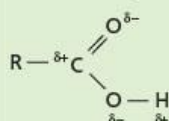


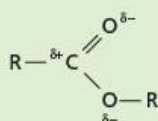
18 Carboxylic acids and esters

Functional groups:



carboxylic acids

In this topic we look at the major class of organic acids, the carboxylic acids, and at some of the compounds derived from them. Apart from acid-base reactions, their chemistry is dominated by nucleophilic substitution reactions, owing to the $\delta+$ carbon atom in the carbonyl group.



esters

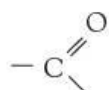
Learning outcomes

By the end of this topic you should be able to:

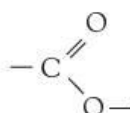
- 14.1a)** interpret and use the general, structural, displayed and skeletal formulae of the carboxylic acids and esters
- 14.2a)** interpret and use the term condensation in relation to organic reactions
- 19.1a)** describe the formation of carboxylic acids from alcohols, aldehydes and nitriles
- 19.1b)** describe the reactions of carboxylic acids in the formation of salts (by the use of reactive metals, alkalis or carbonates), alkyl esters, and alcohols (by the use of LiAlH_4)
- 19.3a)** describe the acid and base hydrolysis of esters
- 19.3b)** state the major commercial uses of esters, e.g. solvents, perfumes, flavourings.

18.1 Introduction

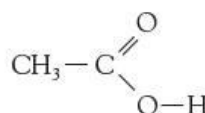
When the carbonyl group is directly joined to an oxygen atom, the **carboxyl group** is formed. This occurs in **carboxylic acids** and **esters**.



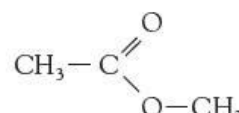
carbonyl group



carboxyl group

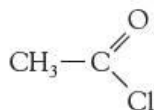


carboxylic acid:
(ethanoic acid)

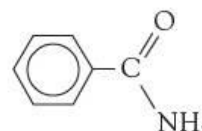


ester:
(methyl ethanoate)

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 as described in Topic 17. The same is true of two other classes of compounds in which the carbonyl group is directly attached to an electronegative atom, namely the **acyl chlorides** and the **amides**:

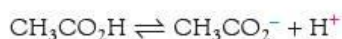


acyl chloride:
(ethanoyl chloride)



amide:
(benzamide)

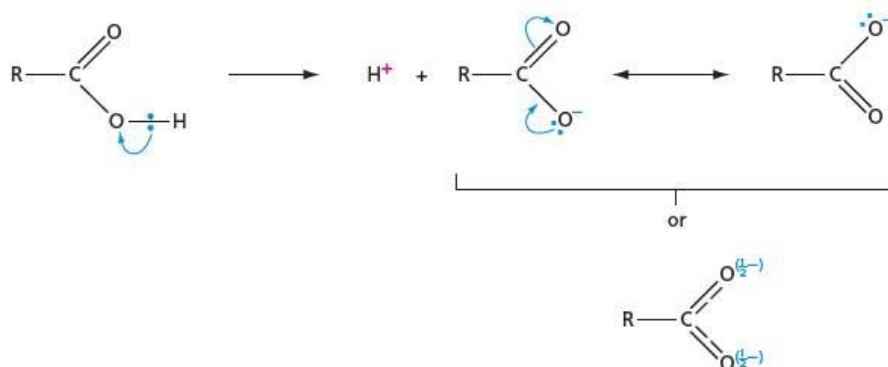
The reactivity of carboxylic acids is dominated by the tendency of the O—H bond to ionise to give hydrogen ions, hence the incorporation of the word 'acid' in their name. The extent of ionisation is small, however. For example, in a 1.0 mol dm^{-3} solution of ethanoic acid, about one molecule in 1000 (0.1%) is ionised:



Carboxylic acids are therefore classed as **weak acids** (see section 6.4).

The O—H bond breaks heterolytically far more easily in carboxylic acids than in alcohols or in phenols (see section 25.5). The negative charge formed by heterolysis can be delocalised over two electronegative oxygen atoms in the carboxylate ion. This spreading out of charge invariably leads to a stabilisation of the anion (see Figure 18.1 and Figure 3.46, page 62). The effect that changes in the structure of a carboxylic acid have on the stability of its anion, and hence its acidity, is dealt with in section 26.1.

Figure 18.1 The charge is spread in the carboxylate anion, stabilising the ion.



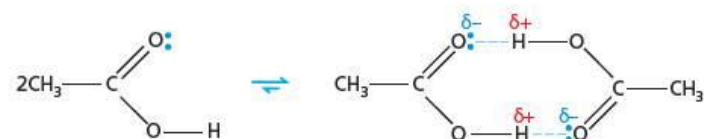
The carboxylic acid group is a strongly hydrogen-bonded one, both to carboxylic acid groups on other carboxylic acid molecules and to solvent molecules such as water. This has effects on two important properties – boiling points and solubilities. Table 18.1 compares these properties for carboxylic acids and the corresponding alcohols.

Table 18.1 Hydrogen bonding increases the boiling points and solubilities in carboxylic acids.

| Number of carbon atoms | Alcohol | | | Carboxylic acid | | |
|------------------------|--|------------------|--------------------------------|---|------------------|--------------------------------|
| | Formula | Boiling point/°C | Solubility in 100 g of water/g | Formula | Boiling point/°C | Solubility in 100 g of water/g |
| 1 | CH ₃ OH | 65 | ∞ | HCO ₂ H | 101 | ∞ |
| 2 | CH ₃ CH ₂ OH | 78 | ∞ | CH ₃ CO ₂ H | 118 | ∞ |
| 3 | CH ₃ CH ₂ CH ₂ OH | 97 | ∞ | CH ₃ CH ₂ CO ₂ H | 141 | ∞ |
| 4 | CH ₃ CH ₂ CH ₂ CH ₂ OH | 118 | 7.9 | CH ₃ CH ₂ CH ₂ CO ₂ H | 164 | ∞ |
| 5 | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH | 138 | 2.3 | CH ₃ CH ₂ CH ₂ CH ₂ CO ₂ H | 187 | 3.7 |

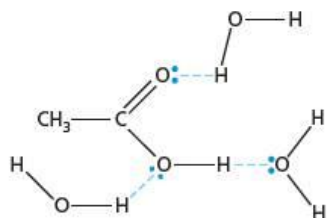
Both in the pure liquid state, and in solution in non-hydrogen-bonding solvents such as benzene, carboxylic acids can form hydrogen-bonded dimers (see Figure 18.2).

Figure 18.2 Carboxylic acids dimerise as two molecules hydrogen bond to each other.



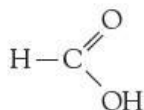
In water, both oxygen atoms and the —OH hydrogen atom of carboxylic acids can hydrogen bond with the solvent (see Figure 18.3).

Figure 18.3 Carboxylic acids hydrogen bond to water molecules.

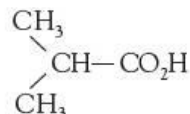


18.2 Isomerism and nomenclature

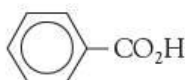
Carboxylic acids are named by finding the longest carbon chain that contains the acid functional group, and adding the suffix '-oic acid' to the stem. Side groups off the chain are named in the usual way:



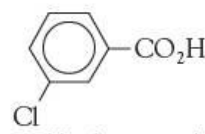
methanoic acid



2-methylpropanoic acid

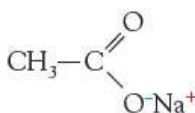


benzoic acid

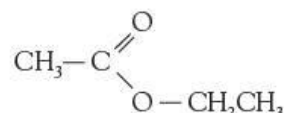


3-chlorobenzoic acid

Esters are named as alkyl derivatives of acids, similar to the naming of salts:

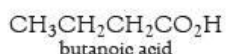


sodium ethanoate



ethyl ethanoate

The isomerism shown by acids is not usually associated with the functional group, but occurs in the carbon chain to which it is attached, as in the following two isomers with the formula $\text{C}_4\text{H}_8\text{O}_2$:

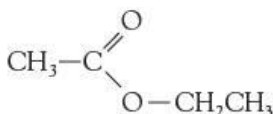


butanoic acid

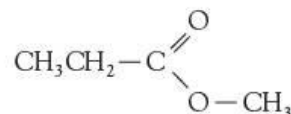


2-methylpropanoic acid

Esters, however, can show a particular form of isomerism, depending on the number of carbon atoms they have in the acid or alcohol part of the molecule. Two isomers of $\text{C}_4\text{H}_8\text{O}_2$ are shown below. Note that although the acid part is usually written first in the formula, by convention, it appears last in the name:



ethyl ethanoate

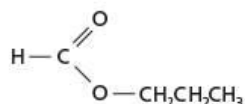


methyl propanoate

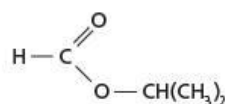
Worked example

Draw the structures of the other two isomeric esters with the formula $\text{C}_4\text{H}_8\text{O}_2$, and name them.

Answer



prop-1-yl methanoate



prop-2-yl methanoate

Now try this

Draw and name possible ester isomers with the formula $\text{C}_5\text{H}_{10}\text{O}_2$. How many ester isomers are there with this formula? Indicate in your answer which of the esters are chiral.

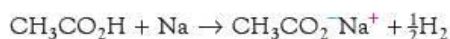
18.3 Reactions of carboxylic acids

Reactions of the O—H group

The acidity of carboxylic acids has already been mentioned. They show most of the typical reactions of acids.

With metals

Ethanoic acid reacts with sodium metal, liberating hydrogen gas (compare with alcohols, section 16.3, and phenols, section 25.5):



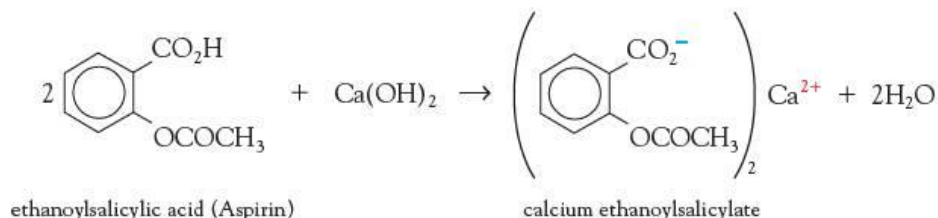
They also react with other reactive metals, such as calcium and magnesium.

With sodium hydroxide

Like phenols, but unlike alcohols, carboxylic acids form salts with alkalis:



Salts are often much more soluble in water than the carboxylic acids from which they are derived. For example, soluble aspirin tablets contain the calcium salt of ethanoysalicylic acid (see section 25.6):

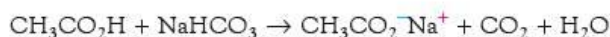


With sodium carbonate and sodium hydrogencarbonate

Like the usual inorganic acids, but unlike both alcohols and phenols, carboxylic acids react with carbonates, liberating carbon dioxide gas:



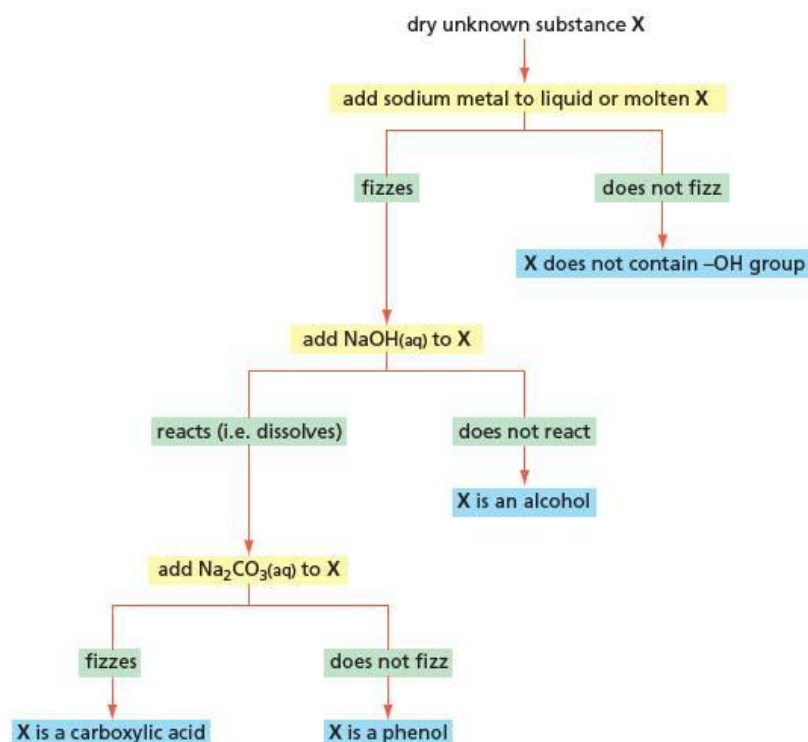
A similar reaction occurs with sodium hydrogencarbonate:



These three reactions form the basis of a series of tests by which alcohols, phenols and carboxylic acids can be distinguished from one another, and from other functional groups (see Figure 18.4).

Acids, phenols and alcohols can be distinguished by their reactions with sodium metal, aqueous sodium hydroxide and aqueous sodium carbonate.

Figure 18.4 How to distinguish between alcohols, phenols and carboxylic acids

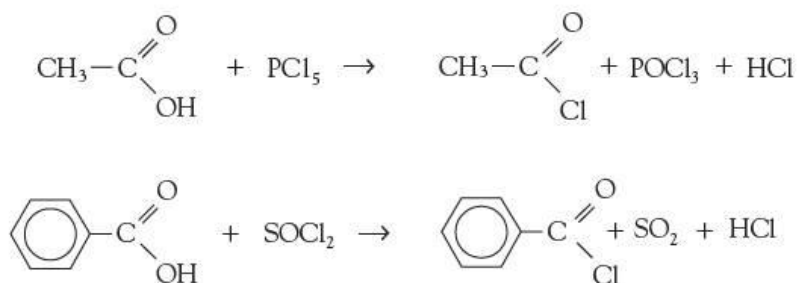


Reactions of the C—OH group

There are two main reactions which replace the —OH group in carboxylic acids with other atoms or groups.

With phosphorus(V) chloride or sulfur dichloride oxide

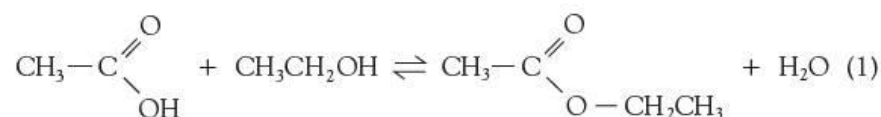
Carboxylic acids react with these reagents in exactly the same way as do alcohols (see section 16.3). Acyl chlorides are produced:



Acyl chlorides are used to make amide. Further reactions and properties of acyl chlorides are described in Topic 26.

With alcohols in the presence of anhydrous acids

Carboxylic acids react with alcohols (but not with phenols) in an acid-catalysed equilibrium reaction to give esters:

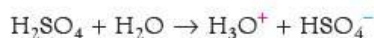


The formation of an ester is an example of a *condensation reaction*. This is when two molecules join together with the elimination of a small molecule (often water) (see also sections 26.4 and 28.2).

Typical reaction conditions are:

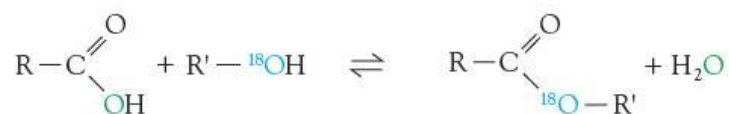
- heat a mixture of carboxylic acid and alcohol with 0.1 mol equivalent of concentrated sulfuric acid under reflux for 4 hours, or
- heat a mixture of carboxylic acid and alcohol under reflux for 2 hours, while passing dry hydrogen chloride gas through the mixture.

The reaction needs an acid catalyst and, like any equilibrium reaction, it can be made to go in either direction depending on the conditions. To encourage esterification, an excess of one of the reagents (often the alcohol) is used, and the water is removed as it is formed (often by the use of concentrated sulfuric acid):



This drives equilibrium (1) over to the right (see section 9.3). To encourage the reverse reaction (the hydrolysis of the ester), the ester is heated under reflux with a dilute solution of sulfuric acid. This provides an excess of water to drive equilibrium (1) over to the left.

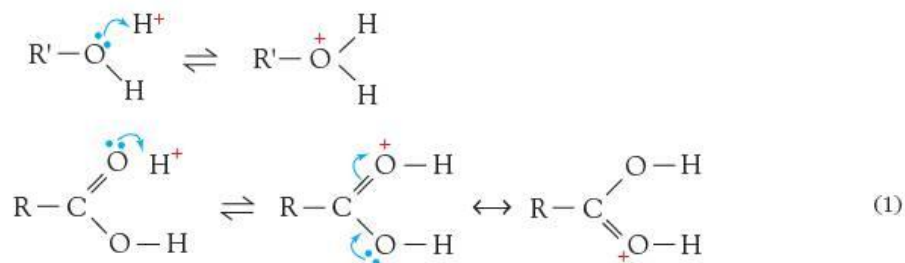
If an ester is made from an alcohol whose —OH group is labelled with an oxygen-18 atom, it is found that the ^{18}O is 100% incorporated into the ester. None of it appears in the water that is also produced. Therefore the water must come from combining the —OH from the carboxylic acid and the —H from the alcohol, rather than vice versa. That is,



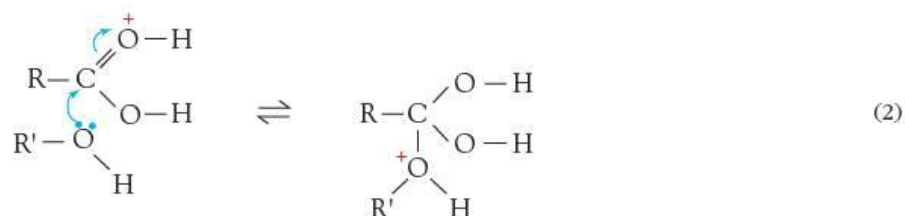
The following mechanism explains why this is the case.

The mechanism of esterification/hydrolysis

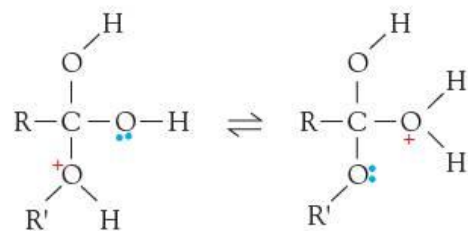
In a strongly acidic medium, both the alcohol and the carboxylic acid can undergo reversible protonation. However, only the protonated carboxylic acid undergoes further reaction.



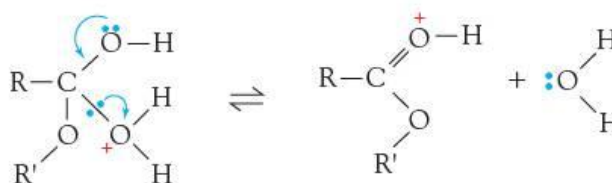
The protonation of the carboxylic acid in step (1) produces a highly δ^+ carbon atom, which can undergo nucleophilic attack by a lone pair of electrons on the oxygen atom of an alcohol molecule:



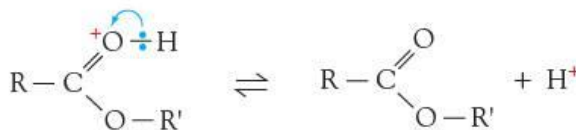
The three oxygen atoms in this intermediate cation are very similar in basicity. Any one of them could be attached to the proton, and proton transfer from one to another can occur readily:



This new cation can undergo a carbon–oxygen bond breaking, which is essentially the reverse of reaction (2), to give a molecule of water, along with the protonated ester:



Lastly, the cation loses a proton to regenerate the H^+ catalyst, and form the ester product:



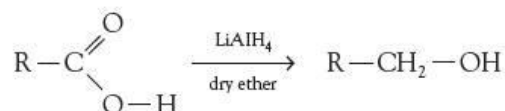
Now try this

Draw the mechanism for the acid-catalysed *hydrolysis* of methyl methanoate.

As mentioned above, the reaction is reversible. So is the mechanism. With an excess of water, esters undergo acid-catalysed hydrolysis. The steps in the mechanism for the hydrolysis reaction are the reverse of the above steps for esterification.

Reduction of the $-\text{CO}_2\text{H}$ group

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

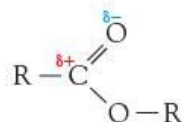


The reaction requires the powerful reducing agent LiAlH_4 ; neither NaBH_4 nor $\text{H}_2 + \text{Ni}$ are strong enough to reduce carboxylic acids. LiAlH_4 will also reduce esters (to alcohols) and amides (to amines – see Topic 27).

18.4 Esters


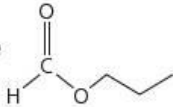
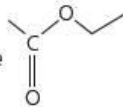
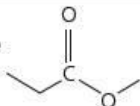
Properties of esters

Esters have the functional group:



Many esters are liquids with sweet, 'fruity' smells. They are immiscible with, and usually less dense than, water. 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, supplemented by a small dipole-dipole contribution. Their boiling points are therefore a few degrees higher than those of the alkanes of similar molecular mass. The position of the carboxyl group along the chain has little effect on the strength of intermolecular bonding, and hence boiling point (see Table 18.2).

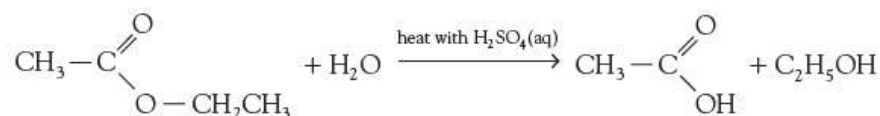
Table 18.2 Esters have boiling points a little higher than those of corresponding alkanes.

| Compound | M_r | Boiling point/ $^{\circ}\text{C}$ |
|---|-------|-----------------------------------|
| hexane  | 86 | 69 |
| propyl methanoate  | 88 | 81 |
| ethyl ethanoate  | 88 | 77 |
| methyl propanoate  | 88 | 79 |

Reactions of esters

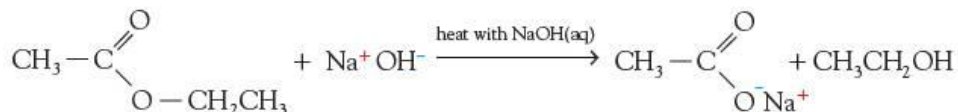
The most common type of reaction that esters undergo is nucleophilic substitution, illustrated here by their hydrolysis.

The hydrolysis of an ester is a slow process, taking several hours of heating under reflux with dilute aqueous acids:



The mechanism of this acid-catalysed hydrolysis has been discussed in section 18.3: it is the reverse of the acid-catalysed esterification described there.

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 base to form the carboxylate anion:

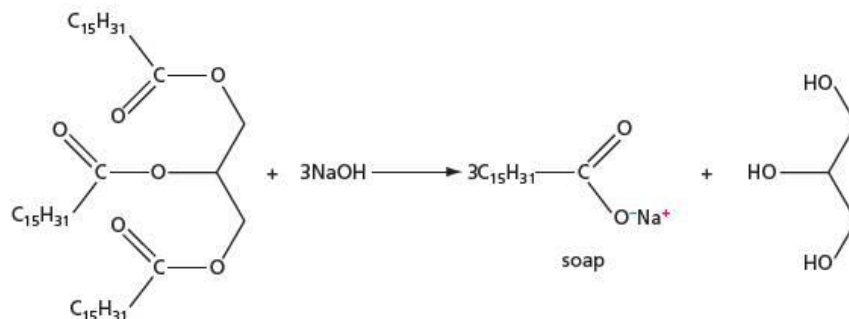


Now try this

Suggest a mechanism for this reaction, using OH^- as the initial nucleophile, and $\text{C}_2\text{H}_5\text{O}^-$ as the base in the last step.

The alkaline hydrolysis of esters has an important application in the manufacture of soap. Fats are glyceryl triesters of long-chain carboxylic acids. Heating fats with strong aqueous sodium hydroxide causes hydrolysis of the triesters. The sodium salts of the long-chain carboxylic acids are precipitated by adding salt (NaCl) to the mixture, and this solid is then washed and compressed into bars of soap (see Figure 18.5). Perfume and colour are also added.

Figure 18.5 Soap is made by the hydrolysis of the glyceryl triesters of fats.

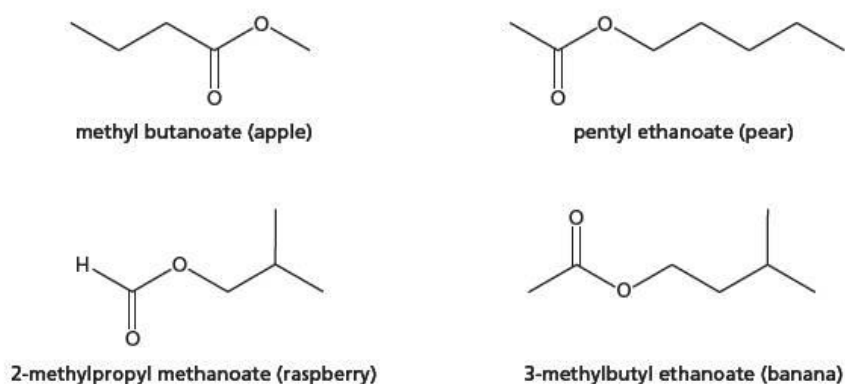


Uses of esters

Esters with small molecular masses find many uses as solvents for paints and varnishes, and also for removing caffeine from coffee and tea to make decaffeinated beverages. Many natural perfumes, flavours and aromas are esters, and many of these are now manufactured commercially to flavour fruit drinks and sweets. It is the ethyl esters formed from alcohol and the various acids in wines that account for much of their 'nose', or aroma, in the glass.

Some of the naturally-occurring esters now made synthetically and used as artificial flavours in foodstuffs are shown in Figure 18.6.

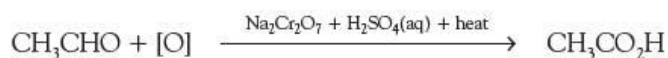
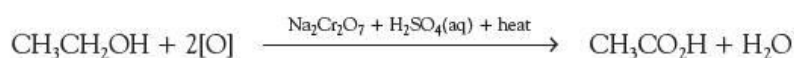
Figure 18.6 Some esters used as flavouring agents



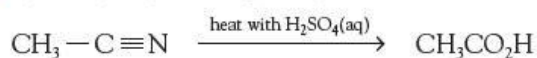
18.5 Preparing carboxylic acids

Carboxylic acids may be prepared by the following reactions.

- By the oxidation of primary alcohols or aldehydes:

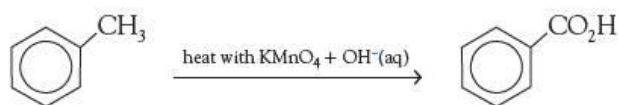


- By the hydrolysis of organic cyanides (nitriles):



- By the hydrolysis of acid derivatives such as esters, acyl chlorides and amides (see Topics 27 and 28). Although these reactions proceed in high yields, they are not normally useful preparative reactions: acid derivatives are usually made from the carboxylic acids in the first place, so their hydrolysis forms no compounds of further use.

- By the oxidation of aryl side chains. When treated with hot alkaline potassium manganate(VII), aryl hydrocarbons produce benzoic acids by oxidation:

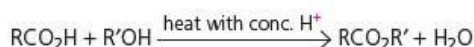
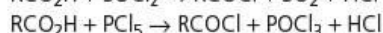
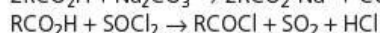
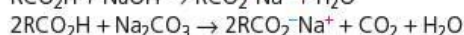
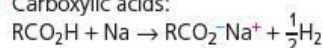


Summary

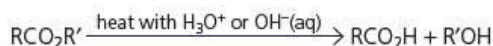
- The **carboxylic acids**, RCO_2H , are weak acids, ionising to the extent of 1% or less in water.
- Carboxylic acids react with alcohols to form **esters**, and with phosphorus(V) chloride to form **acyl chlorides**.
- Esters undergo acid- or base-catalysed **hydrolysis**.

Key reactions you should know

- Carboxylic acids:



- Esters:



Examination practice questions

Please see the data section of the CD for any A_r values you may need.

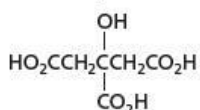
- 1 Isomerism occurs in many organic compounds. The two main forms of isomerism are structural isomerism and stereoisomerism. Many organic compounds that occur naturally have molecules that can show stereoisomerism, that is *cis-trans* or optical isomerism.

- a i Explain what is meant by *structural isomerism*.
 ii State **two** different features of molecules that can give rise to **stereoisomerism**. [3]

Unripe fruit often contains polycarboxylic acids, that is acids with more than one carboxylic acid group in their molecule. One of these acids is commonly known as tartaric acid, $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$.

- b Give the structural formula of the organic compound produced when tartaric acid is reacted with an excess of NaHCO_3 . [1]

Another acid present in unripe fruit is citric acid,



- c Does citric acid show optical isomerism? Explain your answer. [1]

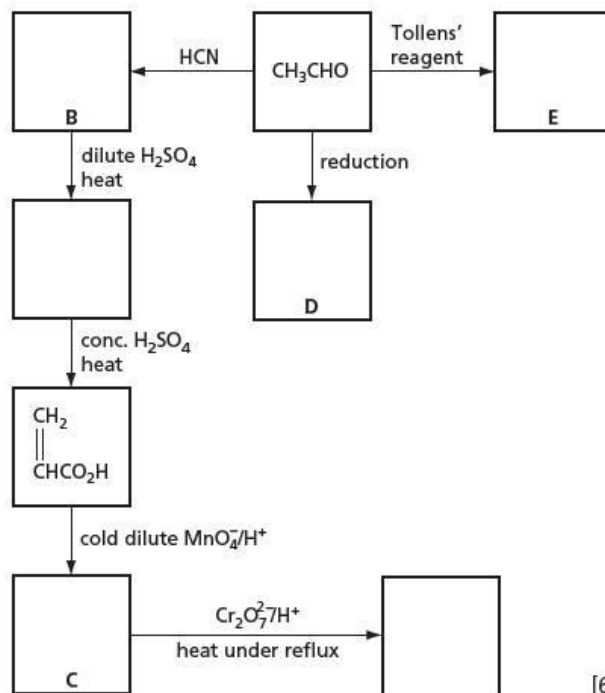
A third polycarboxylic acid present in unripe fruit is a colourless crystalline solid, **W**, which has the following composition by mass: C, 35.8%; H, 4.5%; O, 59.7%.

- d i Show by calculation that the empirical formula of **W** is $\text{C}_4\text{H}_6\text{O}_5$.
 ii The M_r of **W** is 134. Use this value to determine the molecular formula of **W**. [3]

A sample of **W** of mass 1.97 g was dissolved in water and the resulting solution titrated with 1.00 mol dm^{-3} NaOH. 29.4 cm^3 were required for complete neutralisation.

- e i Use these data to deduce the number of carboxylic acid groups present in one molecule of **W**.
 ii Suggest the displayed formula of **W**. [5]
[Cambridge International AS & A Level Chemistry 9701, Paper 21 Q5 June 2010]

- 2 a Draw and complete the following reaction scheme which starts with ethanal. In **each empty** box, write the **structural formula** of the organic compound that would be formed.



- b** Write the structural formula for the organic compound formed when, under suitable conditions,
- i** compound **C** reacts with compound **D**,
 - ii** compound **C** reacts with compound **E**. [2]

- c** Compound **B** is chiral. Draw displayed formulae of the two optical isomers of compound **B**, indicating with an asterisk (*) the chiral carbon atom. [3]

[Cambridge International AS & A Level Chemistry 9701, Paper 2 Q4 June 2009]