difference in boiling points and draw a diagram for the interactions between ethanoic acid molecules:

Esters

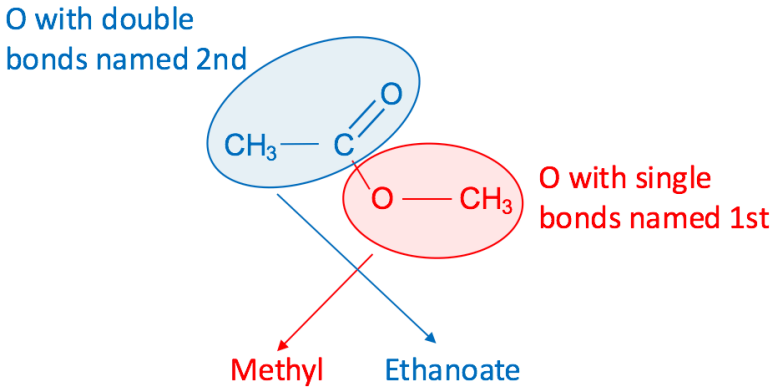
- Esters have the general formula:



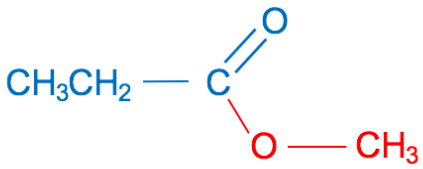
- They are derived from carboxylic acids.
- Esters are called a ***derivative*** of carboxylic acids due to the ***substitution of the hydrogen*** in the hydroxyl group with an ***alkyl*** group.

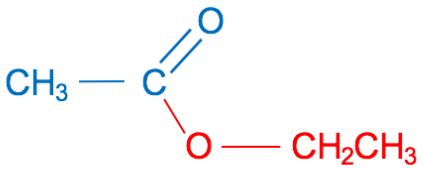


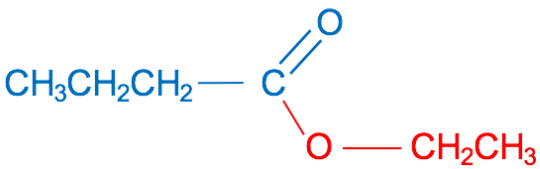
Naming esters

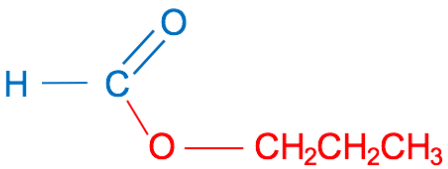


Name the following esters:





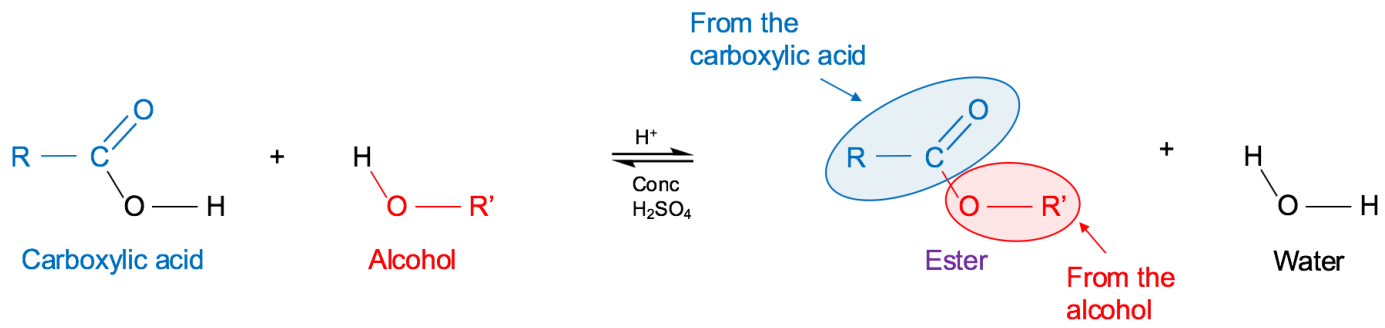




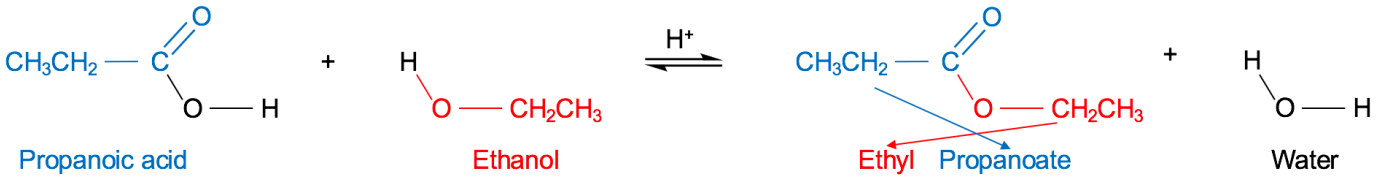
Esterification - making esters:

- The reaction is known as esterification.
- It is a reversible reaction:

Carboxylic acid + Alcohol $\overset{H^+}{\rightleftharpoons}$ Ester + Water

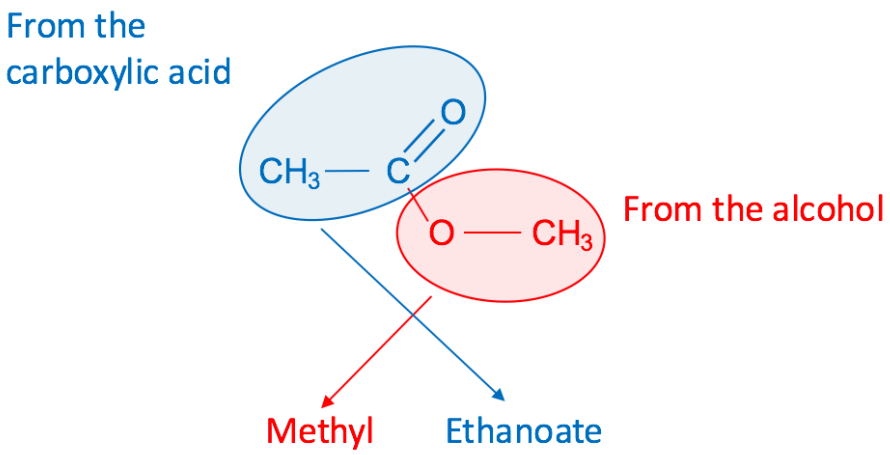


Example:

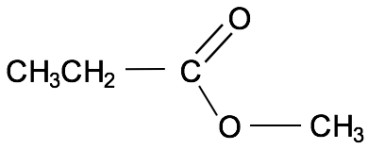


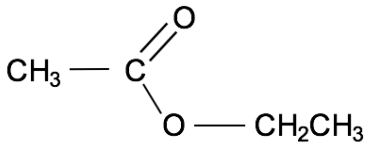
- The name of the ester comes from the alcohol and the carboxylic acid

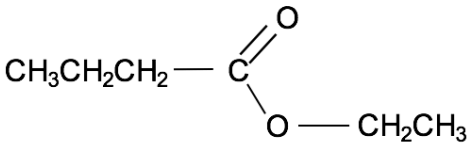
1) Alcohol comes 1st becomes 'yl'
2) Carboxylic acid 2nd becomes 'oate'

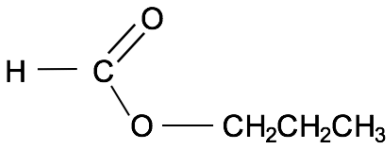


Name the alcohol and carboxylic acids used to make the following esters. Write balanced chemical equation showing the esterification reaction:









Uses of esters

- Flavourings – due to their sweet smells / tastes
- Perfumes – Due to their sweet smells
- Solvents – polar molecules
- Plasticisers

Reactions of esters:

1) Hydrolysis of esters:

- It is the reverse reaction of esterification:
- This is the breaking of a bond (in esters) with water.

Carboxylic acid + Alcohol $\overset{H^+}{\rightleftharpoons}$ Ester + Water

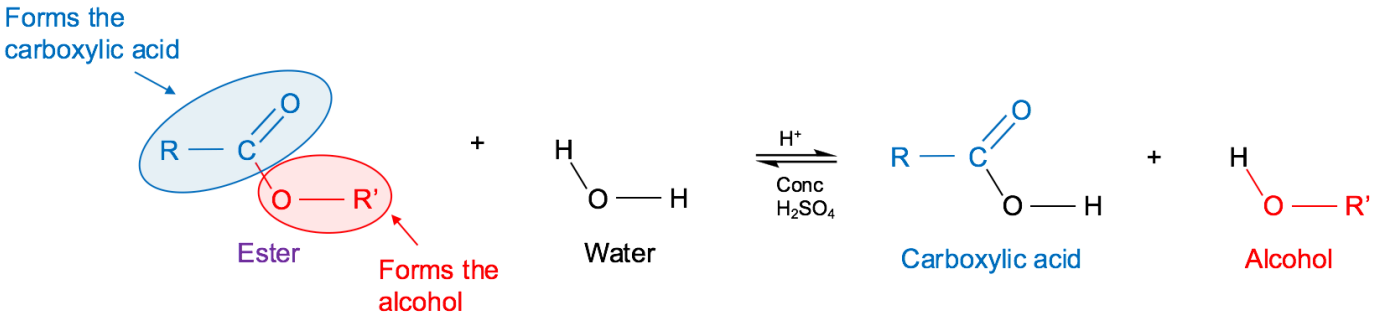
Ester + Water $\overset{H^+}{\rightleftharpoons}$ Carboxylic acid + Alcohol

- It can be done using an acid or alkaline catalyst. The products formed are slightly different:

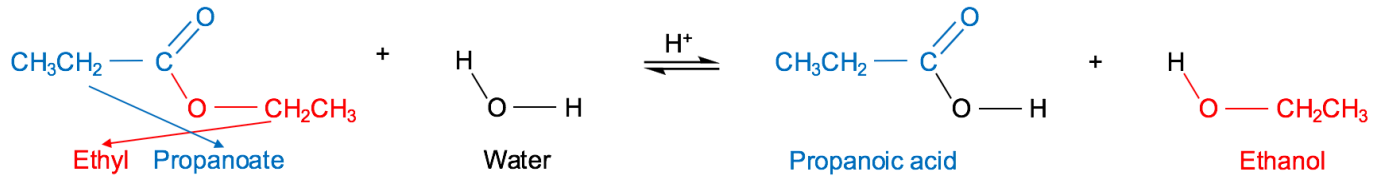
a) Acid hydrolysis:

Reagent: dilute aq sulphuric or hydrochloric acid
Conditions: Ruflux

- The **hydrolysis** of any carboxylic acid **derivative** results in the **carboxylic acid**.



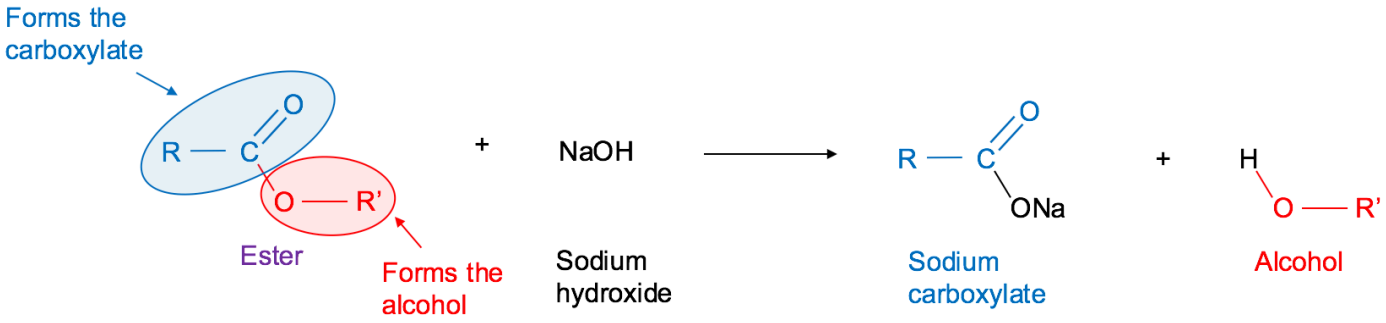
Example:



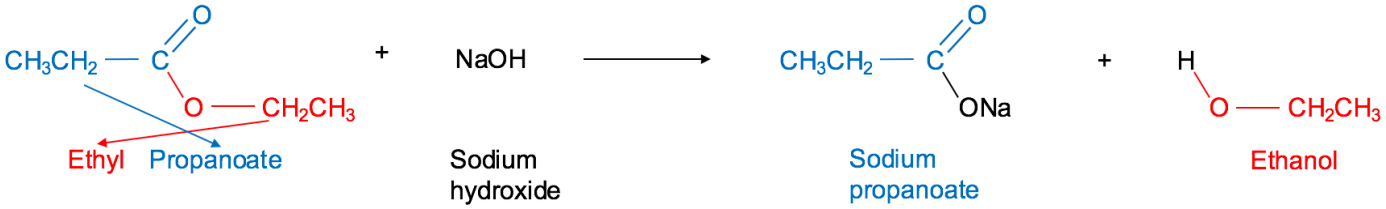
b) Alkaline hydrolysis:

Reagent: dilute aq sodium hydroxide
Conditions: Ruflux

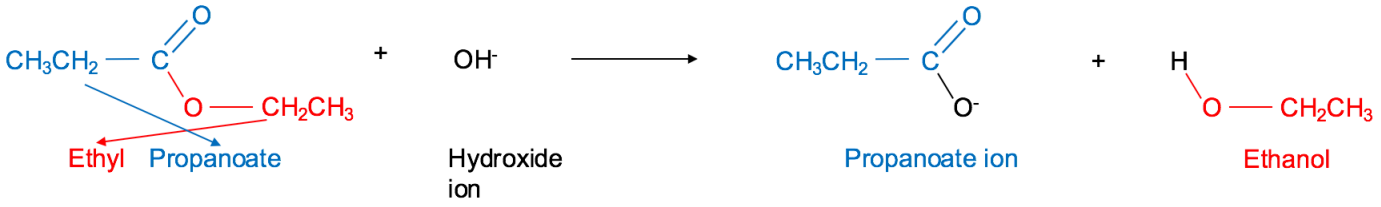
- When a base is used, the product is the carboxylate ion / salt of the carboxylic acid:



Example



or



***Note:** The carboxylate salt can be converted to the carboxylic acid by adding an acid, eg HCl, H_2SO_4

Questions:

1) Write balanced chemical reactions for the acid hydrolysis of the following. Name the products for each reaction:
    a. Ethyl ethanoate

    b. Methyl ethanoate

    c. Propyl methanoate

    d. Methyl propanoate

2) Write balanced chemical reactions for the alkaline hydrolysis of the following. Name the products for each reaction:
    a. Ethyl ethanoate

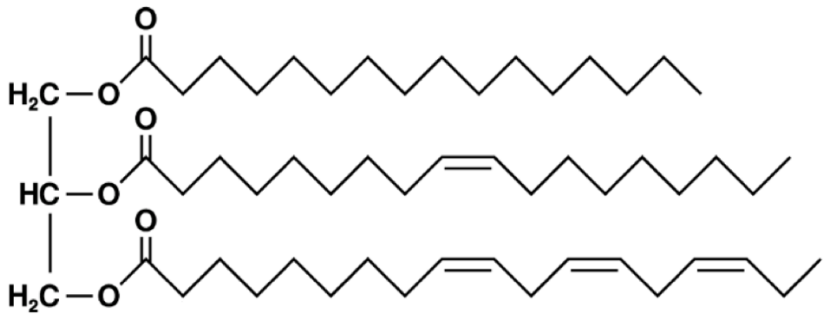
    b. Methyl ethanoate

    c. Propyl methanoate

    d. Methyl propanoate

Fats and oils

- Fats and oils are basically esters made from propan-1,2,3-triol or glycerol (a triol) and long chain carboxylic acids called fatty acids:



- Its melting point determines whether it is a fat or oil.
- Its melting point is determined by the strength of the VDW forces of attraction.

Fats are solids:

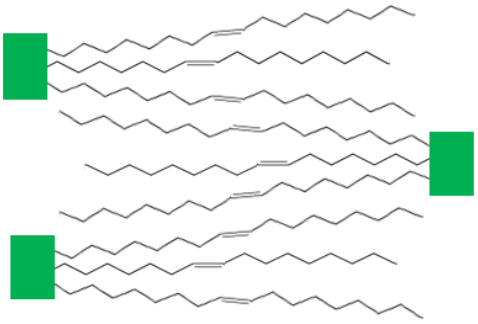
If its melting point is above room temperature it is a solid which makes it a fat, eg margarine and butter.

These tend to have saturated fatty acids allowing them to pack efficiently:

Oils are liquids

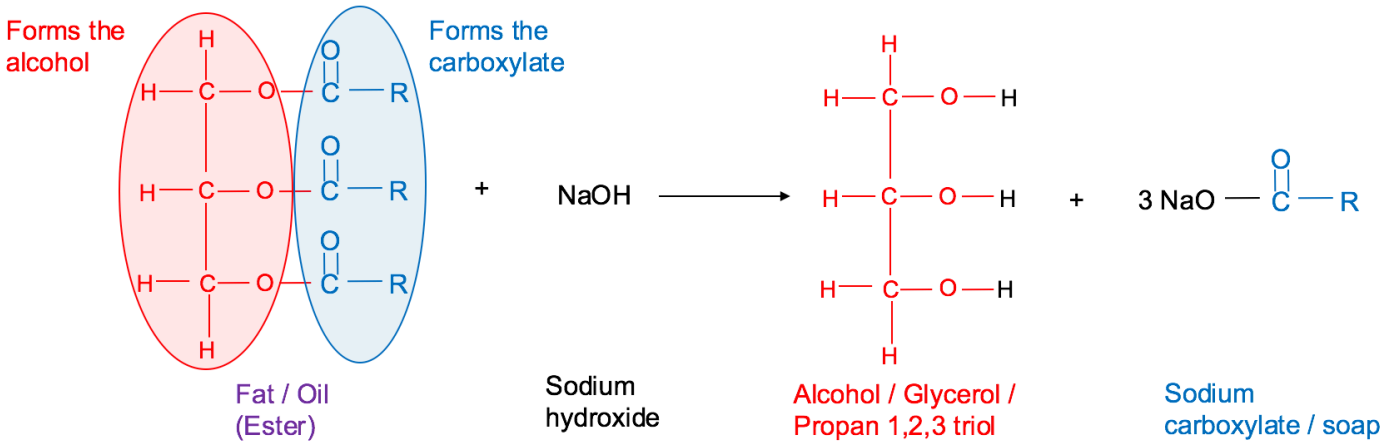
If its melting point is below room temperature it is a solid which makes it an oil, eg olive oil.

These tend to have unsaturated fatty acids. The chains are bent and don't pack together as efficiently:



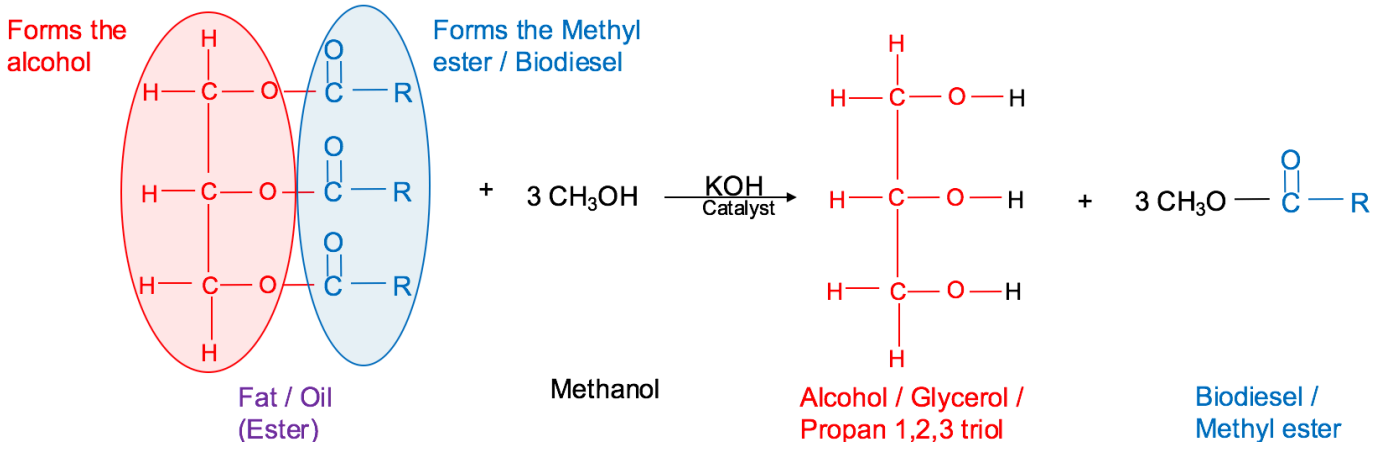
- All fats and oils are basically esters (tri esters) which means they can be hydrolysed:

Hydrolysis of fats and oils:



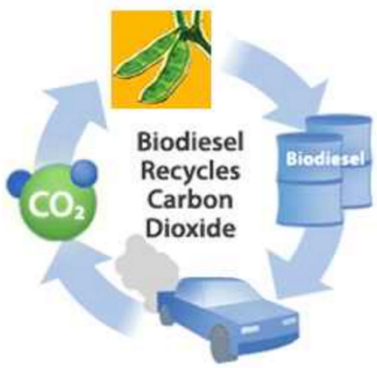
- The sodium carboxylate can be converted back to a carboxylic acid by the reaction with an acid, HCl.

Biodiesel:



- Often referred to as 'transesterification' reactions.
- Vegetable oils like rapeseed are often used.
- The R group in the biodiesel comes from the fatty acid.
- The molecules have the same properties as diesel.

Carbon neutral:



- A common misconception is that biodiesel is carbon neutral.
- In terms of CO_2 taken in to make the fuel and CO_2 given out during combustion, they are?
- It doesn't however include all the processing to take it from seed to biodiesel.
- Planting, watering, harvest, transporting etc

Questions:

1) State and explain the difference between fats and oils. In your answer you should include:
   - The physical states
   - The intermolecular forces
   - Features in the structure responsible for its physical state
   - The packing of the fats / oils

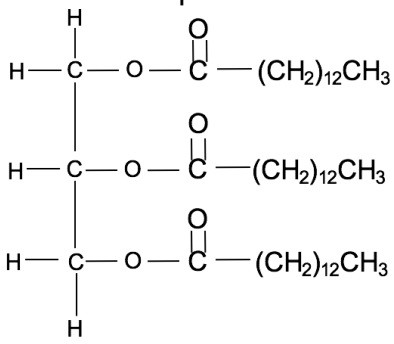
2) Stearic acid is a common fatty acid, $CH_3(CH_2)_{16}COOH$.
   a. Draw the molecule formed when 3 of these molecules react with propan1,2,3 triol:

   b. Would this triester be a fat or an oil? Explain your answer

   c. Write an equation for the alkaline hydrolysis of this triester, draw a circle around the 'soap molecule'

   d. How could the soap be converted into stearic acid? Write an equation to show this:

e. The molecule below is often found in rapeseed oil:



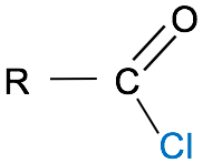
Write a chemical equation for its conversion into biodiesel:

Is this fuel carbon neutral? Explain your answer:

Acyl chlorides

Introduction to acyl chlorides

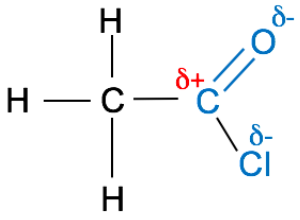
- Acyl chlorides have the general formula:



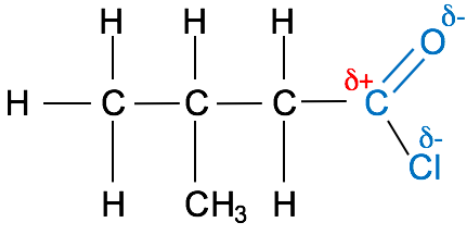
Has the functional group COCl

Naming:

- All acyl chlorides end in 'oyl chloride'
- The COCl group is the priority group so counting starts from this carbon:



Ethanoyl chloride



3 methyl butanoyl chloride

Naming acyl chlorides

- Give the IUPAC name of the following:

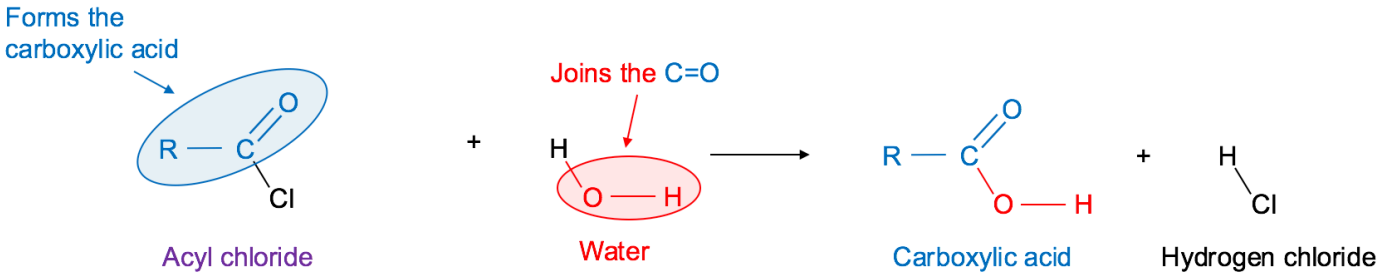
Structure	IUPAC name
$CH_3CH_2CH_2CH_2CH_2COCl$	
$(CH_3)_2CHCH_2COCl$	
$CH_3CH_2CH(CH_3)CH_2COCl$	

Reactions of acyl chlorides:

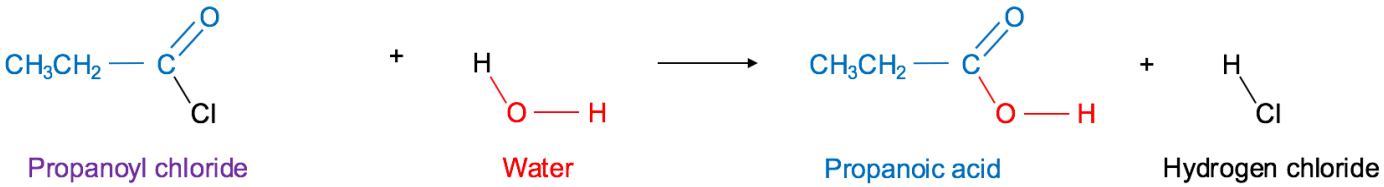
- The acyl chlorides are very reactive.
- The **Cl** is always **substituted** with an **O containing group** or an **N containing group.**
- **HCl is always given off** – white fumes are seen as they react with water vapour in the air

1) With water:

- The reaction with water gives the carboxylic acid:

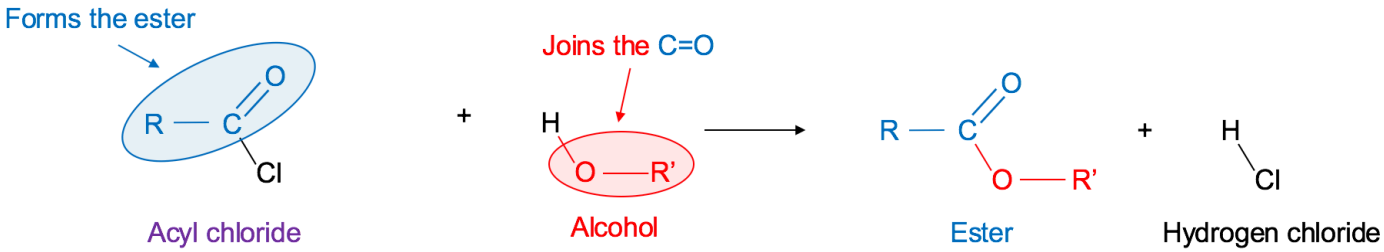


Example:

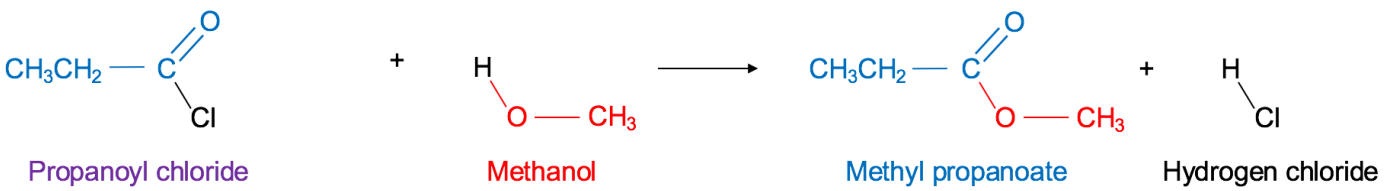


2) With alcohol:

- The reaction with alcohol gives the ester:

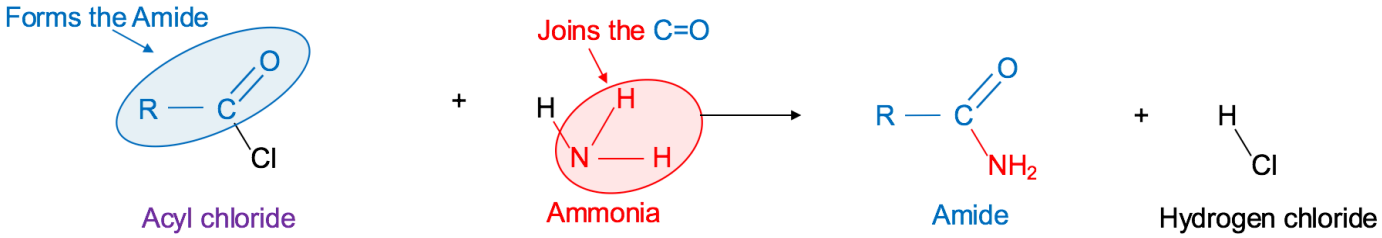


Example:

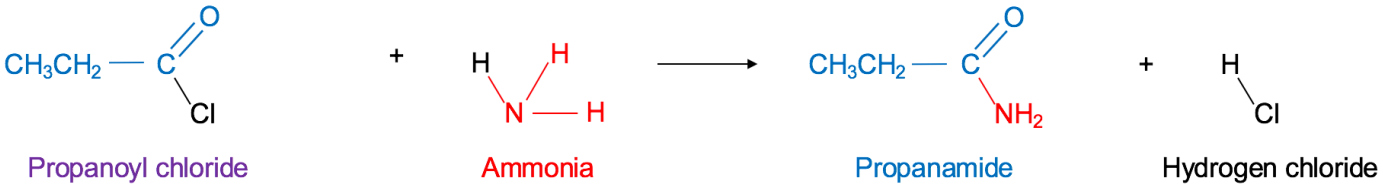


3) With ammonia:

- The reaction with ammonia gives the amide:

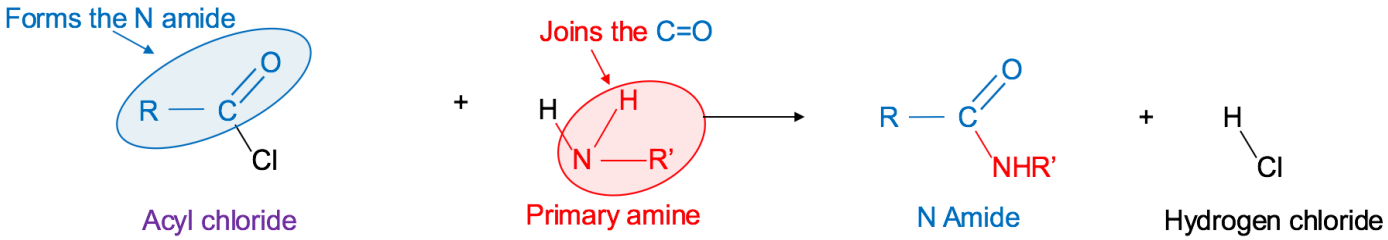


Example:



4) With primary amines:

- The reaction with primary amines gives the N substituted amide:

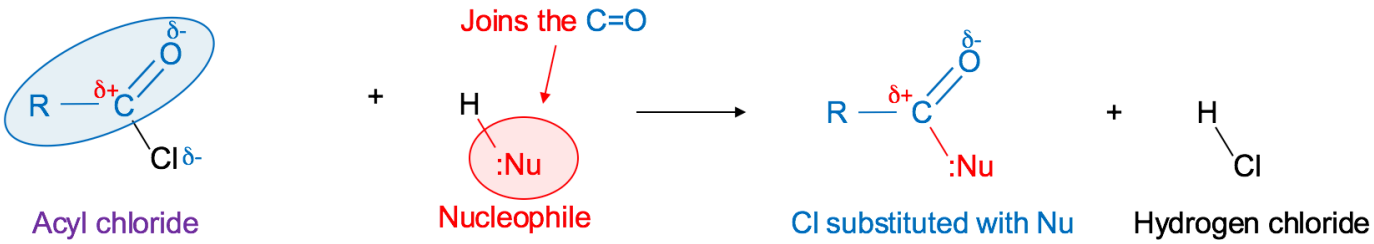


Example:

Nucleophilic addition – elimination reaction of the acyl chlorides

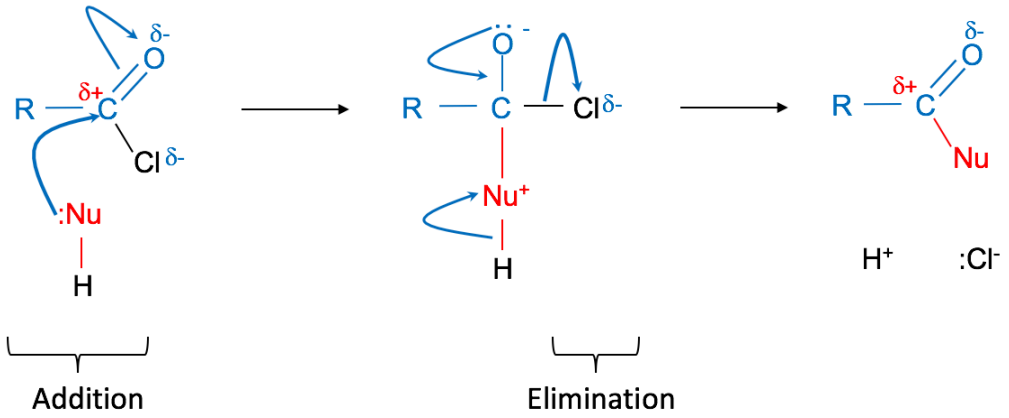
Summary:

- All acyl chlorides undergo the following reaction:

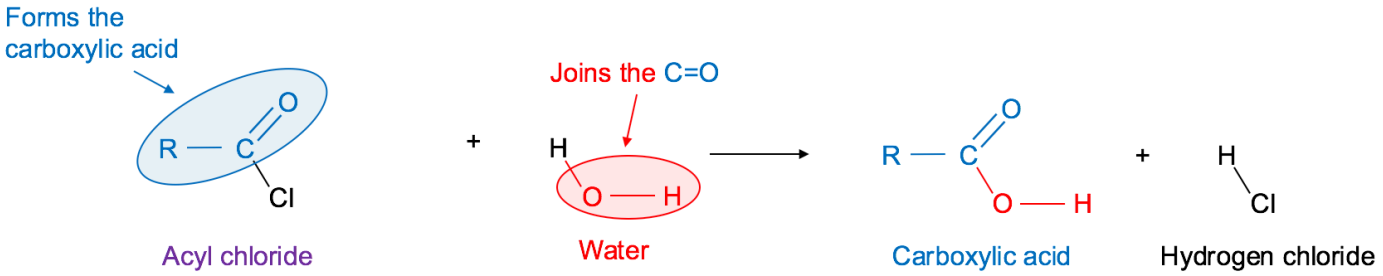


The mechanism:

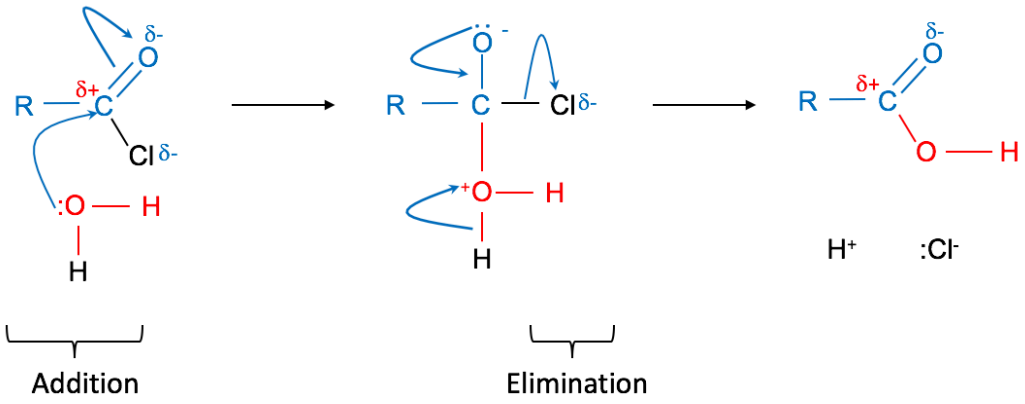
- The mechanism by which this happens is as follows and they all follow this mechanism:



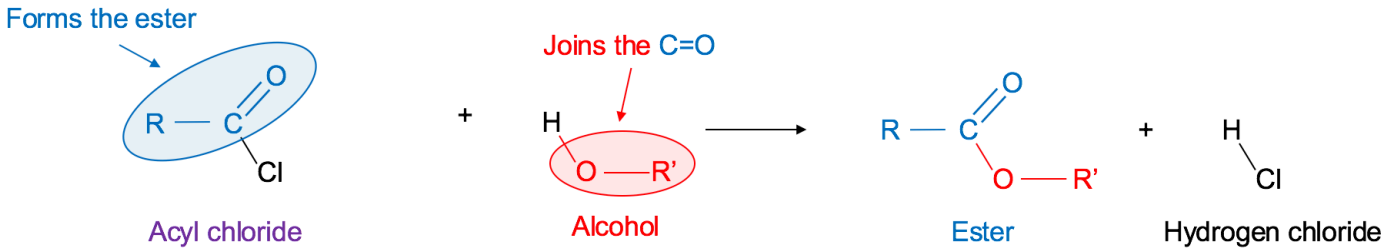
1) With water:



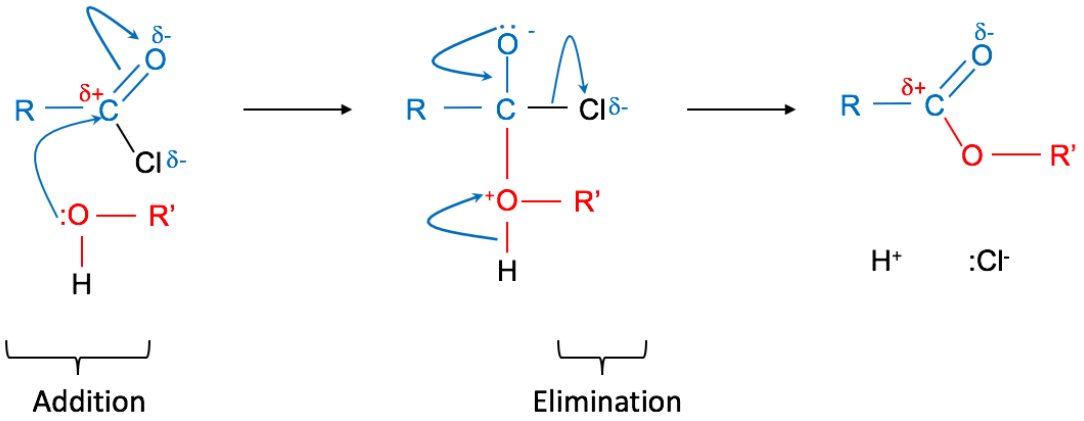
The mechanism:



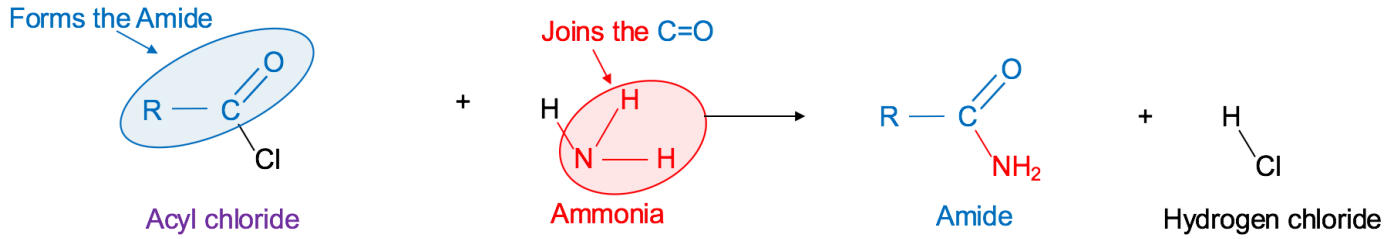
2) With alcohol:



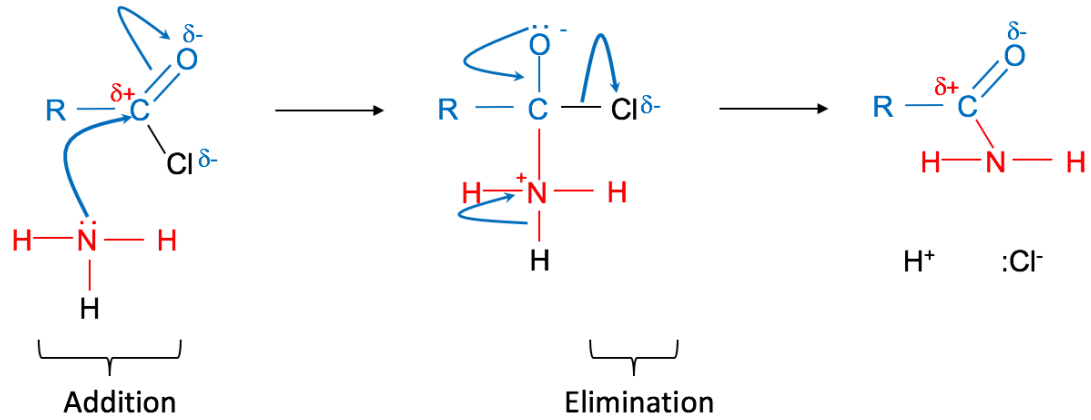
Mechanism:



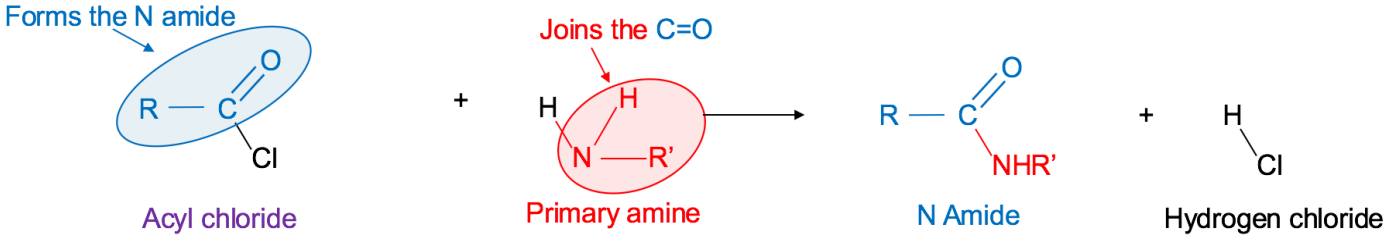
3) With ammonia:



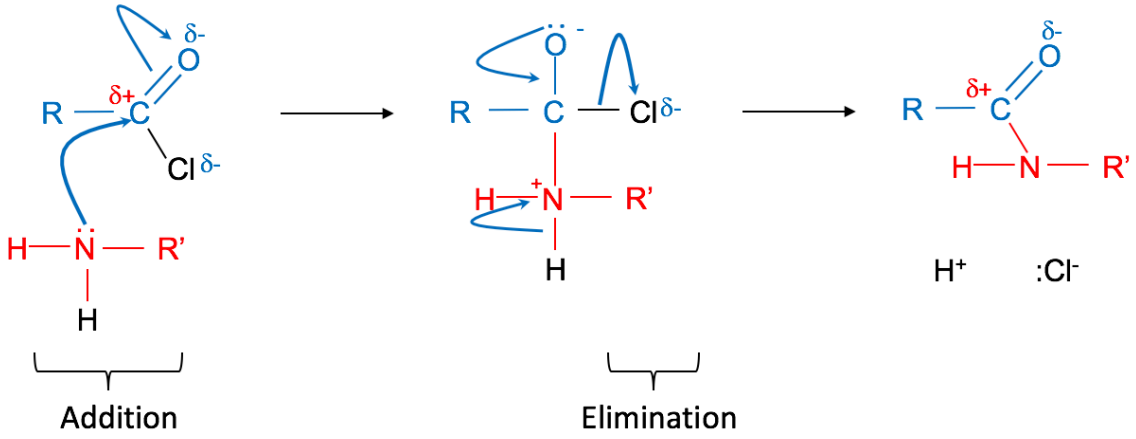
The mechanism:



4) With primary amines:



The mechanism:



Questions:

1) Write balanced chemical equations for the following:
   a. Ethanoyl chloride and water

   b. Methanoyl chloride and ethanol

   c. Ethanoyl chloride and ammonia

   d. Ethanoyl chloride and methylamine

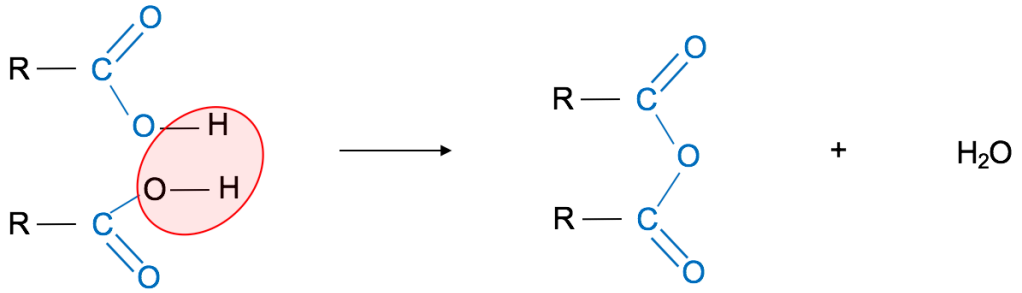
   e. For each of the following reactions above. Name the organic product formed

2) Write out the mechanisms for 1a – d:

Acid anhydrides:

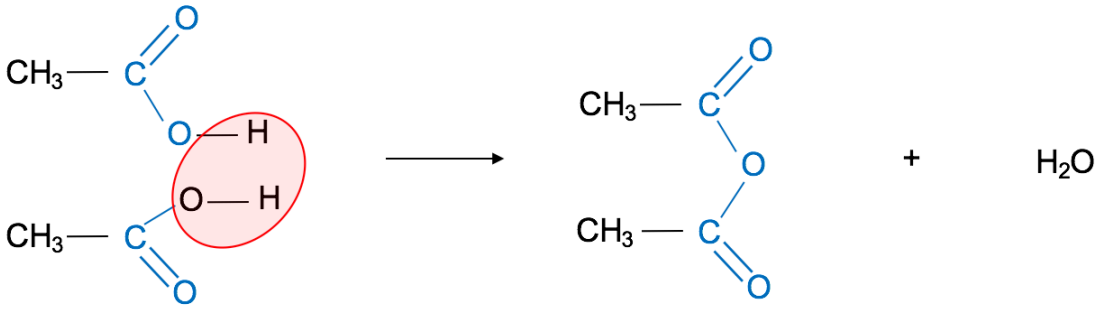
Introduction to acid anhydrides

- Acid anhydrides are made from the elimination of water from 2 carboxylic acids:



Carboxylic acid Acid anhydride

Example:



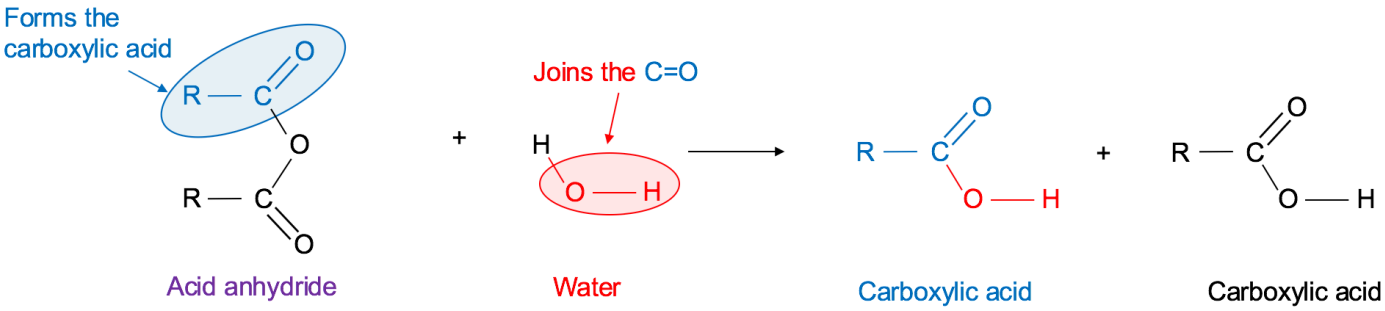
Ethanoic acid Ethanoic anhydride

Reactions of acid anhydrides:

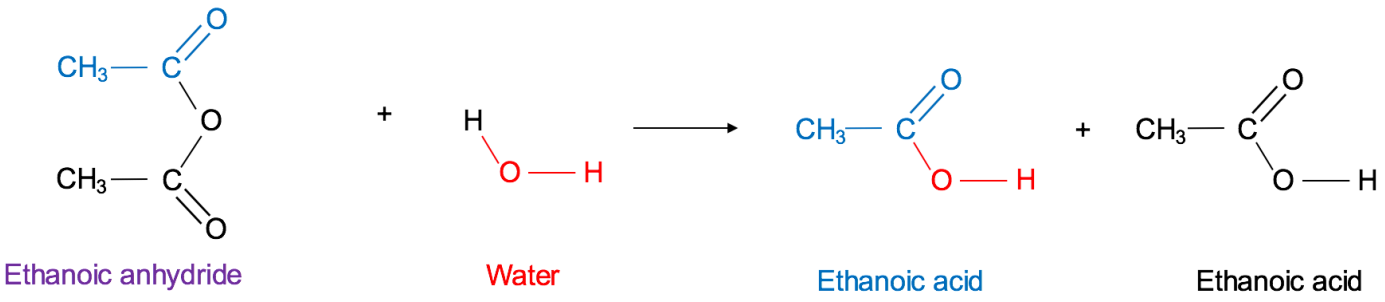
- The acid anhydrides are more reactive than carboxylic acids but less than acyl chlorides.
- The **RCOO** is always **substituted** with an **O containing group** or an **N containing group.** (instead of the Cl in acyl chlorides).
- **A carboxylic acid is always given off** (instead of HCl in the acyl chlorides)

1) With water:

- The reaction with water gives the carboxylic acid:

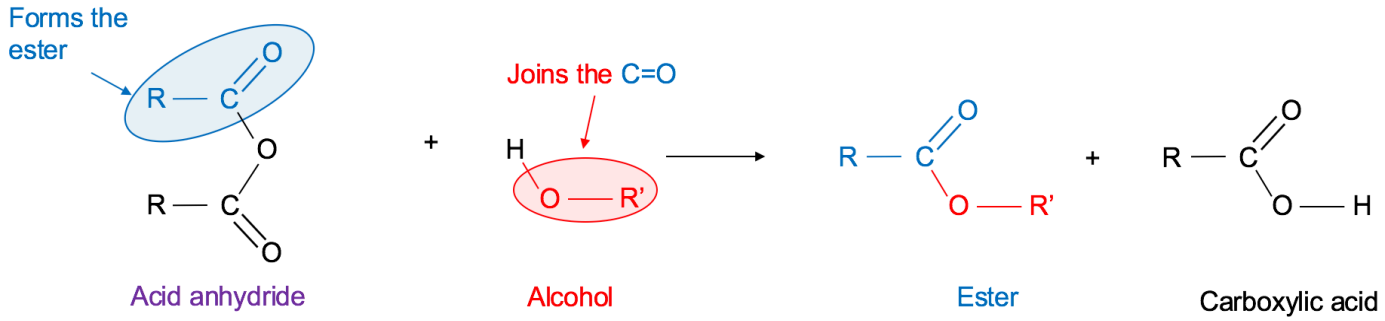


Example:

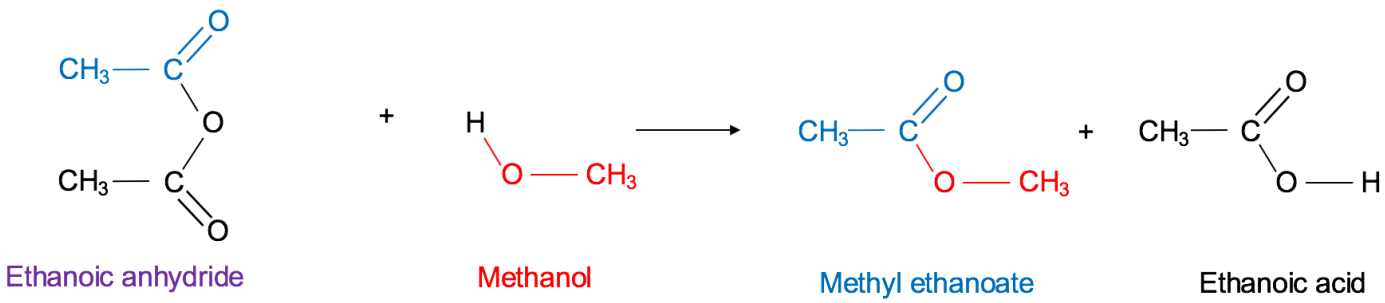


2) With alcohol:

- The reaction with alcohol gives the ester:

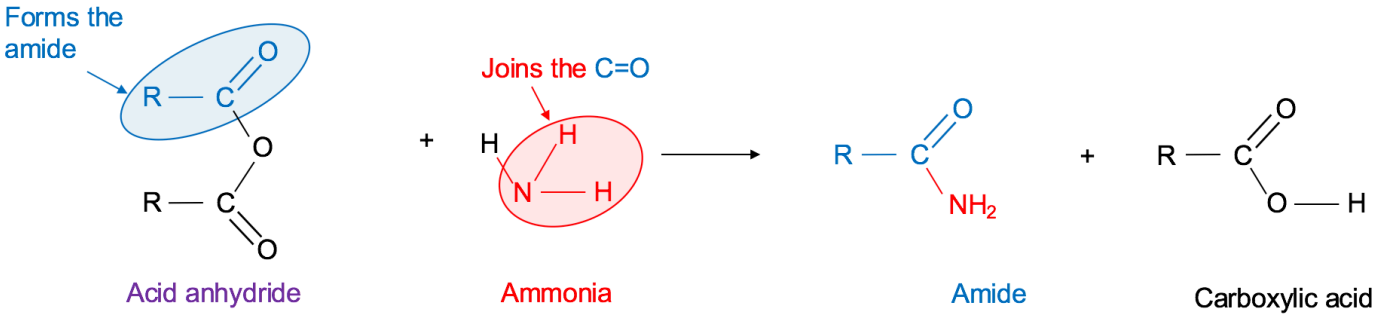


Example:

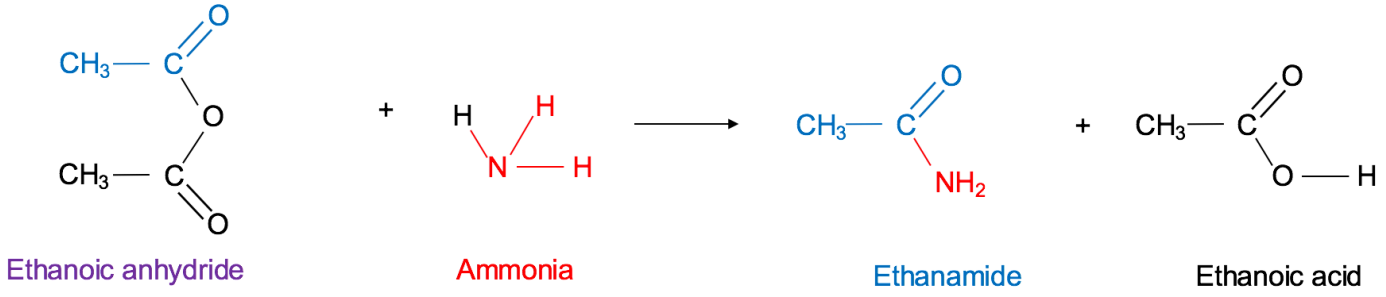


3) With ammonia:

- The reaction with ammonia gives the amide:

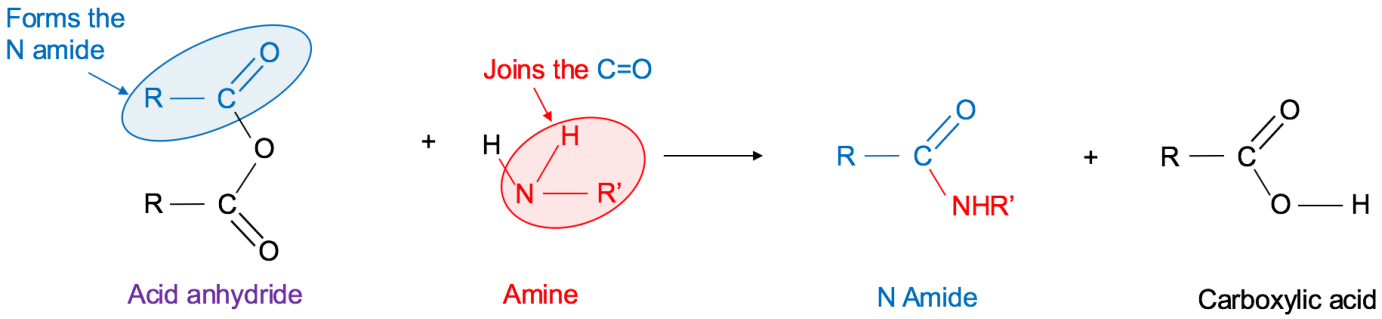


Example:

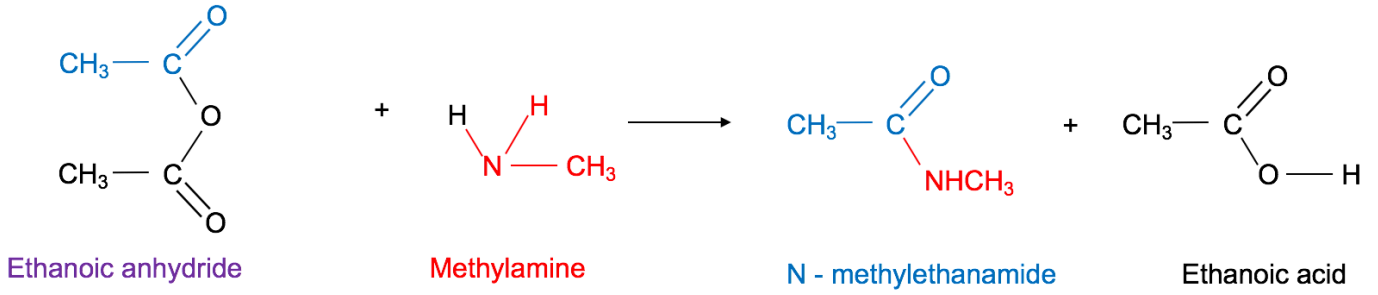


4) With primary amines:

- The reaction with primary amines gives the N substituted amide:



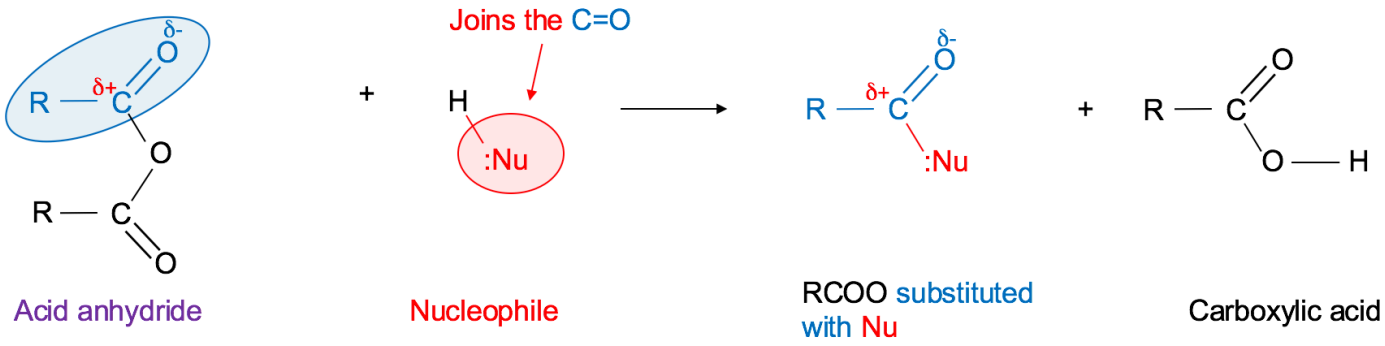
Example:



Nucleophilic addition – elimination reaction of the acid anhydrides

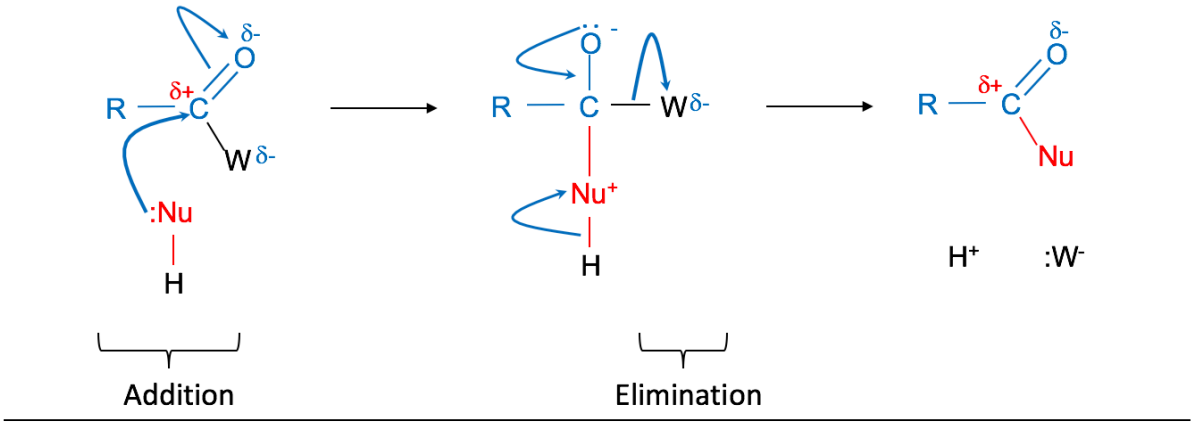
Summary:

- All acid anhydrides undergo the following reaction:



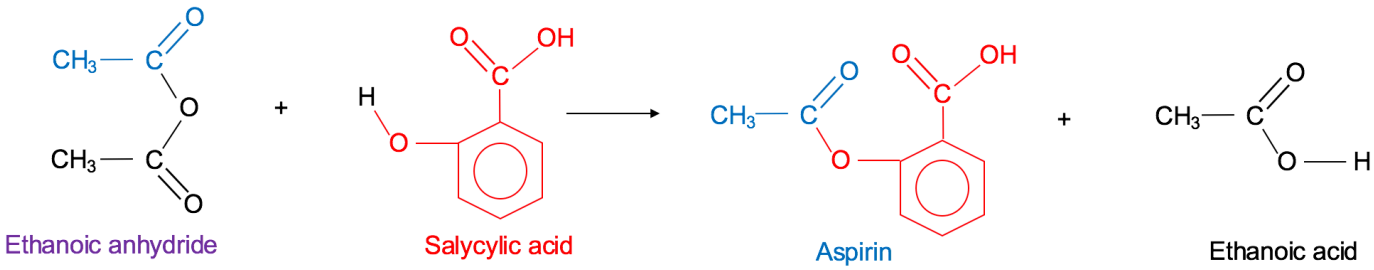
The mechanism:

- The mechanism Is not required but they ***all*** follow the general mechanism:



Nucleophiles: Nu — H		Leaving groups: W
HO — H	H_2N — H	Cl
RO — H	RHN — H	RCOO

Aspirin:



- Ethanoic anhydride is used instead of the acyl chloride as it is:
  - Cheaper
  - Less reactive / corrosive therefore safer to use
  - Doesn't form HCl fumes

Questions:

1) Write balanced chemical equations for the following:
   a. Ethanoic anhydride and water

   b. Methanoic anhydride and ethanol

   c. Ethanoic anhydride and ammonia

   d. Ethanoic anhydride and methylamine

   e. For each of the following reactions above. Name the organic products formed

2) Have a go at the mechanism for 1b: