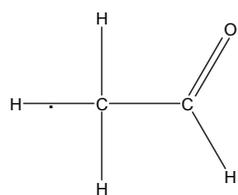


Module 4 revision guide: Compounds with C=O group

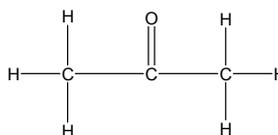
Carbonyls: Aldehydes and Ketones

Carbonyls are compounds with a C=O bond, they can be either aldehydes or ketones



If the C=O is on the end of the chain with an H attached it is an aldehyde.
The name will end in **-al**

CH₃CHO ethanal

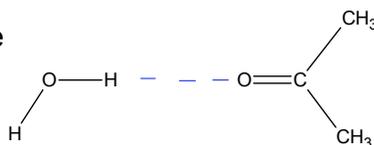


If the C=O is in the middle of the chain it is a ketone.
The name will end in **-one**

CH₃COCH₃ propanone

Solubility in water

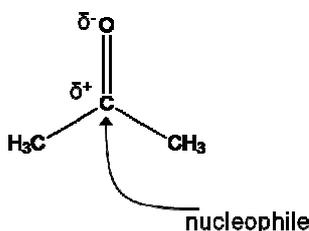
The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



Pure carbonyls cannot hydrogen bond, but bond instead by permanent dipole bonding.

Reactions of carbonyls

The C=O bond is polarised because O is more electronegative than carbon. The positive carbon atom attracts nucleophiles.



In comparison to the C=C bond in alkenes, the C=O is stronger and does not undergo addition reactions easily.

This is in contrast to the electrophiles that are attracted to the C=C.

Oxidation Reactions

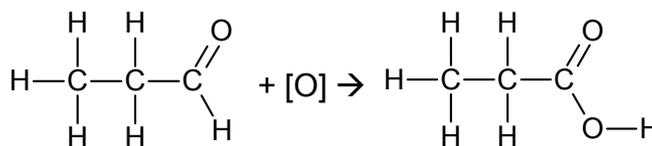
Potassium dichromate K₂Cr₂O₇ is an oxidising agent that causes alcohols and aldehydes to oxidise.

Primary alcohol → aldehydes → carboxylic acid
Secondary alcohol → ketones
Tertiary alcohols do not oxidise

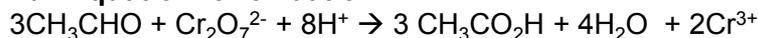
Key point: Aldehydes can be oxidised to carboxylic acids but ketones cannot be oxidised.

Oxidation of Aldehydes

Reaction: aldehyde → carboxylic acid
Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.
Conditions: heat under reflux



Full Equation for oxidation



Observation: the orange dichromate ion (Cr₂O₇²⁻) reduces to the green Cr³⁺ ion

Aldehydes can also be oxidised using Fehling's solution or Tollen's Reagent. These are used as tests for the presence of aldehyde groups

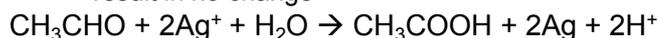
Tollen's Reagent

Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)₂]⁺.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to a silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube Ketones result in no change



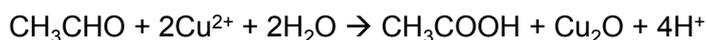
Fehling's solution

Reagent: Fehling's Solution containing blue Cu²⁺ ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide.

Observation: Aldehydes: Blue Cu²⁺ ions in solution change to red precipitate of Cu₂O. Ketones do not react



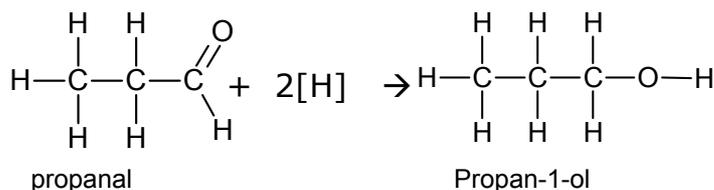
Reduction of carbonyls

Reagents: NaBH₄ in aqueous ethanol

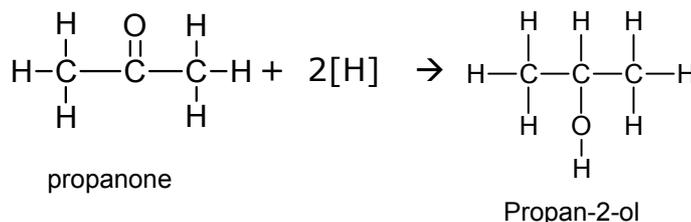
Conditions: Room temperature and pressure

Reducing agents such as NaBH₄ (sodium tetrahydridoborate) or LiAlH₄ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

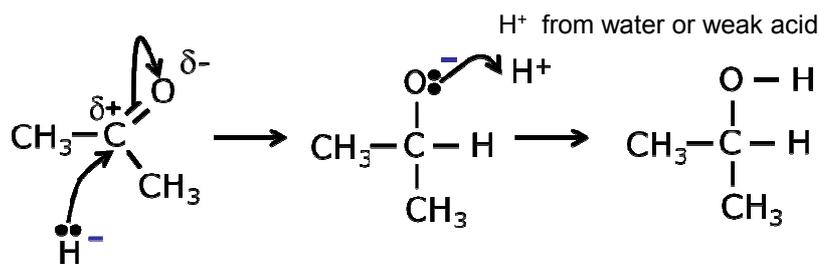
Aldehydes will be reduced to primary alcohols



Ketones will be reduced to secondary alcohols.



Nucleophilic Addition Mechanism



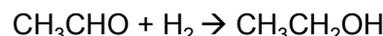
NaBH₄ contains a source of nucleophilic hydride ions (H⁻) which are attracted to the positive carbon in the C=O bond.

Catalytic Hydrogenation

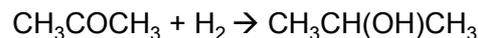
Carbonyls can also be reduced using catalytic hydrogenation

Example Equations

Reagent: hydrogen and nickel catalyst



Conditions: high pressure



Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

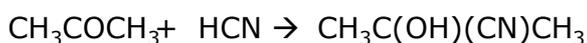
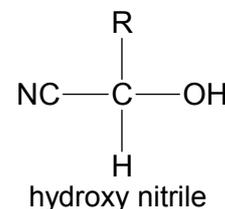
Reaction: carbonyl → hydroxynitrile

Reagent: sodium cyanide (NaCN) and dilute sulphuric acid.

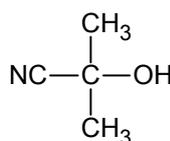
Conditions: Room temperature and pressure

Mechanism: nucleophilic addition

The NaCN supplies the nucleophilic CN⁻ ions. The H₂SO₄ acid supplies H⁺ ions needed in second step of the mechanism



2-hydroxy-2-methylpropanenitrile

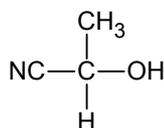


When naming hydroxy nitriles the CN becomes part of the main chain

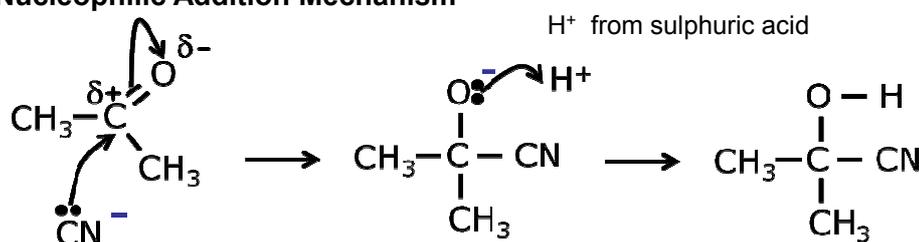
We could use HCN for this reaction but it is a toxic gas that is difficult to contain. The KCN/NaCN are still, however, toxic, because of the cyanide ion



2-hydroxypropanenitrile

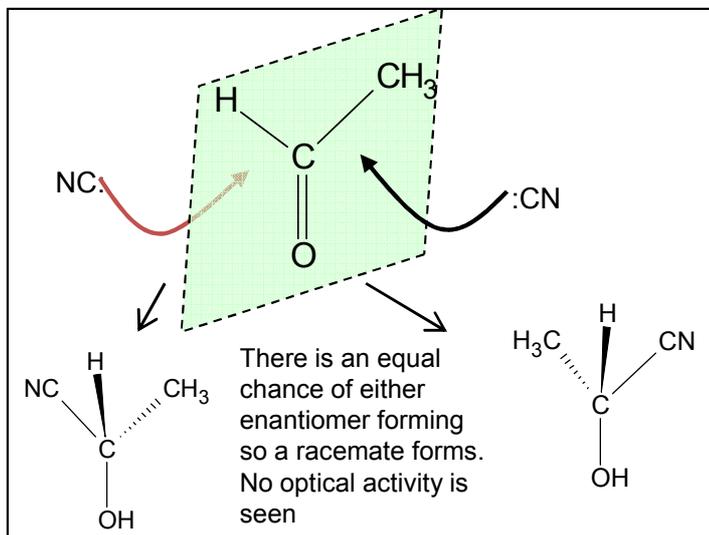
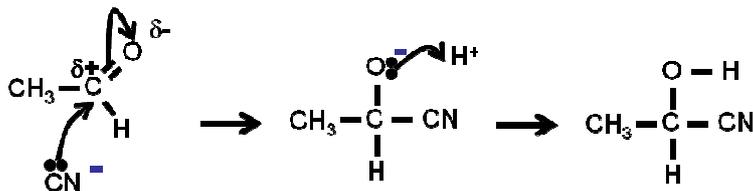


Nucleophilic Addition Mechanism



Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate

Mechanism for the reaction (drawn the same for both enantiomers)



Carboxylic Acids

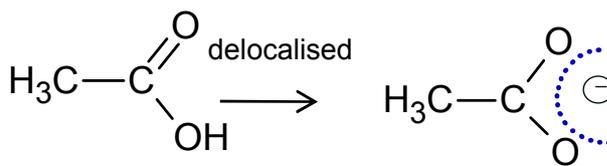
Acidity

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



Delocalisation

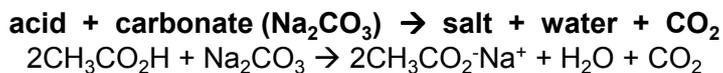
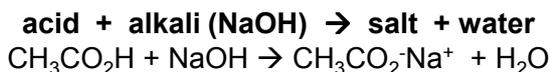
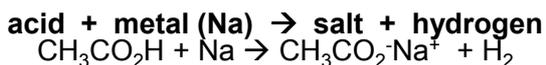
The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.



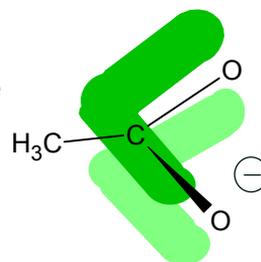
The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.

Salt formation reactions of carboxylic acids

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



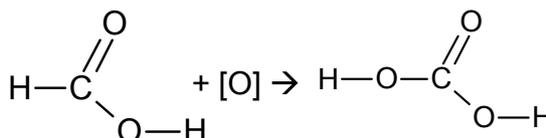
The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form.



The effervescence caused by production of CO₂ with carboxylic acids with solid Na₂CO₃ or aqueous NaHCO₃ can be used as a functional group test for carboxylic acids

Oxidation of methanoic acid

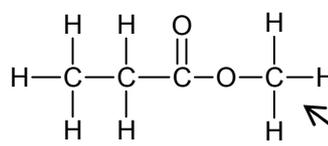
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group



It forms carbonic acid (H₂CO₃) which can decompose to give CO₂

Esterification

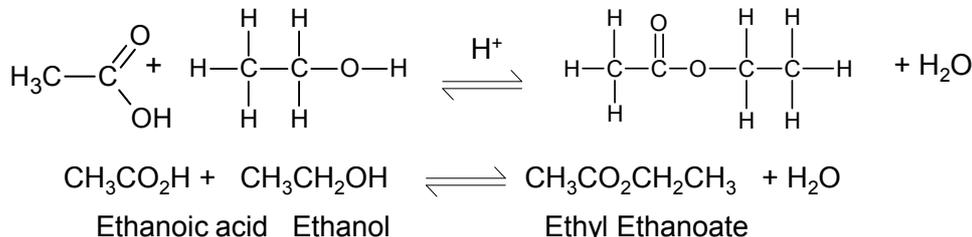
Carboxylic acids react with alcohols, in the presence of a strong acid catalyst, to form esters and water.



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 (H_2SO_4) is needed.

Uses of Esters Esters can have pleasant smells

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

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

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

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

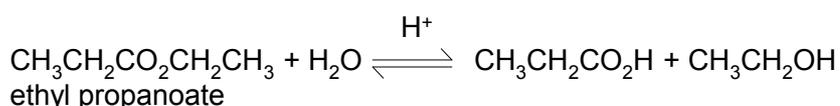
Often pure polymers have limited flexibility because the polymer chains cannot move over each other. Incorporating some plasticiser into the polymer allows the chains to move more easily and the polymer can become more flexible.

Hydrolysis of esters

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

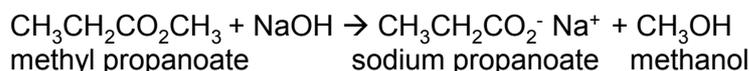
i) with acid
reagents: dilute acid (HCl)
conditions: heat under reflux

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



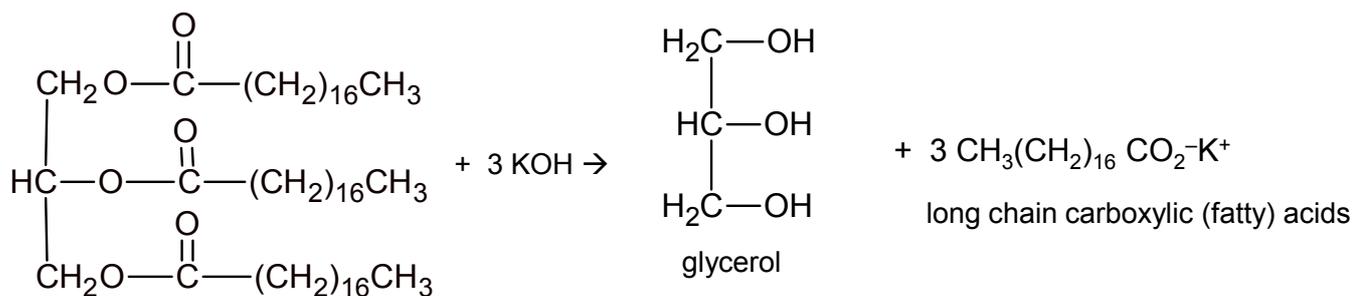
This reaction goes to completion.

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)

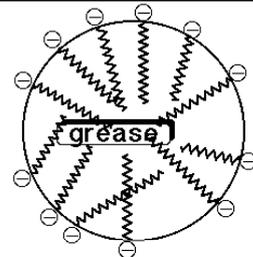
Vegetable oils and animal fats can be hydrolysed to give soap, glycerol and long chain carboxylic (fatty) acids



Glycerol forms hydrogen bonds very easily and is readily soluble in water. It is used in cosmetics, food and in glues

Soap

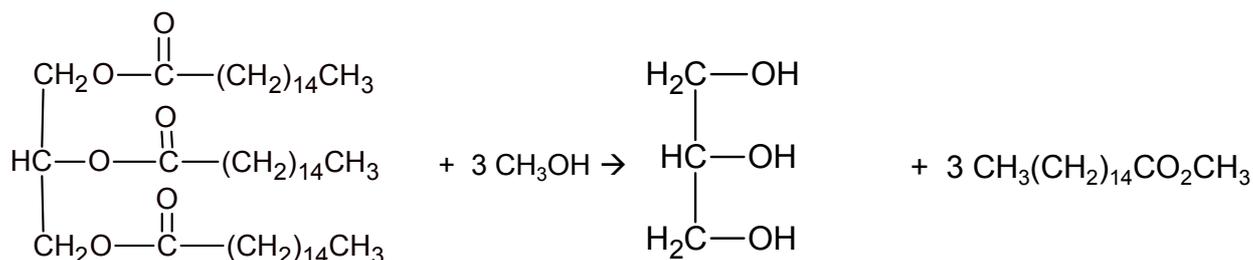
Long chain carboxylic (fatty) acids act as soaps. The polar CO_2^- end is hydrophilic and mixes with water. The long non-polar hydrocarbon chain is hydrophobic and mixes with grease. So this allows the grease and water to mix and be washed away



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



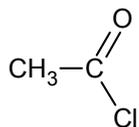
It can be argued that biodiesel produced from this method is classed as carbon-neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

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

Carboxylic acid derivatives: acyl chlorides and acid anhydrides

Acyl Chlorides

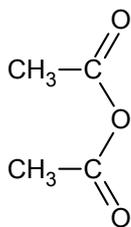


Acyl chlorides are much more reactive than carboxylic acids

ethanoyl chloride

The Cl and $-\text{OCOCH}_3$ 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.

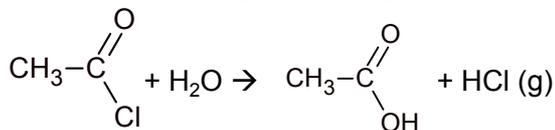
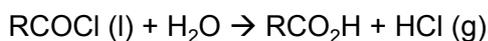
The main difference is the by-products. Acyl chlorides mostly give off HCl. Acid anhydrides give off RCOOH

Reaction with water

Change in functional group: **acyl chloride** \rightarrow **carboxylic acid**

Reagent: **water**

Conditions: **room temp.**

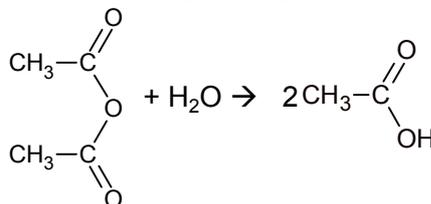
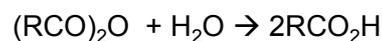


Observation: Steamy white fumes of HCl are given off

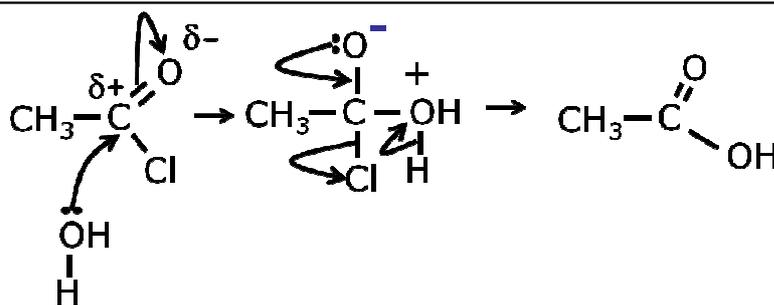
Change in functional group: **acid anhydride** \rightarrow **carboxylic acid**

Reagent: **water**

Conditions: **room temp.**



Nucleophilic Addition Elimination Mechanism

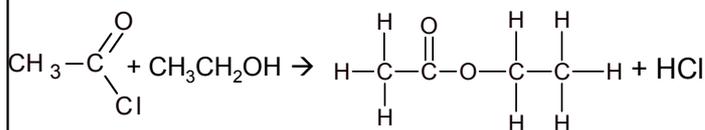
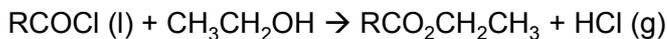


Reaction with alcohol

Change in functional group: **acyl chloride** \rightarrow **ester**

Reagent: **alcohol**

Conditions: **room temp.**

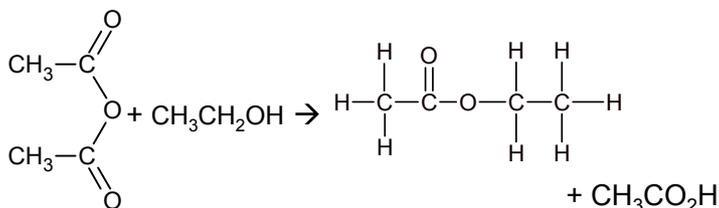
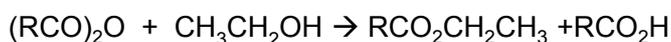


Observation: Steamy white fumes of HCl are given off

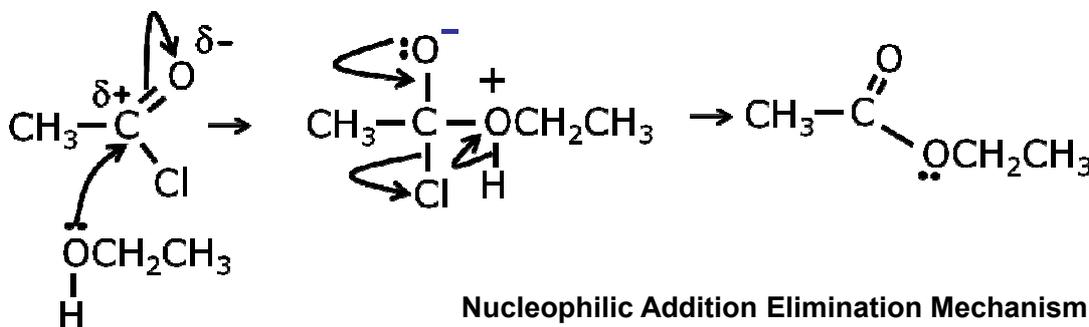
Change in functional group: **acid anhydride** \rightarrow **ester**

Reagent: **alcohol**

Conditions: **room temp.**



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



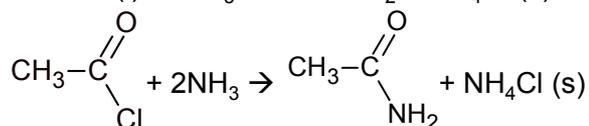
Nucleophilic Addition Elimination Mechanism

Reaction with ammonia

Change in functional group: **acyl chloride** → **primary amide**

Reagent: **ammonia**

Conditions: **room temp.**

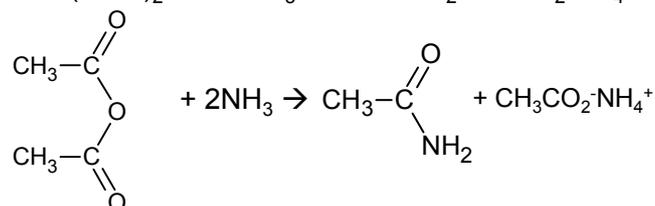


Observation: white smoke of NH_4Cl is given off

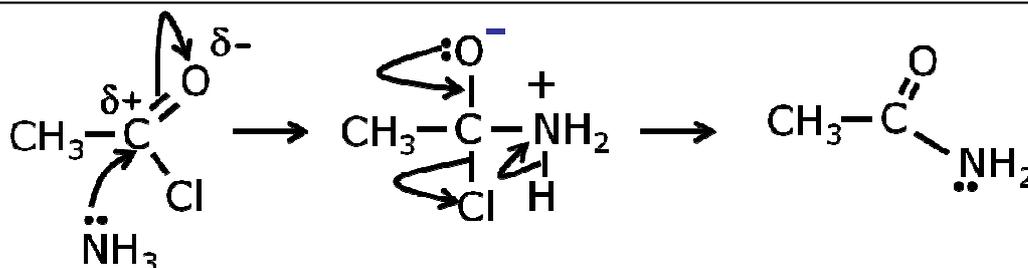
Change in functional group: **acid anhydride** → **primary amide**

Reagent: **ammonia**

Conditions: **room temp.**



**Nucleophilic
Addition
Elimination
Mechanism**

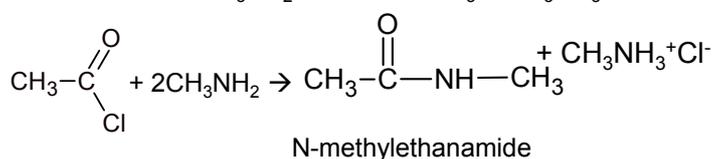


Reaction with primary amines

Change in functional group: **acyl chloride** → **secondary amide**

Reagent: **primary amine**

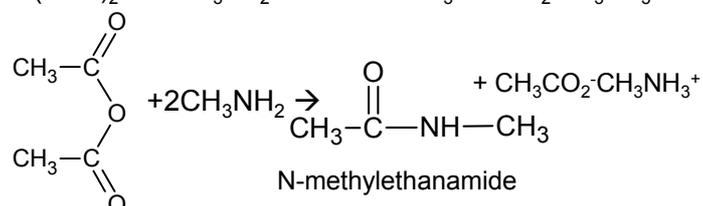
Conditions: **room temp.**



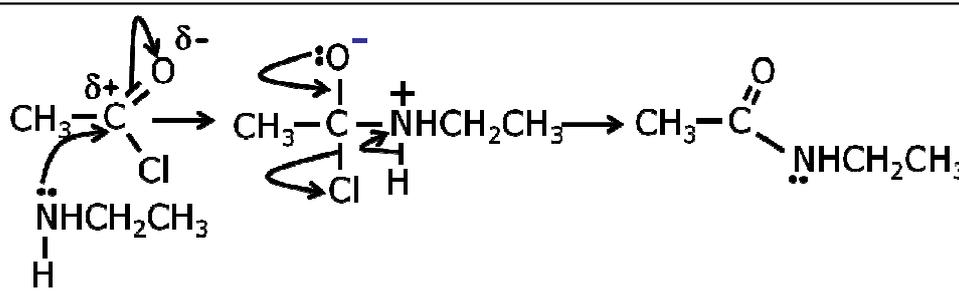
Change in functional group: **acid anhydride** → **secondary amide**

Reagent: **primary amine**

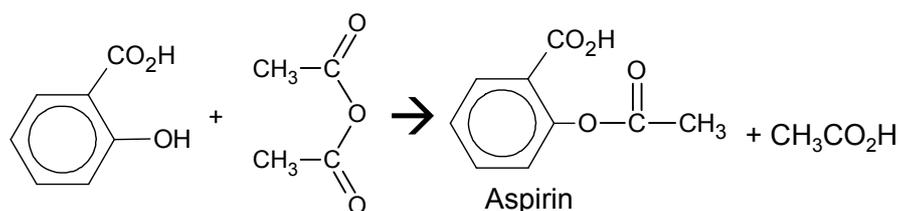
Conditions: **room temp.**



**Nucleophilic
Addition
Elimination
Mechanism**



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.