Carboxylic acids

a describe the formation of carboxylic acids from alcohols, aldehydes and nitriles ☐

b describe the reactions of carboxylic acids in the formation of:

(i) salts, by the use of reactive metals, alkalis or carbonates ☐

(ii) alkyl esters ☐

(iii) alcohols, by use of $LiAlH_4$ ☐

(iv) acyl chlorides ☐

c recognise that some carboxylic acids can be further oxidised:

(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents ☐

(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm acidified manganate(VII) ☐

d explain the relative acidities of carboxylic acids, phenols and alcohols ☐

e use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids ☐

Esters

a describe the acid and base hydrolysis of esters ☐

b state the major commercial uses of esters, e.g. solvents, perfumes, flavourings ☐

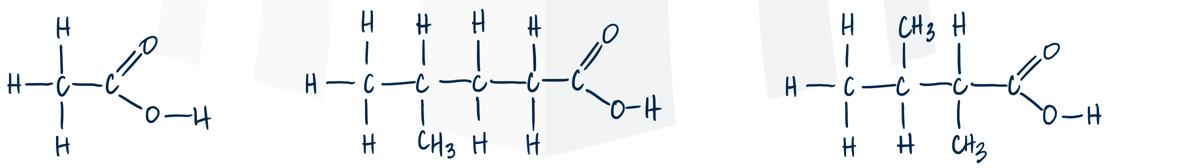
CARBOXYLIC ACIDS

19.1 Carboxylic acids	a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles b) describe the reactions of carboxylic acids in the formation of: (i) salts, by the use of reactive metals, alkalis or carbonates (ii) alkyl esters (iii) alcohols, by use of $LiAlH_4$ **(iv) acyl chlorides** **c) recognise that some carboxylic acids can be further oxidised:** **(i) the oxidation of methanoic acid, HCO_2H, with Fehling's and Tollens' reagents** **(ii) the oxidation of ethanedioic acid, HO_2CCO_2H, with warm acidified manganate(VII)** **d) explain the relative acidities of carboxylic acids, phenols and alcohols** **e) use the concept of electronegativity to explain the acidities of chlorine-substituted ethanoic acids**
19.2 Acyl chlorides	**a) describe the hydrolysis of acyl chlorides** **b) describe the reactions of acyl chlorides with alcohols, phenols, ammonia and primary amines** **c) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides including the condensation (addition-elimination) mechanism for the hydrolysis of acyl chlorides**
19.3 Esters	a) describe the acid and base hydrolysis of esters b) state the major commercial uses of esters, e.g. solvents, perfumes, flavourings

CARBOXYLIC ACIDS AND ESTERS

CARBOXYLIC ACIDS

When the carbonyl group is directly joined to an oxygen atom, the carboxyl group is formed. This occurs in carboxylic acids and esters.



ethanoic acid   4-methyl pentanoic acid   2,3-dimethylbutanoic acid

CARBOXYLIC ACIDS

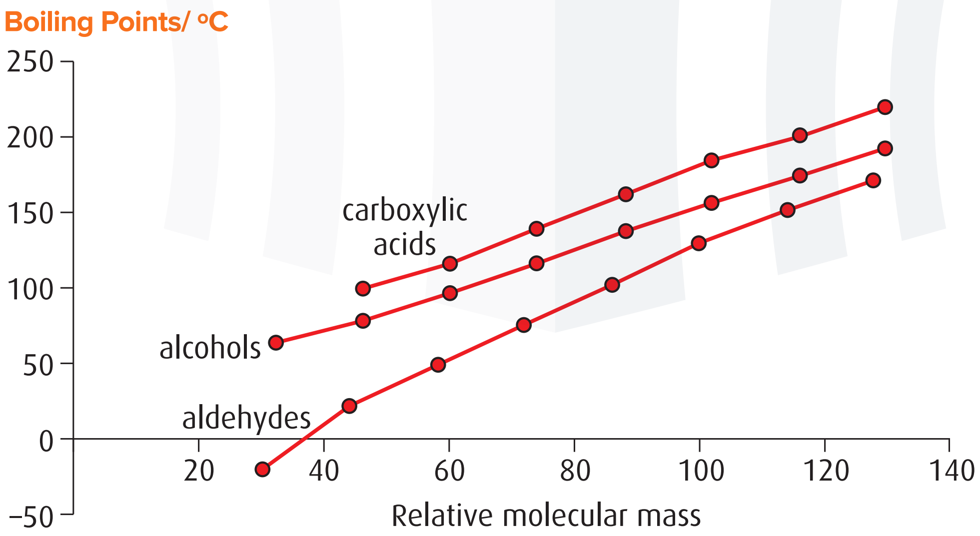
The reactions of the carbonyl group are drastically changed by the presence of the electronegative oxygen atom.

These compounds have virtually none of the reactions of carbonyl compounds.

The reactivity of carboxylic acids is dominated by the tendency of the O—H bond to ionise to give hydrogen ions, hence the incorporation of the word 'acid' in their name.

The extent of ionisation is small, however.

BOILING POINT

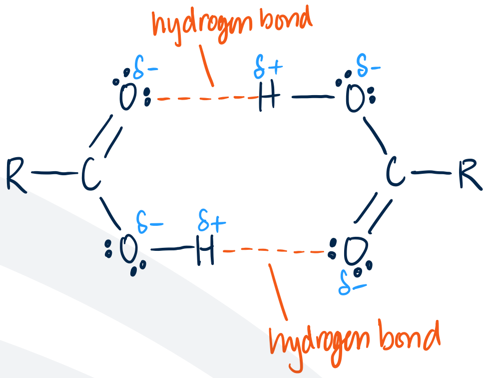


BOILING POINT

Carboxylic acids have hydrogen bonding between molecules and therefore have higher boiling points than aldehydes of similar relative molecular mass.

Carboxylic acids have hydrogen bonding between molecules and therefore have higher boiling points than aldehydes of similar relative molecular mass.

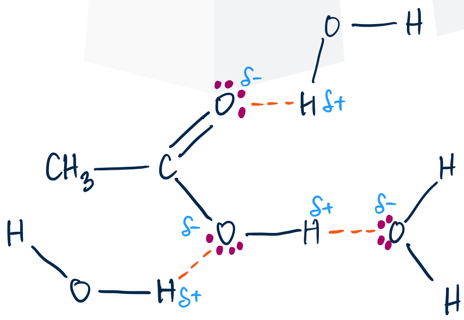
They also have higher boiling points than alcohols of the same relative molecular mass, as they have two O atoms per molecule and therefore have stronger hydrogen bonding than alcohols, which have only one O atom per molecule.



SOLUBILITY

Carboxylic acids with lower relative molecular mass are generally soluble in water, owing to the ability to hydrogen bond to water.

However, the solubility decreases as the length of the hydrocarbon chain (non-polar) increases, so octanoic acid is essentially insoluble in water.

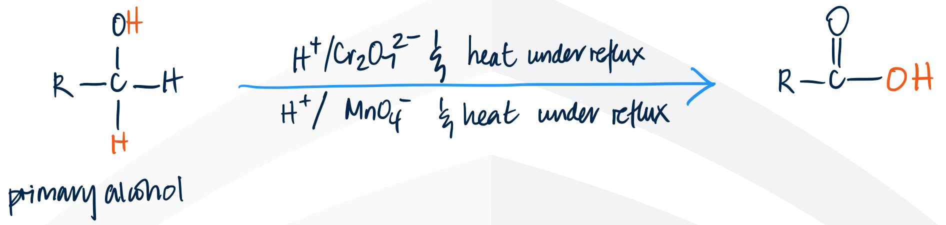


FROM OXIDATION OF PRIMARY ALCOHOLS

Reagent acidified potassium dichromate, $K_2Cr_2O_7$ (OR acidified potassium manganate(VII), $KMnO_4$)

Condition heat under reflux

Type oxidation



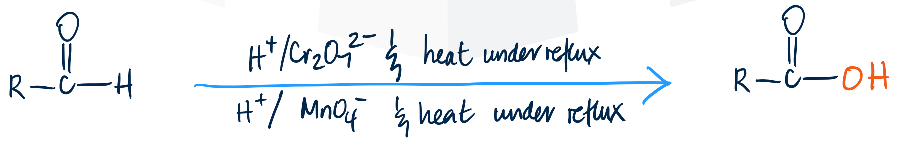
7

FROM OXIDATION OF ALDEHYDES

Reagent acidified potassium dichromate, $K_2Cr_2O_7$ (OR acidified potassium manganate(VII), $KMnO_4$) OR Fehling;s reagent OR Tollen's solution

Condition heat under reflux

Type oxidation



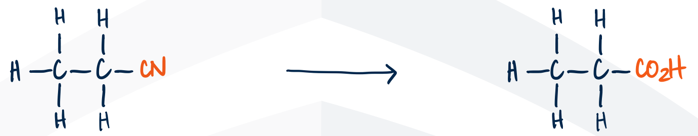
8

FROM HYDROLYSIS OF CYANIDES

Hydrolysis of nitriles formed after the reaction of halogenoalkanes with CN^- produces carboxylic acids.

Reagent	dilute HCl or NaOH (aq)
Condition	heat under reflux
Type	hydrolysis

$$CH_3CH_2CN + 2H_2O \longrightarrow CH_3CH_2CO_2H + NH_3$$



with acids $CH_3CH_2CN + 2H_2O + H^+ \longrightarrow CH_3CH_2CO_2H + NH_4^+$

with alkalis $CH_3CH_2CN + H_2O \quad OH^- \longrightarrow CH_3CH_2CO_2^- + NH_3$

ACID REACTIONS

Carboxylic acids are weak acids.

Equation $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$

Carboxylic acids neutralised alkalis to form salts

Equation $CH_3CO_2H + NaOH \longrightarrow CH_3CO_2^-Na^+ + H_2O$

Carboxylic acids neutralised carbonates to form salts, carbon dioxide and water

Equation $2\,CH_3CO_2H + Na_2CO_3 \longrightarrow 2CH_3CO_2^-Na^+ + CO_2 + H_2O$

Carboxylic acids react with most metals (e.g. Na) to form salt and hydrogen gas

Equation $CH_3CO_2H + Na \longrightarrow CH_3CO_2^-Na^+ + \frac{1}{2} H_2$

ESTERIFICATION

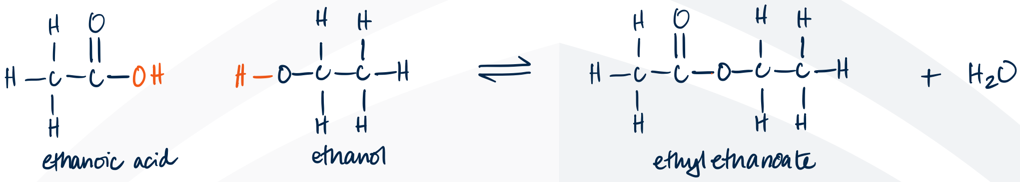
When an alcohol is heated with a carboxylic acid in the presence of a small amount of concentrated sulfuric acid as a catalyst, an ester is formed.

Reagent carboxylic acid and conc. sulfuric acid, H_2SO_4

Condition 60°C / heat

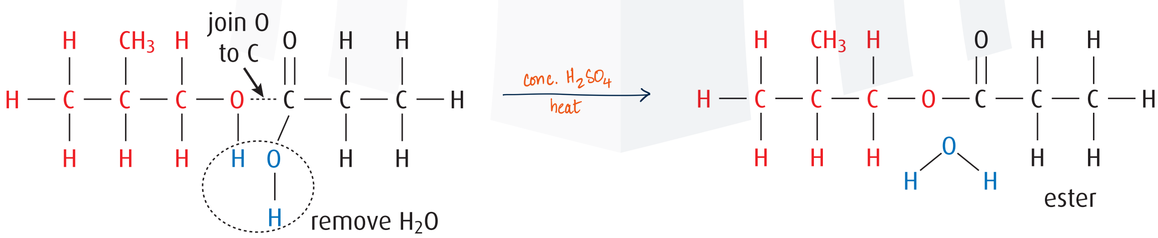
Type of reaction esterification / condensation / nucleophilic substitution

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

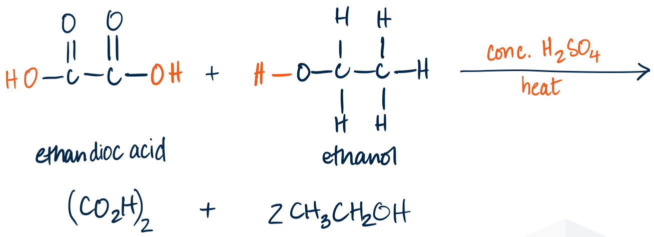


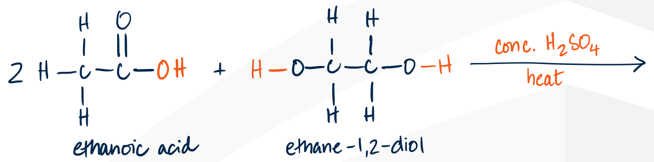
ESTERIFICATION

The alcohol and the carboxylic acid have been joined together and water has been eliminated (one H atom from the alcohol and –OH from the carboxylic acid molecule).



ESTERIFICATION





HYDROLYSIS OF ESTERS

The most common type of reaction that esters undergo is nucleophilic substitution, illustrated by their hydrolysis.

The hydrolysis of an ester is a slow process, taking several hours of heating under reflux with dilute aqueous acids. Acid catalysed hydrolysis does not go completion.

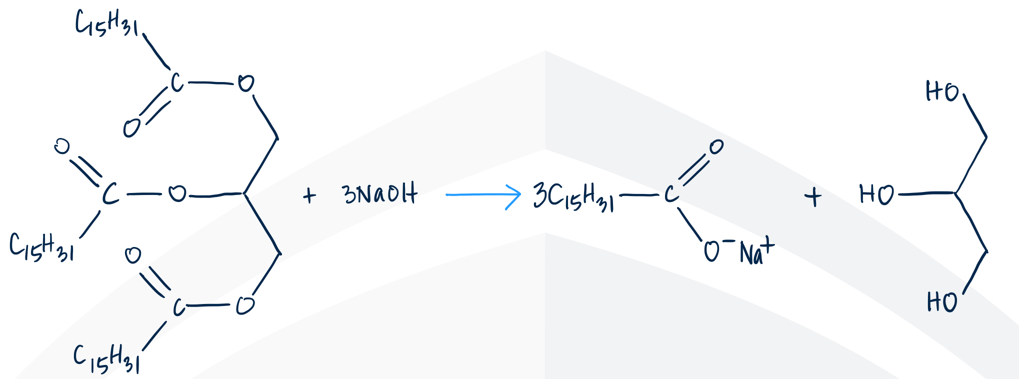
Ester hydrolysis can also be carried out in alkaline solution. The reaction is quicker than in acid solution: OH^- is a stronger nucleophile than water. Additionally, it does not reach equilibrium, but goes to completion.

This is because the carboxylic acid produced reacts with an excess of the alkali to form the carboxylate salt.

HYDROLYSIS OF ESTERS

with HCl $CH_3CH_2CO_2CH_3 + H_2O \longrightarrow CH_3CH_2CO_2H + CH_3OH$

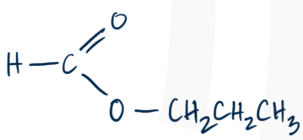
with NaOH $CH_3CH_2CO_2CH_3 + H_2O \longrightarrow CH_3CH_2CO_2^- + CH_3OH$

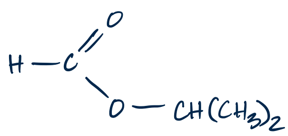


15

HYDROLYSIS OF ESTERS

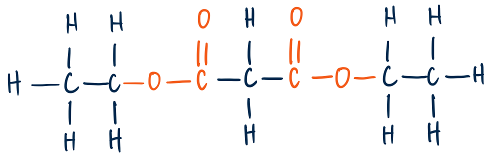
Hydrolyse the following esters using dil HCl.





16

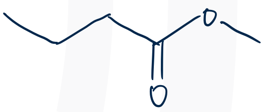
HYDROLYSIS OF ESTERS

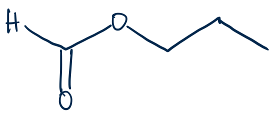


$CH_3CH_2OCOCH_2CO_2CH_2CH_3$

HYDROLYSIS OF ESTERS

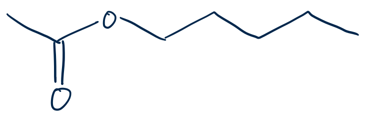
Hydrolyse the following esters using NaOH (aq).

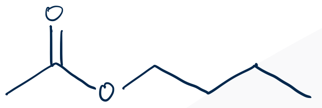




HYDROLYSIS OF ESTERS

Hydrolyse the following esters using dil HCl.





ESTERS

Esters often have a sweet, fruity smell and are used as artificial flavours and odours. Esters are good organic solvents.

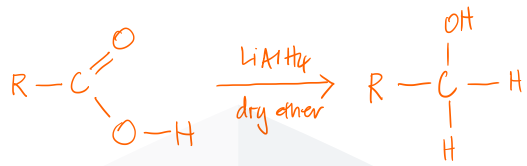
Fats and oils are esters of propane-1,2,3-triol (glycerol) and long-chain carboxylic acids (fatty acids).

Despite containing two oxygen atoms, they do not form strong hydrogen bonds with water molecules. Neither do they form hydrogen bonds with other ester molecules (because they do not contain δ+ hydrogen atoms).

Their major intermolecular bonding is van der Waals. Their boiling points are therefore a few degrees higher than those of the alkanes of similar molecular mass lower than those of corresponding carboxylic acids.

REDUCTION OF THE –CO_2H GROUP

Carboxylic acids can be reduced to alcohols by reacting with lithium tetrahydridoaluminate(III) (lithium aluminium hydride), $LiAlH_4$, in dry ether.



The reaction requires the powerful reducing agent $LiAlH_4$: neither $NaBH_4$ nor H_2 + Ni are strong enough to reduce carboxylic acids.

REDUCTION OF CARBOXYLIC ACIDS

Carboxylic acids can be reduced to their corresponding primary alcohol by using the reducing agent lithium tetrahydridoaluminate, $LiAlH_4$, in dry ether at room temperature. Dry ether is used because $LiAlH_4$ reacts violently with water.

In the simplified reduction equation, the symbol [H] can be used to represent the hydrogen atoms from the reducing agent (remember that in organic chemistry, reduction can be thought of as the addition of hydrogen atoms). So for ethanoic acid being reduced to ethanol, we can show the reaction as:

$$CH_3CO_2H + 4[H] \longrightarrow CH_3CH_2OH + H_2O$$