



# Higher Chemistry

HSN12100  
Unit 2 Topic 1

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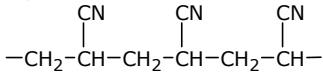
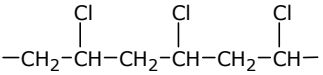
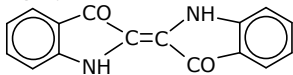
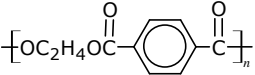
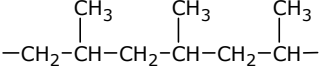
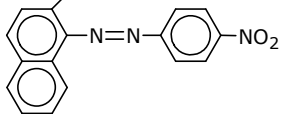
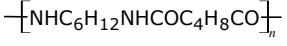
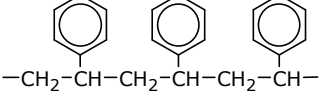
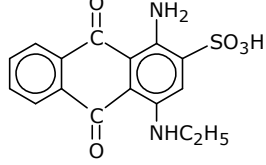
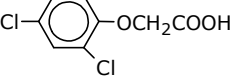
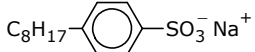
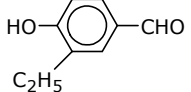
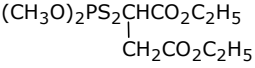
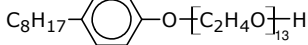
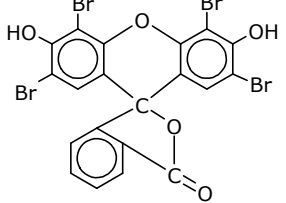
# Topic 1 – Fuels, Homologous Series and Naming

## Fuels and Feedstocks

This topic assumes you know and understand the work done in Standard Grade on Fuels and Hydrocarbons. Coal, oil and natural gas are finite resources – they are not renewable. From these resources we get carbon compounds that can be used as fuels or feedstocks. A feedstock is simply a chemical from which other chemicals can be manufactured. Sometimes one chemical can be used both as a fuel or a feedstock.

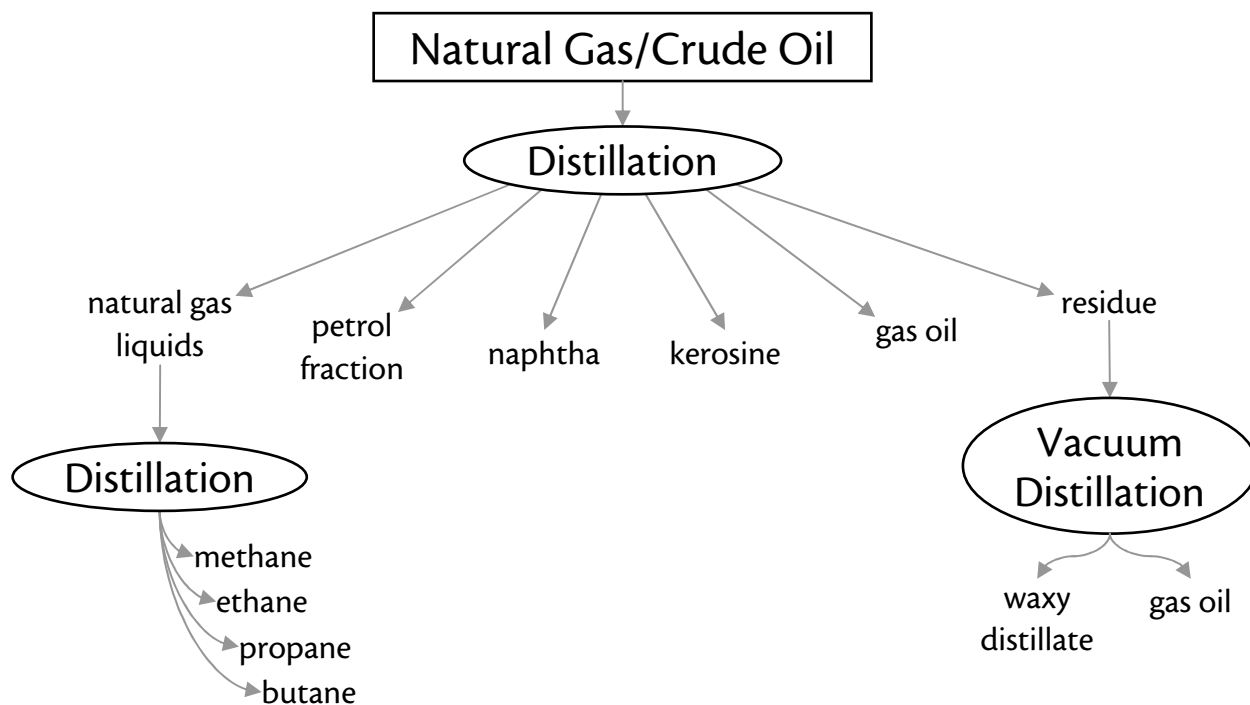
eg. the naphtha fraction from crude oil distillation can produce petrol (a fuel) or it can be used as a feedstock to produce ethene and then polythene.

The table below shows some of the vast range of consumer products containing carbon compounds.

Textiles	Plastics	Dyes
a) <i>Acrylic</i> 	a) <i>PVC</i> 	a) <i>Indigo (for blue denim)</i> 
b) <i>Polyester</i> 	b) <i>Polypropene</i> 	b) <i>Azodyes eg 'Para Red'</i> 
c) <i>Nylon</i> 	c) <i>Polystyrene</i> 	c) <i>Anthraquinone dyes</i> 
Agricultural Chemicals	Detergents	Cosmetics
a) <i>Herbicides eg '2,4-D'</i> 	These contain a) <i>Anionic surfactants</i> 	a) <i>Perfumes may include ethyl vanillin</i> 
b) <i>Pesticides eg 'Malathion'</i> 	b) <i>Non-ionic surfactants</i> 	b) <i>Lipsticks include coloured compounds</i> 

These large complex molecules have been synthesised (built up) from small reactive molecules.

In this country, crude oil is our main source of these compounds. Crude oil undergoes an initial separation by fractional distillation as shown in the flow diagram on the next page.



Some of these fractions are used to make fuels (petrol, diesel etc) and some of the fractions are used to make a whole range of other chemicals. Let us consider the important facts and features of the fuels first – dealing mainly with petrol.

## Petrol

The petrol fraction produced by distillation of crude oil is still not ready to use as a car fuel. There are two problems with it:

- it is a low quality fuel.
- there is not enough of it to satisfy market demand for petrol.

The petrol fraction contains mostly straight chain hydrocarbons and this makes a poor quality petrol. When ignited in the combustion chamber of the engine, straight chain hydrocarbons tend to explode rather than burn smoothly. These explosions are called 'auto-ignition' or 'knocking' and can damage the engine. Petrol burns more smoothly if it contains branched, cyclic and aromatic hydrocarbons. Leaded petrol contains the additive lead tetra-ethyl,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ . This is an antiknock agent and helps poor quality petrol to burn smoothly. Petrol also contains dibromoethane. This combines with the lead which then leaves the exhaust as volatile lead (II) bromide. Lead is poisonous and pressure was put on the oil companies to produce unleaded petrol. To make it burn smoothly unleaded petrol must have an even greater amount of branched and aromatic hydrocarbons.

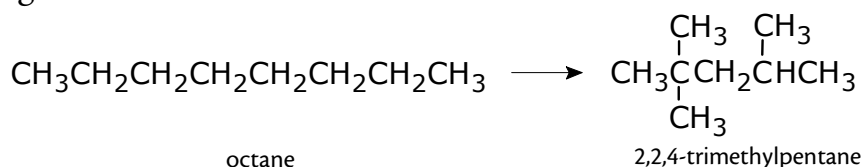
The quantity of the petrol fraction is increased by using the naphtha fraction and waxy distillate but first their quality must be improved. This is done as follows:

The naphtha fraction is mostly straight chain  $\text{C}_5$  to  $\text{C}_{10}$  hydrocarbons. This is the correct size of molecules for petrol.

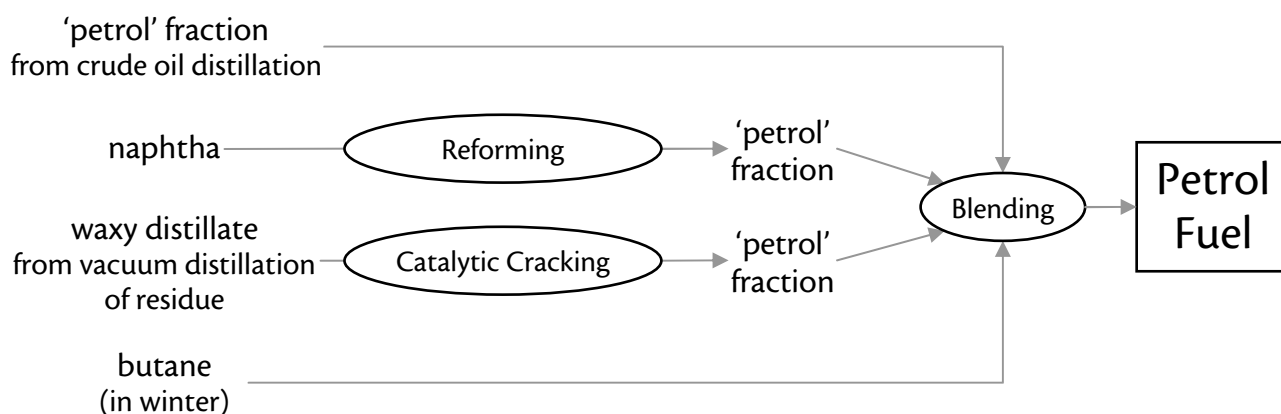
The waxy distillate consists of  $\text{C}_{20}$  to  $\text{C}_{40}$  hydrocarbons. These are first cracked to reduce the chain length. We now have molecules which are the correct size for petrol but they are still straight chained.

Reforming is a chemical reaction which changes the structure of molecules without changing their size. Reforming of the naphtha fraction and the products of cracking gives aromatics, cycloalkanes and branched chain products as well as some straight chain compounds.

eg the reforming of octane



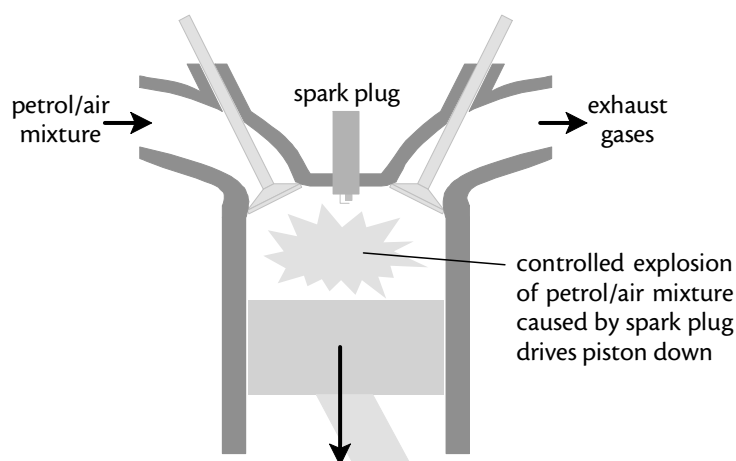
These are blended with the original petrol fraction to increase both the quality and the amount. The flow diagram shows these processes:



This better quality fuel can be burned much more smoothly in a petrol engine without lead compounds and is therefore referred to as 'unleaded' petrol. As we will see in the next section, petrol is drawn in to an engine as a vapour so it is important to have the correct mix of volatile compounds and this actually depends on the time of year – in winter more volatile compounds are added (eg butane and pentane) and in summer, the blend has a larger proportion of slightly larger hydrocarbons.

## Petrol Engines

Petrol contains small ( $C_5$  to  $C_{10}$ ) volatile hydrocarbon molecules. They are drawn into the engine as a petrol vapour/air mixture. They are ignited by an electric spark from the spark plug. We have seen the importance of branched and aromatic molecules in providing a smooth combustion. The following diagram shows part of the workings in a petrol engine.



## Pollution due to burning Fuels

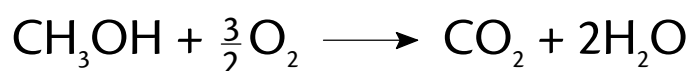
This has been studied at Standard Grade but is an important issue so is worth a brief reminder at this point:

The burning of fossil fuels yields products that can harm the environment.

- **Carbon dioxide** contributes to the green house effect.
- **Carbon monoxide** produced by incomplete combustion is toxic.
- **Sulphur dioxide:** Sulphur is a common impurity in fuels and, unless it is removed, it produces sulphur dioxide when the fuel is burned. Sulphur dioxide is a major contributor to acid rain.
- **Nitrogen oxides:** The spark in a car engine, as well as igniting the petrol, produces nitrogen oxides ( $\text{NO}_x$ ) from the nitrogen and oxygen of the air. They cause respiratory problems and also dissolve in water and add to the “acid rain” problem.
- **Lead compounds** resulting from leaded petrol are poisonous. Evidence suggests that accumulations of lead in the body can cause brain damage especially in young children.

## Alternatives to petrol

We know that, one day, the sources of crude oil will run out – fossil fuels are finite resources. There are some alternative liquid fuels such as ethanol and methanol. These belong to a homologous series called alkanols which we will study later. We have already met ethanol at Standard Grade as the alcohol which is formed when sugar (glucose) ferments. In countries where sugar cane can be grown in great quantities (eg Brazil), ethanol is produced and mixed with petrol. It is also possible to manufacture methanol on an industrial scale; this can be used as a fuel directly or mixed with petrol. Methanol burns according to the following equation:



Advantages and disadvantages of using methanol are outlined below:

### Advantages

- The burning of methanol is complete so reducing the carbon monoxide in the air.
- Petrol contains benzene and other aromatic hydrocarbons which are carcinogenic; methanol does not contain these compounds.
- Methanol is relatively quite cheap and renewable.
- Methanol is less volatile and less likely to be an explosion risk.

### Disadvantages

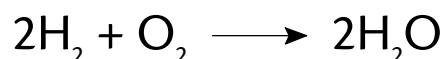
- Methanol is toxic and can cause blindness/brain damage
- Methanol produces less energy than petrol (for equivalent volumes)
- Methanol absorbs water – this gives a corrosive mixture
- Methanol and petrol are quite immiscible (don't mix readily)

The industrial preparation of methanol is an important chemical process and it is discussed in more detail on page 17.

## The Hydrogen Economy

Hydrogen has for a long time now been recognised as potentially a very useful fuel for a number of good reasons:

Internal combustion engines could be designed to use hydrogen burning instead of petrol. This would be very efficient and reduce the amount of carbon dioxide in the atmosphere.



If we compare the burning of hydrogen with the burning of petrol then, weight for weight, hydrogen produces far more energy than petrol. However, hydrogen is the lightest and least easily liquefied gas. Volume for volume, hydrogen is less energy efficient than petrol. Much research is being done to overcome this problem.

Hydrogen can be used to make electricity from a hydrogen/oxygen fuel cell, which would involve allowing the hydrogen and oxygen to react in two separate parts of the cell and making electricity instead of heat – this can be fairly easily done.

Hydrogen could be stored and distributed like natural gas and used for heating in houses. This could be cheaper than using electricity.

Using hydrogen in these ways as our main fuel source is known as a ‘hydrogen economy’ and could be very efficient compared with our present use of fossil fuels if only we did not need fossil fuels to make the hydrogen in the first place (electricity is required to make the hydrogen and this electricity is still made largely by burning fossil fuels). However, the use of solar energy to ‘split’ water into hydrogen and oxygen would be a perfect solution to this problem and is being investigated as a long term possibility.

## Biogas

Biomass is a general term for plant material. When waste plant material (e.g. manure, straw, vegetables) decays in the absence of air, bacteria produce biogas. The process is called anaerobic (without air) fermentation. Biogas is a mixture consisting mainly of methane (60%) and carbon dioxide.

## The Chemistry of Carbon

Fuels are important uses of hydrocarbon compounds but the chemistry of carbon extends far beyond what has been covered so far. There are over 15,000,000 different carbon compounds (containing not only C and H atoms but often O, N and many other types of atom). This arises from carbon's ability to join in straight chains, branched chains and rings as well as its ability to form strong bonds with many types of atom. The chemistry of carbon compounds is made simpler because the compounds are studied in families called homologous series. Members of a homologous series are called homologues. A homologous series has the following features:

- there is a gradual change in physical properties from one member to the next. The most common example of this is the increasing melting and boiling points as we go up a series. The reason of course is the increasing van der Waals forces as the molecules get larger.
- members have similar chemical properties and methods of preparation.
- the formula increases by  $\text{CH}_2$  from one member to the next up the series.
- the series has a general formula.
- all members possess the same functional group. It is the functional group that gives the series its characteristic reactions.

We have met two important series of hydrocarbons – the alkanes and the alkenes.

### Alkanes

The alkanes are a series of hydrocarbons with the general formula  $\text{C}_n\text{H}_{2n+2}$ . The table below shows the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
methane	$\text{CH}_4$	<pre>       H             H-C-H               H           </pre>
ethane	$\text{C}_2\text{H}_6$	<pre>       H H               H-C-C-H                 H H           </pre>
propane	$\text{C}_3\text{H}_8$	<pre>       H H H                 H-C-C-C-H                   H H H           </pre>
butane	$\text{C}_4\text{H}_{12}$	<pre>       H H H H                   H-C-C-C-C-H                     H H H H           </pre>

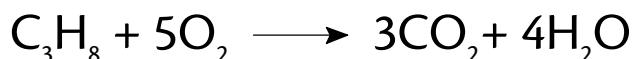
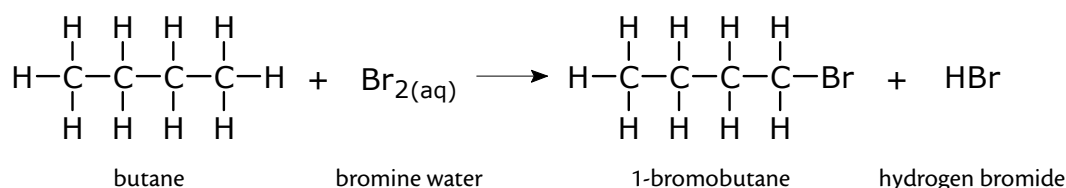
They are called saturated hydrocarbons because all the carbon atoms have formed the maximum number of single covalent bonds (4).

### Chemical Reactions of Alkanes

This is revision of Standard Grade work. Alkanes can undergo two main types of reaction – combustion and substitution.

*Combustion*

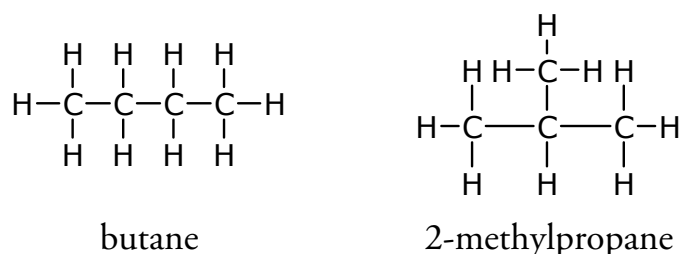
Alkanes burn in plenty oxygen to form carbon dioxide and water

*Substitution*

Substitution reactions of alkanes are slow. In this reaction with butane, the brown colour of the bromine disappears slowly. Note that all halogens (chlorine, fluorine and iodine also) can react with alkanes in this way.

**Isomers and Systematic Nomenclature (names)**

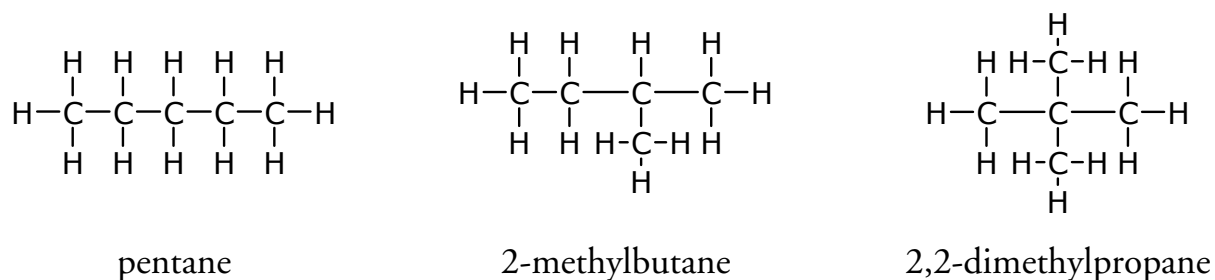
Isomers are molecules with the same molecular formula but different structural formulae. For the first three members of the alkanes only one structure is possible but butane,  $\text{C}_4\text{H}_{10}$ , has two isomers, shown below with their systematic names.



The rules for naming are:

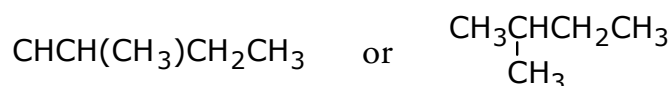
1. Find the longest carbon chain in the molecule – the name is based on the alkane with this number of carbon atoms.
2. Number the chain to give any branches the lowest possible number.
3. Name the branches: methyl ( $-\text{CH}_3$ ), ethyl ( $-\text{C}_2\text{H}_5$ ) etc.

We can see how this works by naming the three isomers of pentane ( $\text{C}_5\text{H}_{12}$ ):



As well as the full structural formulae we have used to show the different isomers of pentane, you should also be able to represent organic compounds in the form of shortened structural formulae.

eg 2-methylbutane as shown earlier can also be drawn:



Try writing other shortened structural formulae for practice.



## Alkenes

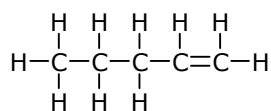
The alkenes are a homologous series of hydrocarbons with the general formula  $C_nH_{2n}$ . The table below has the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
ethene	$C_2H_4$	<pre>       H   H                   C=C                   H   H           </pre>
propene	$C_3H_6$	<pre>       H   H   H                       H-C-C=C-H                   H           </pre>
butene	$C_4H_8$	<pre>       H   H   H   H                           H-C-C-C=C-H                       H   H           </pre>

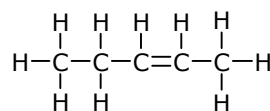
They are unsaturated because each member has a C=C bond. This feature is the functional group in the alkenes and gives the alkenes their characteristic reactions.

### Isomers and Naming

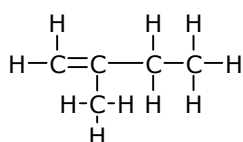
Isomers arise both by branching the chain and by varying the position of the double bond. Naming is similar to the alkanes but the main chain (the longest chain) must contain the double bond, whose position is indicated by a number. The chain is numbered to make this number as small as possible. The isomers of pentene and their names are given below.



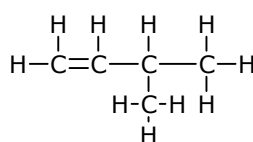
pent-1-ene



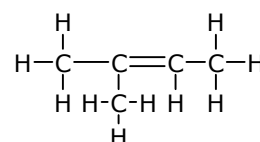
pent-2-ene



2-methylbut-1-ene



3-methylbut-1-ene



2-methylbut-2-ene

### Industrial Source of Alkenes

Ethene and propene are made by cracking of either ethane or naphtha (check where these feedstocks come from on the previous flow diagram). This involves heating the feedstock to a very high temperature (800°C). Both feedstocks give the same products but the proportions are different:

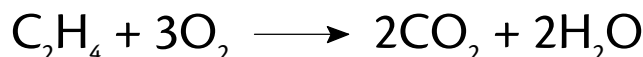
Product	Approximate percentage obtained from cracking	
	Ethane	Naphtha
Ethene	80	30
Fuel Gases ( $CH_4$ , $H_2$ )	10	25
Propene	5	15
Gasoline	5	30

As we can see ethane provides a much higher percentage of ethene but naphtha gives other valuable by products. Note that if propane is cracked the main product is propene.

## Chemical reactions of alkenes

### Combustion

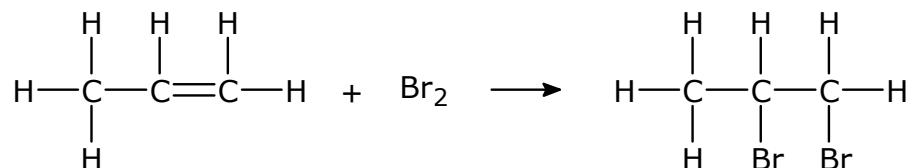
In common with all hydrocarbons, the alkenes burn in plenty oxygen to form carbon dioxide and water.



### Addition

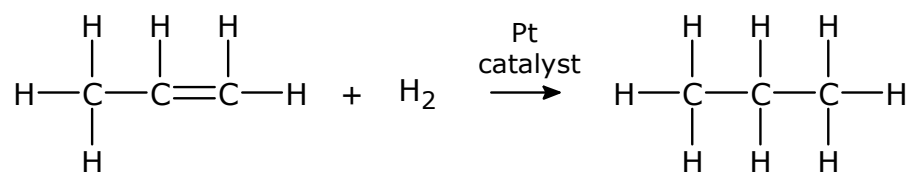
The characteristic reaction of alkenes are addition reactions – in these a molecule adds across the double bond.

#### a) with bromine water – bromination



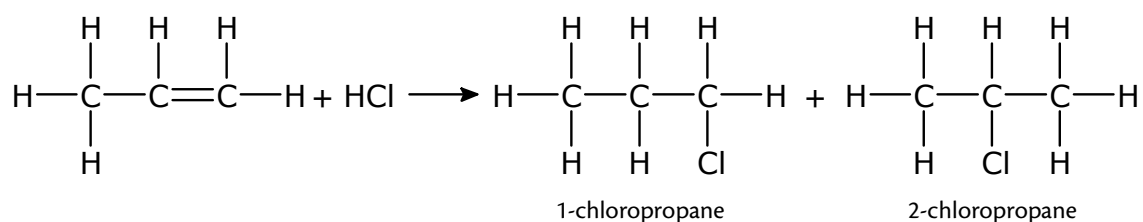
In this reaction the bromine loses its brown colour very quickly. This reaction is used as a test for unsaturation. Contrast it with the slow substitution reaction with bromine given by the saturated alkanes.

#### b) with hydrogen – hydrogenation



This addition of hydrogen across a double bond happens only in the presence of a catalyst – usually platinum is used in the lab reaction. This process converts an alkene into an alkane.

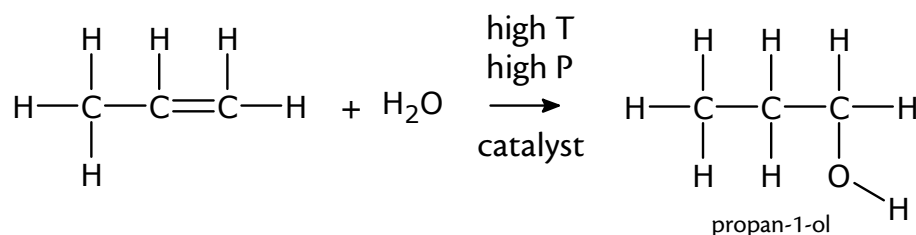
#### c) with hydrogen halides



Note the possibility of isomeric products in this case.

In this reaction we end up with a substituted alkane – a haloalkane.

#### d) with water – hydration



In all of the above addition reactions, an unsaturated compound becomes fully saturated.

## Alkynes

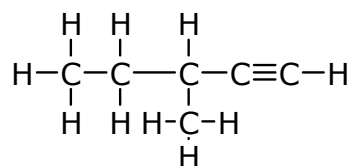
The alkynes are another homologous series, which you have not met before. The important functional group of these is the  $C\equiv C$  'triple bond'. These molecules are obviously even more unsaturated than alkenes. The naming of the alkyne isomers is exactly similar to the naming of alkenes apart from the ending being 'yne' rather than 'ene'. The general formula of the alkynes is  $C_nH_{2n-2}$  and the table below has the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
ethyne	$C_2H_2$	$H-C\equiv C-H$
propyne	$C_3H_4$	$\begin{array}{c} H \\   \\ H-C-C\equiv C-H \\   \\ H \end{array}$
butyne	$C_4H_6$	$\begin{array}{c} H & H \\   &   \\ H-C & -C-C\equiv C-H \\   &   \\ H & H \end{array}$

### Isomerism and Naming

The naming of the isomers of alkynes is exactly similar with the naming of alkenes, except that the ending -yne is used instead of -ene.

The isomer 3-methylpent-1-yne is shown below:

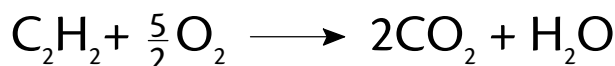


Try to write structural formulae for as many other isomers of the above and give the systematic names.

### Chemical reactions of alkynes

#### Combustion

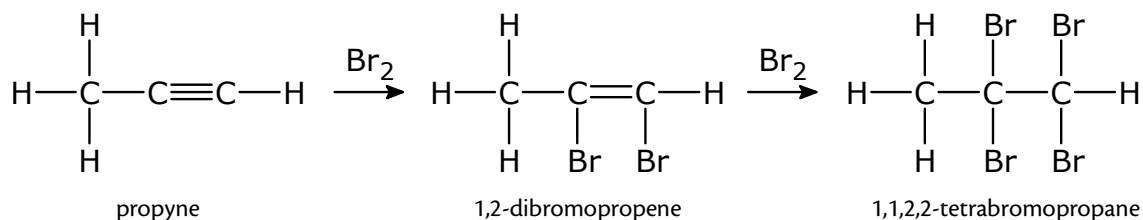
This is as expected for the combustion of a hydrocarbon



#### Addition

As the alkynes are unsaturated we might expect that they will undergo addition reactions like the alkenes. This is indeed the case but the reaction can happen in two stages and, with care, can be stopped after the first stage.

a) **with halogens** – to make dihaloalkenes, then tetrahaloalkanes.





**Blowing agents**

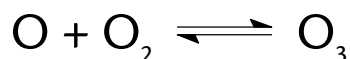
If a volatile CFC is included in the formation of a plastic, the heat generated in the polymerisation vaporises the CFC and this creates tiny bubbles in the plastic, making foam – eg expanded polystyrene. This process must involve the release of much CFC into the atmosphere.

**Cleaning solvents**

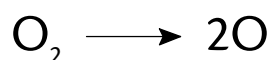
CFCs are very good solvents for grease and are used as dry cleaning solvents and for cleaning electric circuits. Again, some of the solvent ends up in the atmosphere.

The release of CFCs into the atmosphere has become a huge environmental issue in the last few years and steps have been taken to control the use and the release of these chemicals into the atmosphere because of its effect on the 'ozone layer' in the upper atmosphere.

Ozone, O<sub>3</sub>, is a vital natural sunscreen gas which protects us from very harmful UV radiation by absorbing it. It is formed between oxygen atoms and oxygen molecules and breaks back down to oxygen molecules and atoms by absorption of UV light:



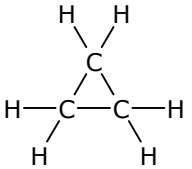
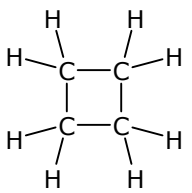
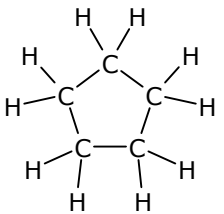
The oxygen atoms are produced by oxygen molecules, also by absorbing some UV radiation.



The ozone is constantly being formed and destroyed through the absorption of UV light and the balance of these processes is important in shielding us from too much UV radiation. It is widely accepted that certain CFCs in the atmosphere can destroy the ozone layer and this would allow more UV radiation to reach the earth. This would result in more incidents of skin cancer, eye cataracts and could have many other wide ranging effects on the environment of the earth.

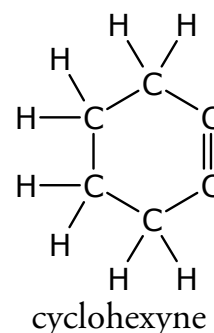
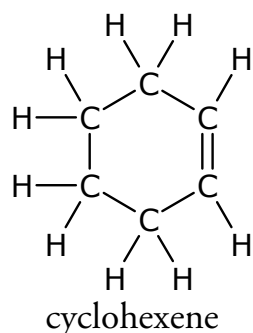
## Ring Compounds

All the hydrocarbon compounds mentioned so far have been straight chain or branched compounds. We also know that one of the reasons that there are so many carbon compounds is that ring compounds can also easily be formed cyclic compounds. There are homologous series of these and we have already met one at Standard Grade – the cycloalkanes (general formula  $C_nH_{2n}$ ). The smallest cycloalkane is cyclopropane (3 is the smallest number of carbons that can join to form a ring!). The structure of this is shown below as well as the next few members of the series:

Name	Molecular Formula	Structural Formula
cyclopropane	$C_3H_6$	
cyclobutane	$C_4H_8$	
cyclopentane	$C_5H_{10}$	

Note that cycloalkanes have the same molecular formula as the alkene with the same carbon number – they are isomeric.

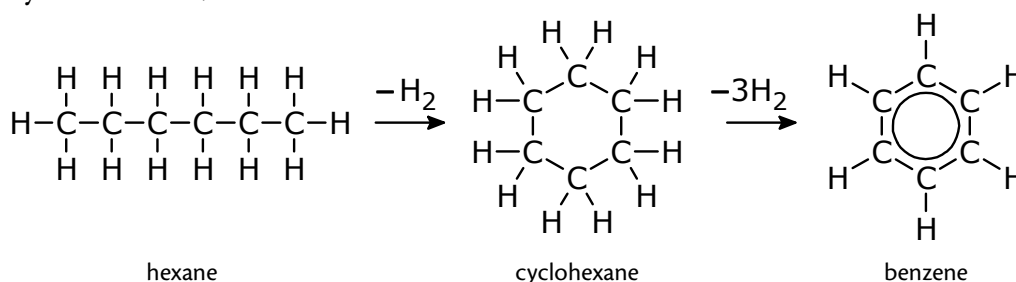
Cycloalkanes react in exactly the same way as the alkanes – combustion and substitution. Cycloalkenes and cycloalkynes are other possible homologous series of cyclic compounds. They react respectively like the alkenes and alkynes. The structures of the 6 carbon members of these series are shown.



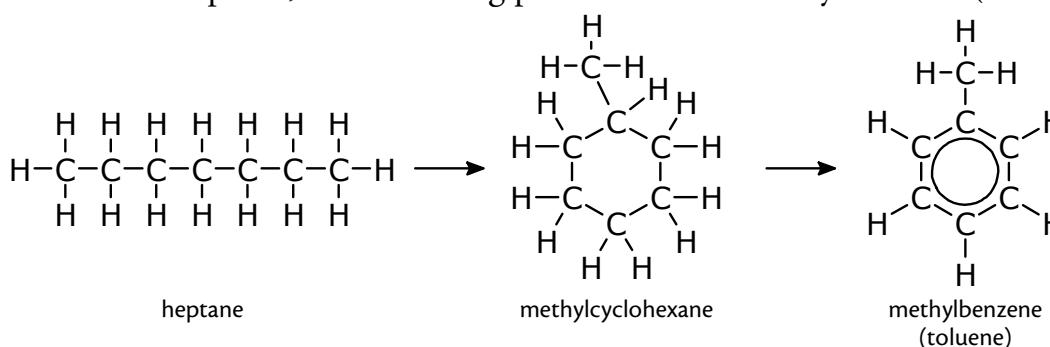
Note that cycloalkenes are isomeric with alkynes.

## Aromatic Hydrocarbons

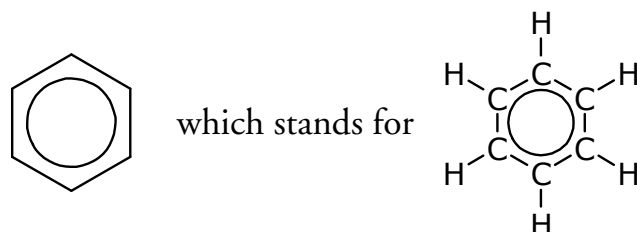
Naphtha, from the distillation of crude oil, can be used for the production of a very important group of compounds called aromatic hydrocarbons. Straight chain alkanes in naphtha undergo cyclisation to form cycloalkanes which then lose hydrogen to form aromatic hydrocarbons, like benzene.



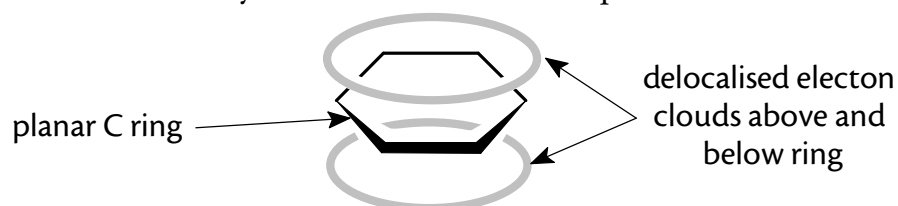
The process is called reforming – the structure of the molecules alters without any change in their size. With heptane, the reforming process leads to methylbenzene (toluene).



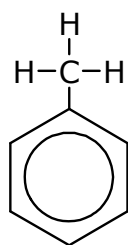
In practice the process of reforming gives a mixture of aromatic compounds that must be carefully separated. Benzene,  $\text{C}_6\text{H}_6$ , is the simplest aromatic compound. It has a ring structure usually drawn as shown:



At each corner there is a carbon with a hydrogen attached. Although this formula seems very unsaturated, the benzene ring is very resistant to addition reactions – there is no fast reaction with bromine water. The structure can be thought of as a ring of six carbon atoms, each with a hydrogen atom. This takes up three of the four bonding electrons from each carbon atom. The fourth electron can be imagined as being shared over the whole ring, above and below as shown in the diagram below. The electrons are said to be delocalised and it is thought that this delocalisation of the electrons gives the benzene ring great stability. It is therefore very resistant to attack and quite unreactive.



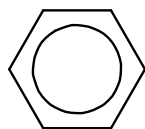
There is an enormous range of aromatic molecules but all are based on the benzene unit. Several of the important groups of molecules shown on the first page are aromatic.



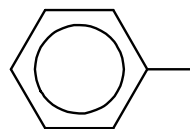
In the molecule methylbenzene (toluene),  $C_6H_5CH_3$ , one of the hydrogens in benzene has been replaced with a methyl group ( $-CH_3$ ).

Another way of looking at this molecule is to regard the methane molecule as having a hydrogen replaced with the aromatic part  $-C_6H_5$ . The  $-C_6H_5$  group is called the phenyl group.

Below we summarise the relationship between benzene and the phenyl group:

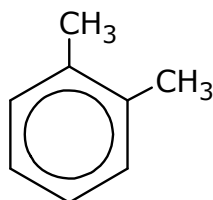


benzene,  $C_6H_6$

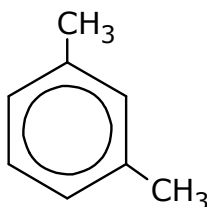


phenyl group,  $C_6H_5$

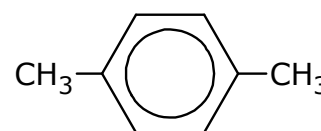
If two hydrogen atoms in benzene are replaced with methyl groups, then three isomeric dimethylbenzenes are possible:



1,2-dimethylbenzene



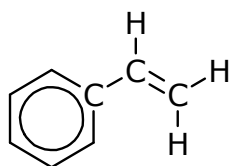
1,3-dimethylbenzene



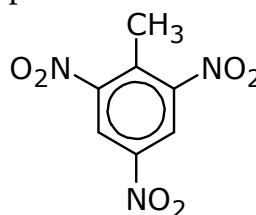
1,4-dimethylbenzene

These three molecules are also called xylenes. They are used in the manufacture of paints, fibres and dyes.

Benzene is a very important feedstock. Most of the benzene made is reacted with ethene to form phenylethene (styrene). This, as we know, is used to make the polymer, poly(phenylethene), more commonly known as polystyrene. Methylbenzene (toluene) is used to make TNT (trinitrotoluene) which is an explosive:

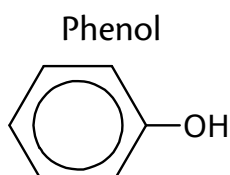


phenylethene (styrene)



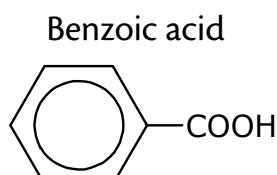
trinitrotoluene

Other examples of derivatives of benzene are:



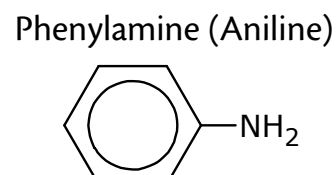
$C_6H_5OH$

- Used in the manufacture of
- bakelite
  - nylon monomers
  - drugs (eg Aspirin) and dyes
  - germicides (eg Dettol)



$C_6H_5COOH$

- Used as a food additive (E210)



$C_6H_5NH_2$

- Used in the manufacture of dyes and drugs

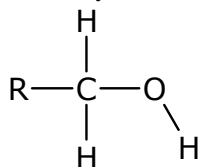


## Alkanols

Alcohols are molecules that contain the hydroxyl (-OH) functional group. The alkanols are a homologous series of alcohols with the general formula  $C_nH_{2n+1}OH$ . They can be thought of as derived from the parent alkanes by substituting a hydrogen atom with an -OH group.

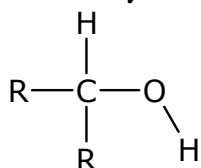
Alkanols can be classified in three groups:

### Primary alkanols



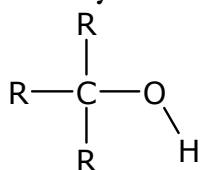
The carbon bearing the -OH group is directly bonded to only one alkyl group.

### Secondary alkanols



The carbon bearing the -OH group is directly bonded to two alkyl groups.

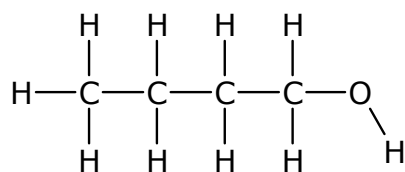
### Tertiary alkanols



The carbon bearing the -OH group is directly bonded to three alkyl groups.

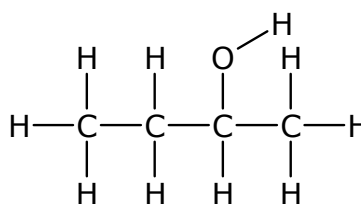
### Isomers and names

Isomers can result from both chain branching and varying the position of the -OH group. In naming, the main chain must contain the -OH group, whose position is indicated by a number. We can see this by looking at the four isomers of butanol,  $C_4H_9OH$ :



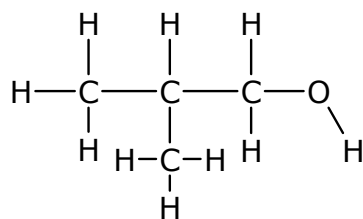
butan-1-ol

(primary)



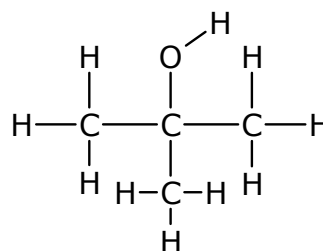
butan-2-ol

(secondary)



2-methylpropan-1-ol

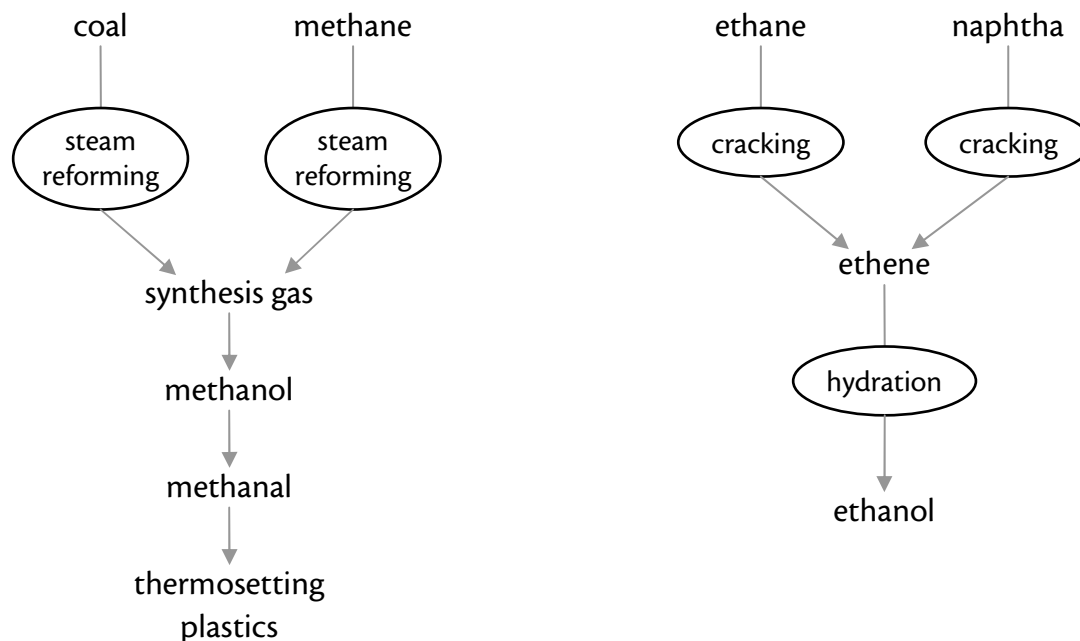
(primary)



2-methylpropan-2-ol

(tertiary)



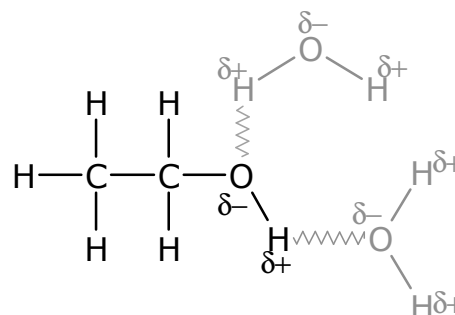


Thermosetting plastics will be dealt with later, in the section on polymers.

## Physical Properties of Alkanols

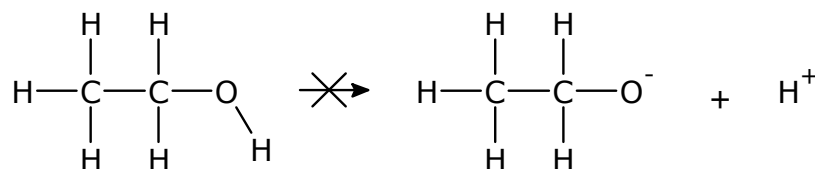
### Solubility in water

The first three alkanols are miscible with water because the polar hydroxyl group can hydrogen bond with water molecules.



### Acidity

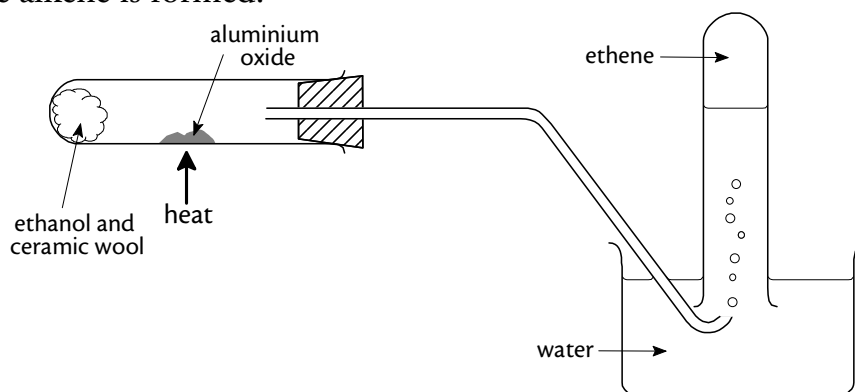
Alkanols are not acidic in water and so do not give any of the usual acid reactions.



## Chemical Reactions of Alkanols

### Dehydration to alkenes

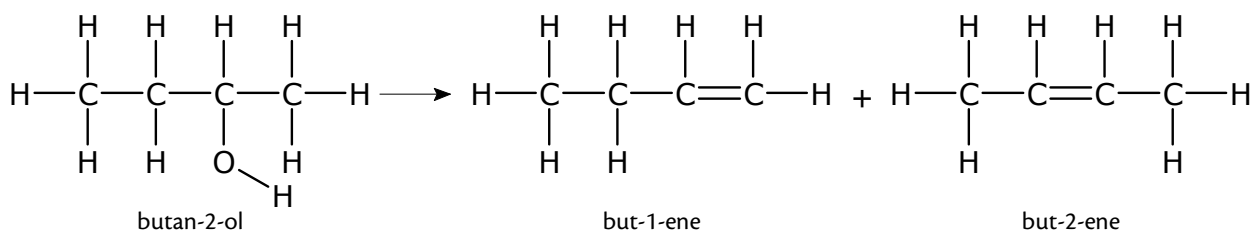
If an alcohol is passed over hot aluminium oxide as catalyst, water is removed from the alcohol and the alkene is formed.



eg



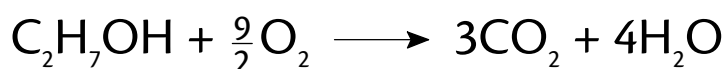
Concentrated sulphuric acid, which has a strong attraction for water, can also be used as the catalyst for this dehydration. Note that with larger alkanols, when dehydration is performed, the -OH and -H from adjacent carbon atoms are removed to form the double bond. This can sometimes result in different isomers being possible:



## Oxidation

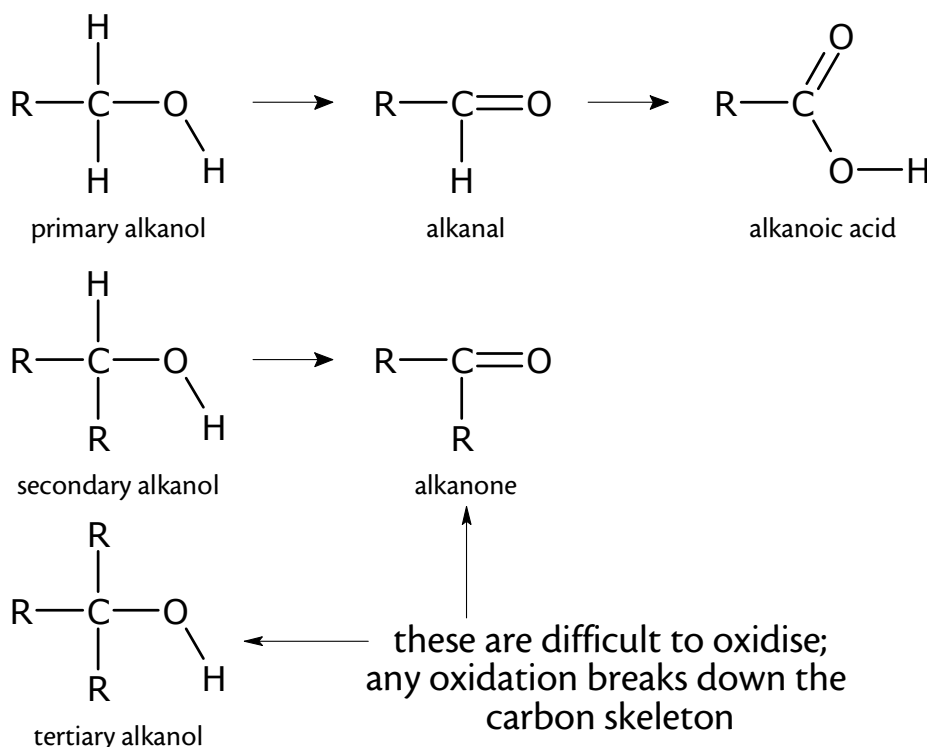
### a) Complete oxidation

Combustion Alcohols burn and in excess oxygen the products are carbon dioxide and water.



### b) Partial Oxidation

The products of the oxidation of alcohols depend on whether the alcohol is primary, secondary or tertiary. The equations below show this:

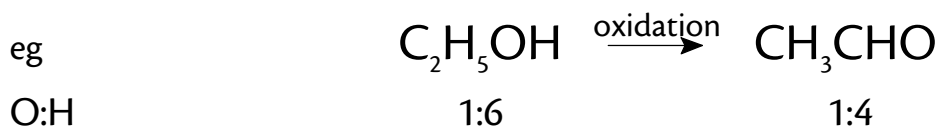


The Oxidising Agent for these reactions can be:

- acidified potassium permanganate solution ( $\text{KMnO}_4$ ). During the reaction the purple permanganate ( $\text{MnO}_4^-$ ) ion is reduced to colourless  $\text{Mn}^{2+}$  ions.
- acidified potassium dichromate solution ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). During the reaction the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) is reduced to green  $\text{Cr}^{3+}$  ions
- copper (II) oxide and heat. The black oxide is reduced to reddish copper metal during the reaction.

## Oxidation and reduction – a new definition

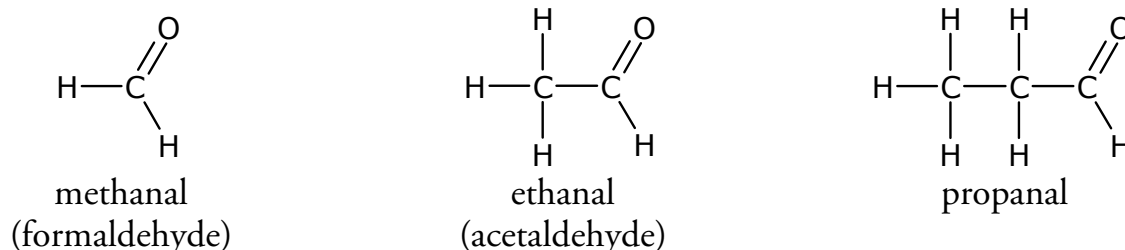
In carbon chemistry, oxidation is defined as increasing the O:H ratio and reduction is defined as decreasing the O:H ratio. These are different definitions from those met previously and only apply in carbon chemistry.



Oxidation of ethanol to ethanal has increased the O:H ratio. Ethanal can also be reduced back to ethanol and this would be a decrease of the ratio.

## Alkanals

Alkanals have the functional group -CHO. Clearly this group must be at the end of a chain. They are named by replacing the -ol of the alkanol with -al. The first three members are:



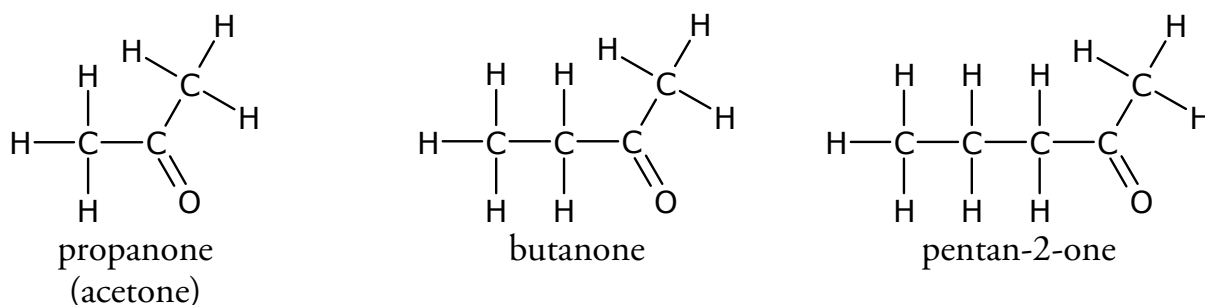
Note that the C=O group is called the carbonyl group. Any compound containing the -CHO group is called an aldehyde. The alkanals which are derivatives of alkanes are a sub-group of aldehydes.

### Preparation and uses

Alkanals are made by oxidising primary alkanols. The main industrial use is in the making of thermosetting plastics eg phenol/methanal resins and urea/methanal resins (more on this later). Methanal (formaldehyde) is also used in the preservation of bodies of dead animals.

## Alkanones

Alkanones also have the functional group C=O, the carbonyl group. This group must be within a chain. Names are formed by replacing the -ol of the alkanol with -one. A number usually has to be used to indicate the position of the carbonyl group. The first three members are:



Alkanones are a subset of the more general ketones.

**Preparation**

Alkanones are made by oxidising secondary alkanols.

**Uses of ketones**

Mainly as solvents for varnishes and plastics.

eg Propanone is the solvent in nail varnish remover.

**Distinguishing aldehydes and ketones**

In many reactions, aldehydes and ketones behave similarly because they both contain the carbonyl group, C=O. However aldehydes can be oxidised to carboxylic acids whereas ketones cannot be oxidised. This provides a method of distinguishing them. The table below lists the oxidising agents that can be used and the results of the tests:

Oxidising Agent	Observation and reason
Benedict's or Fehling's solution	Blue solution $\longrightarrow$ Orange-red precipitate Cu <sup>2+</sup> ions reduced to Cu <sub>2</sub> O ie copper (I) oxide
Tollen's reagent ie AgNO <sub>3(aq)</sub> + NH <sub>3(aq)</sub>	A 'silver mirror' is formed Ag <sup>+</sup> ions reduced to Ag atoms
Acidified potassium dichromate solution	Orange solution $\longrightarrow$ Blue-green solution Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> reduced to Cr <sup>3+</sup>

Note that glucose, fructose etc. give positive tests with Benedicts solution because they contain the aldehyde group -CHO.

**Alkanoic acids**

Compounds whose molecules contain the carboxyl functional group (-COOH) are generally called carboxylic acids. A homologous series based on the parent alkanes exists, and is called the alkanoic acids. The names, molecular and structural formulae of the first few members are given below.

Name	Molecular Formula	Structural Formula
Methanoic acid	HCOOH	
Ethanoic acid	CH <sub>3</sub> COOH	
Propanoic acid	C <sub>2</sub> H <sub>5</sub> COOH	
Butanoic acid	C <sub>3</sub> H <sub>7</sub> COOH	

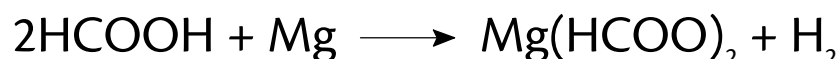
The carboxyl group in alkanolic acids is able to release a hydrogen ion when in water and this gives rise to acid reactions.



The negative ion above is called the ethanoate ion. Generally, the ion produced from alkanolic acids when they ionise is called an alkanoate ion.

These organic acids react in the same way as the other acids that we have met in the past: With MAZIT metals; with metal oxides/hydroxides; with metal carbonates.

eg The reaction of methanoic acid with magnesium



The salt formed in this case is magnesium methanoate.

eg The reaction of ethanoic acid with copper(II) carbonate

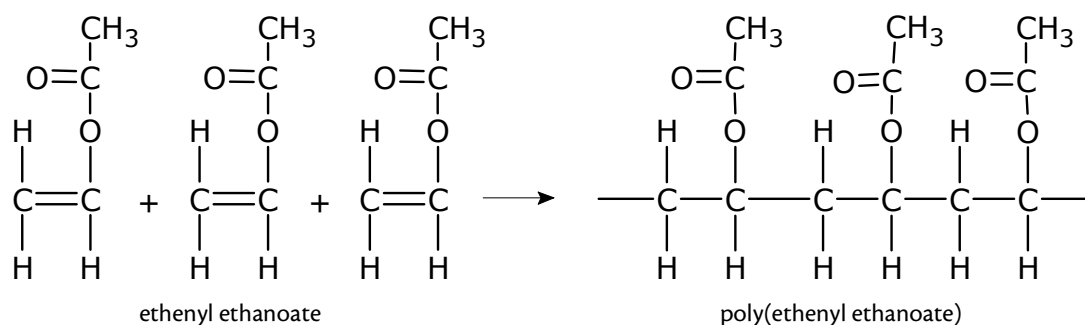


The salt formed in this case is called copper(II) ethanoate.

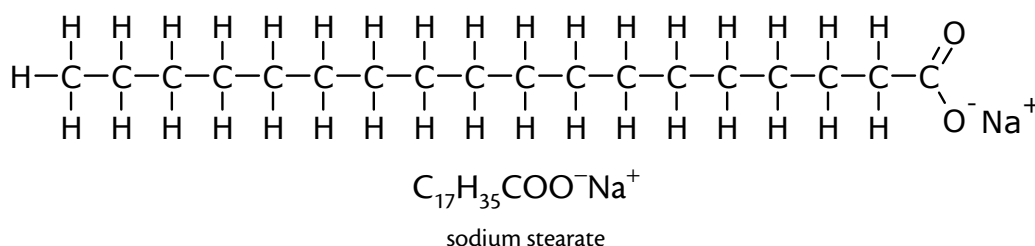
### The Industrial uses of Carboxylic Acids

Ethanoic acid is also known as acetic acid, and when in a fairly dilute solution it is used as vinegar.

Ethanoic acid is used as a feedstock for the production of ethenyl ethanoate (an unsaturated ester) and this can be used to make a polymer poly(ethenyl ethanoate), which is used extensively in paints. This polymer is mentioned later.



Soaps are made from carboxylic acids which have fairly long chains – eg stearic acid can be easily reacted to make sodium stearate, a common compound in soap.

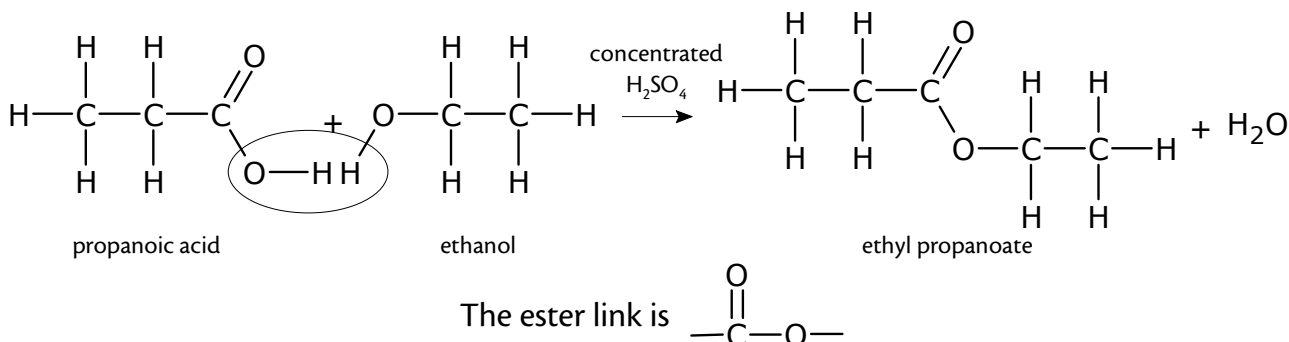


We will also see later that molecules with two carboxyl groups on their molecules (dicarboxylic acids) can be used to make the polymers 'Terylene' and nylon-6,6.

## Ester Formation

There is a PPA on this.

Esters are compounds formed by a condensation reaction between alcohols and carboxylic acids. In a condensation reaction two molecules join and a small molecule (often water) is removed.

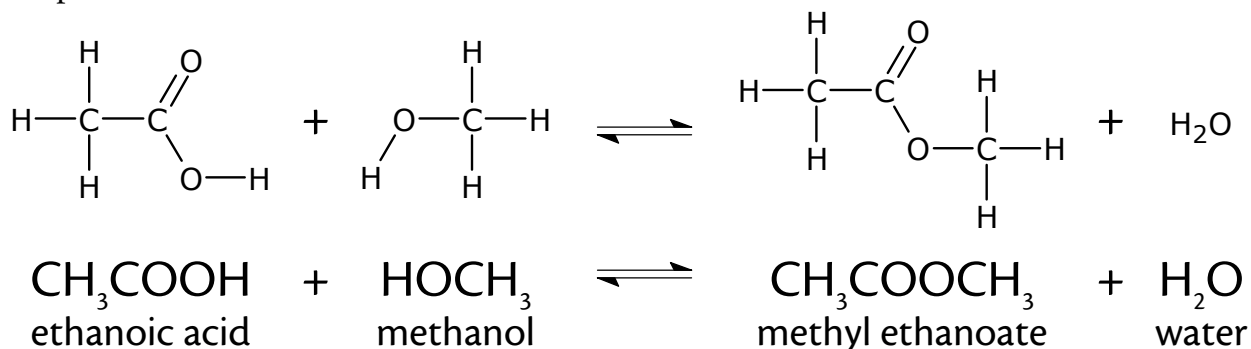


## Naming Esters

The name of an ester indicates the alkanol and acid which go into making it. The first name is derived from the alkanol: -anol becomes -yl. The second name is derived from the alkanonic acid: -oic becomes -oate.

## Reactions of Esters

The main reaction of esters is the reaction given by all compounds formed from condensation reactions – hydrolysis, which is the reverse of condensation. Esters are formed as a result of the loss of water molecule between an alkanol and alkanonic acid. It is possible, under the right conditions, to react the ester with a water molecule. This would reform the original acid and alkanol. So the formation and hydrolysis of an ester is an example of a reversible reaction.

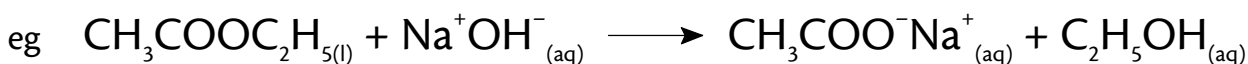


We will study reversible reactions in detail in Unit 3.

The formation of the ester is favoured by removing the other product, water. Concentrated sulphuric acid is a powerful dehydrating agent; this means that it absorbs water. If the alkanol/alkanoic acid mixture is heated with a few drops of concentrated sulphuric acid it is possible to get a good quantity of ester. The ester can be separated from the rest by pouring it into a solution of sodium carbonate – this neutralises the acid and the oily ester layer forms on top.



To reverse the formation of ester (ie hydrolyse it) we need to react the ester with water. However in practice the ester is heated in the apparatus below with either dilute acid or dilute alkali. The ester is said to be heated under “reflux”. When sodium hydroxide solution is used the ester is ‘split up’ into the alkanol and the sodium salt of the acid. The alkanol can be removed by distillation and the alkanolic acid can be regenerated by reacting the sodium alkanoate with dilute hydrochloric acid. The equations for these reactions are also shown below.

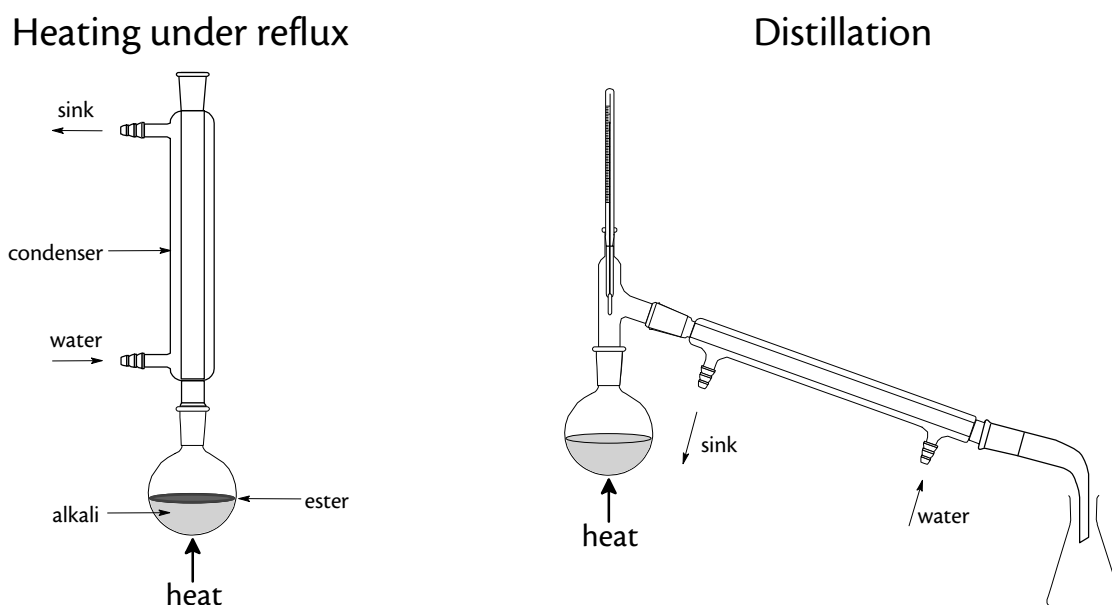


then,



## Apparatus for Hydrolysis

The apparatus usually used is shown:



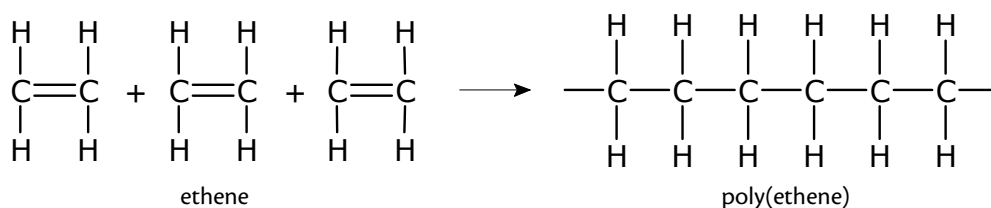
## Properties and Uses of Esters

Esters are generally very pleasant smelling compounds and have a range of uses. Some of the smaller ones are quite volatile and are used as solvents in adhesives, inks and paints – pentyl ethanoate is used in nail varnish for example. Many esters are used as flavourings and in perfumes. Natural fruit flavours contain subtle blends of some of the esters in the table below:

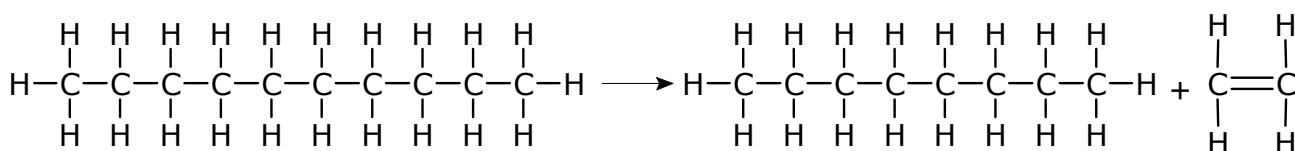
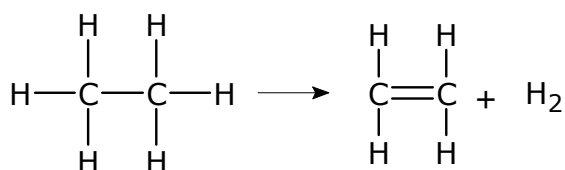
Name	Shortened Structural Formula	Odour/Flavour
Pentyl Ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	Banana
Octyl Ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_7\text{CH}_3$	Orange
Methyl Butanoate	$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_3$	Pineapple
3-Methylbutyl Butanoate	$\text{CH}_3(\text{CH}_2)_2\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	Apple



## Addition Polymerisation

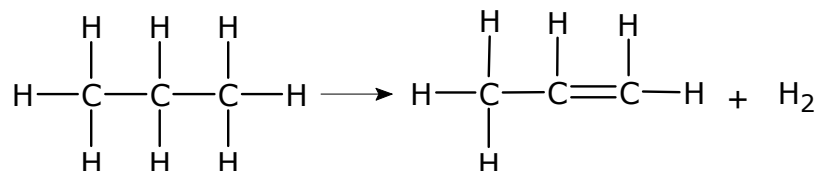


The above example used ethene, which is obtained by cracking of the ethane from the gas fraction from crude oil or by cracking the naphtha fraction. (Note that ethene is a feedstock of very major importance in the chemicals industry). Equations to show the cracking process of ethane and naphtha are shown:

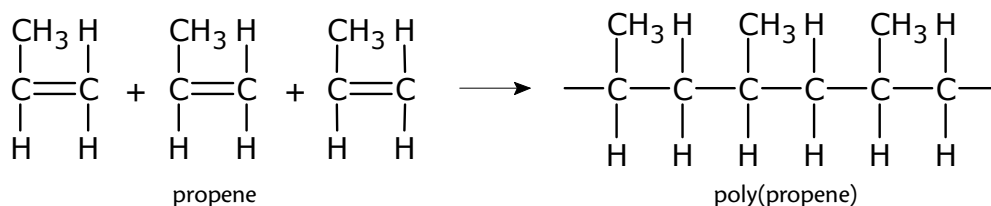


A similar polymerisation can be done using propene, which is obtained from the cracking of propane, or again from the cracking of the naphtha fraction.

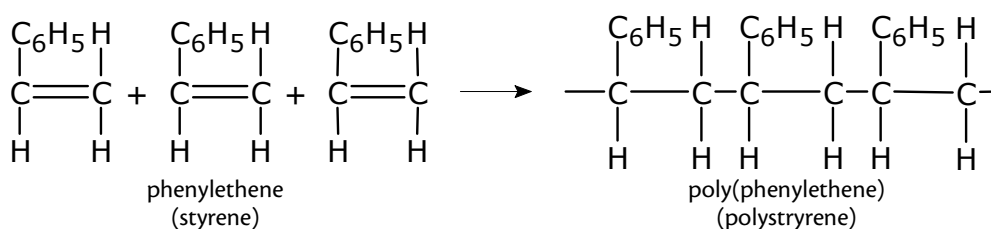
eg cracking propane produces propene and hydrogen:



The polymerisation reaction of propene is shown below. (Note that it is important to draw the propene structure in such a way that the C=C bonds can 'get at' each other edge to edge.)

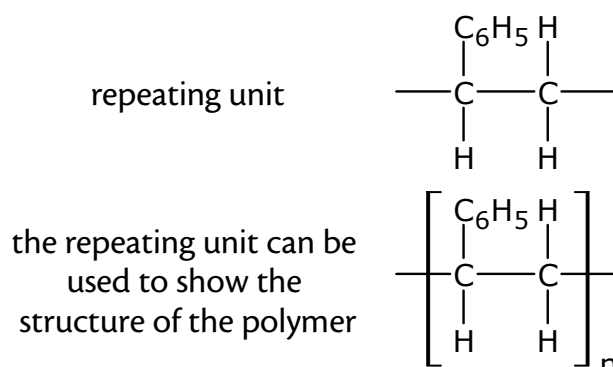


Phenylethene (styrene) has already been mentioned as important in the making of poly(phenylethene), or polystyrene as it is more commonly known, and the reaction scheme is also shown below:



Please refer to your Standard Grade notes (topic 6) for other examples.

All of these polymerisations involve using the addition reaction of the C=C double bond thousands of times. Another feature worth pointing out in the examples is that the small molecules (monomers) were of the same type, and this allows us to identify a small 'repeating unit' which can be enclosed in square brackets to denote the formula of the polymer:

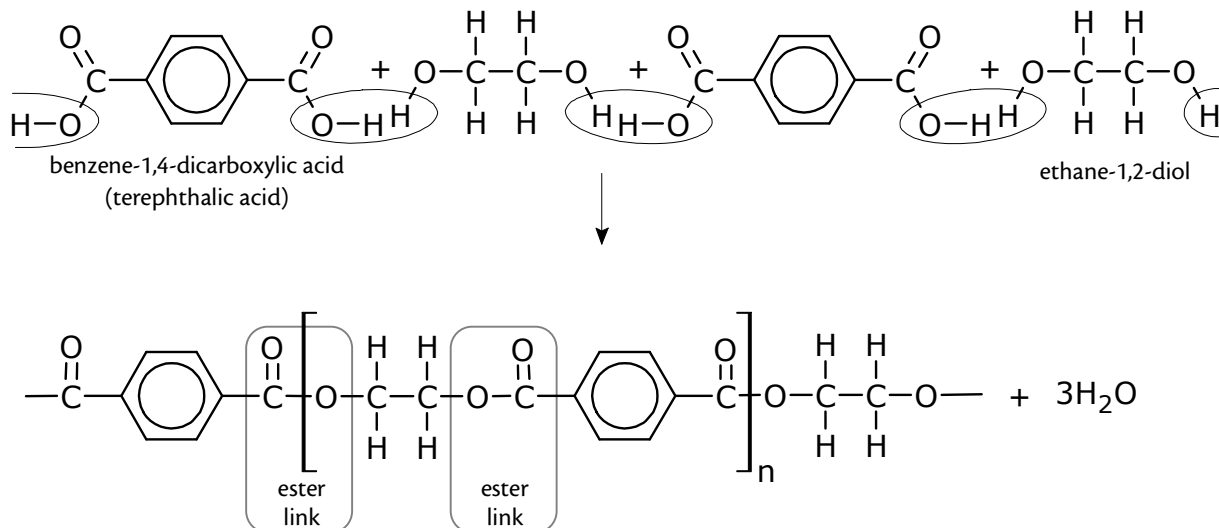


## Condensation Polymerisation

The other reaction which can be used to make polymers involves condensation; where a small molecule (often water) is lost from between the two joining molecules. We have already seen an example of this in making esters.

### Polyester Formation

If we use a small molecule with two acid groups and another small molecule with two hydroxyl groups it is possible to make thousands of ester links and form long chains.

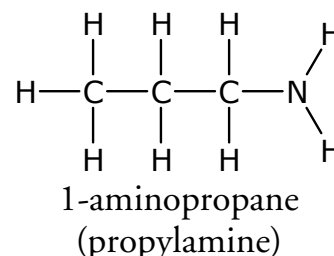
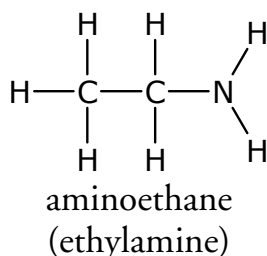
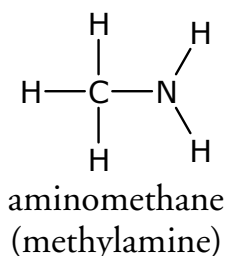


This polymer (terylene) is a linear polymer (a fibre). The fibres can be spun together to give a strong, flexible product used in clothing. This polymer can also be used in making photographic films and recording tapes.

It is also possible to get resins made from polyesters. Here, the di-carboxylic acid has C=C double bonds (ie is unsaturated) so the fibres can 'cross link', giving a three dimensional network. These resins, unlike the polyester fibres, are thermosetting. They are commonly used in conjunction with glass fibre to form glass reinforced plastic (GRP), which is light, inexpensive and hard wearing. It is used in boats, car bodies and in building.

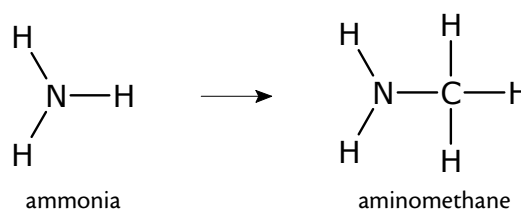
Another example of condensation polymerisation can be seen with molecules having an amine (or amino) functional group. This group has not been met before so we need to introduce it here. Molecules with this type of group give rise to a new homologous series called the **amines**.

The first few members with their names are given:



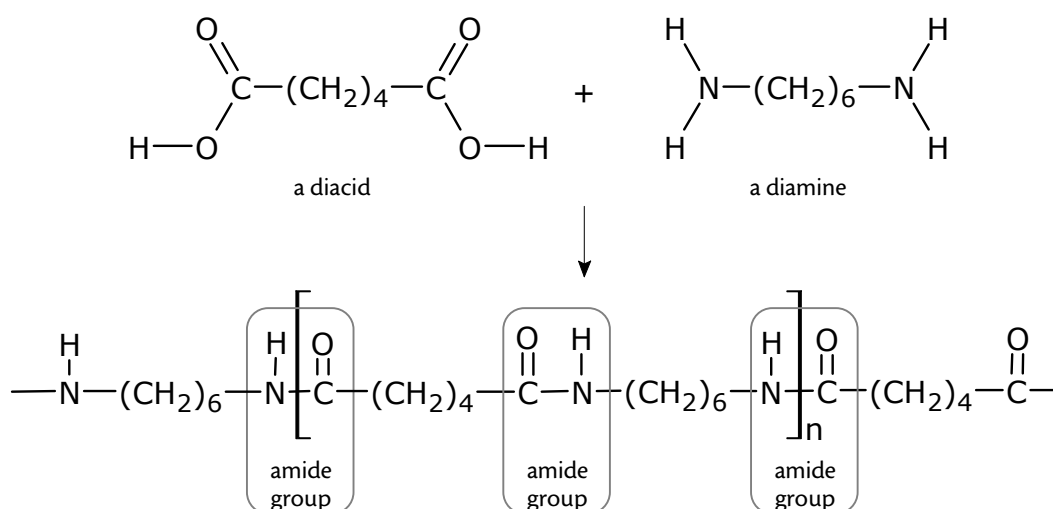
Amines can be thought of as arising from ammonia by replacing a hydrogen with an alkyl group.

The similarity between amines and ammonia is shown by their reaction with copper (II) sulphate solution. Both amines and ammonia give a deep blue solution.



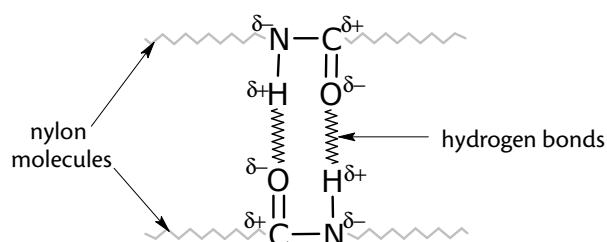
### Polyamide Formation

In this, a di-amine condenses with a di-acid.



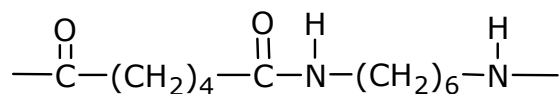
(Note: This is called 'nylon-6,6' because each monomer has six carbon atoms.)

The link formed is an amide link, hence the name polyamide. The best known polyamide has the trade name Nylon. Again, since condensation is the 'joining' reaction, polyamides are classed as condensation polymers. Note that nylon is an extremely important engineering polymer with great strength for its weight. This strength for such a light material is due to strong hydrogen bonding between the chains and along the length of the polymer chains. The  $\text{O}^{\delta-}$  of the polar  $\text{C}=\text{O}$  groups are strongly attracted to the  $\text{H}^{\delta+}$  of the polar  $\text{N}-\text{H}$  groups on adjacent chains.

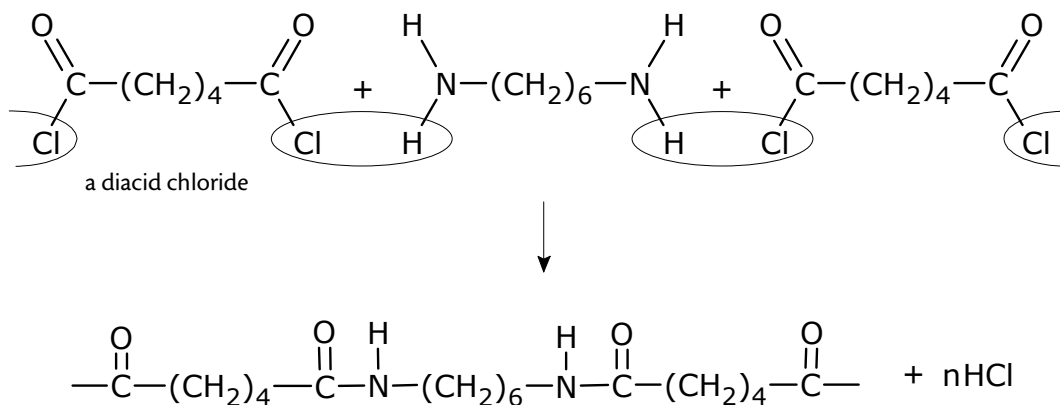


When we are dealing with condensation polymers, the monomers must both have two functional groups. Also, the 'repeating unit' is not as simple as with the addition polymers. The repeating unit must indicate the structures of both the monomers used.

eg The repeating unit for nylon 6,6:



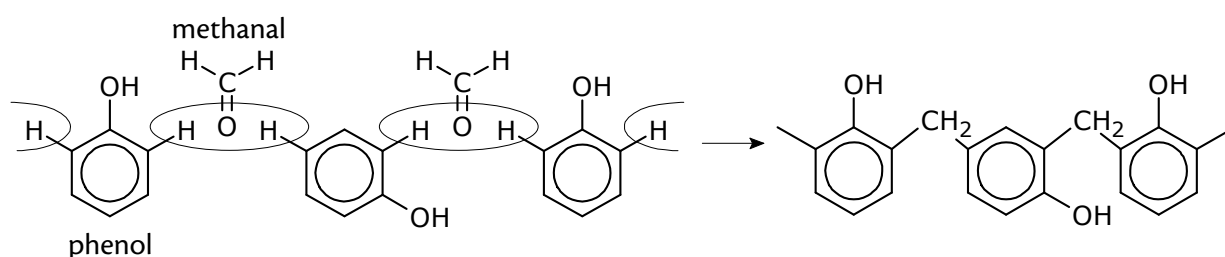
Nylon can also be made using a di-acid chloride instead of a di-acid:



## Thermosetting Plastics

The polymers we have met so far have been thermoplastic.

Methanal and phenol react together to form bakelite, a thermosetting plastic. The reaction is another example of condensation polymerisation – as the monomers join, molecules of water are formed as shown:



The reaction goes further than shown. The chains cross link to give a 3-dimensional covalent network. This is a very strong structure which does not soften on heating – in other words a thermosetting plastic.

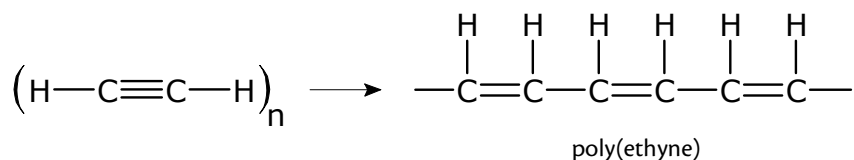
Methanal and urea also react by a condensation polymerisation to produce urea methanal resin, another thermosetting plastic. These plastics are found in pot handles, light fittings, formica work tops and other situations where thermoplastics would soften or melt.

## Recent Polymers

A great deal of research has gone into polymer chemistry and some very interesting new materials have been made as a result, such as water soluble polymers and conducting polymers. Here are some examples of recent developments:

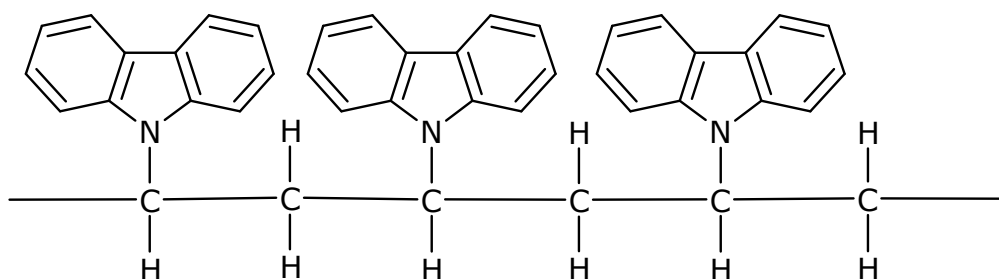
### A Conducting Polymer

If ethyne is used to make an addition polymer, we still have a chain which is very unsaturated – with alternating single and double bonds along the chain – poly(ethyne):



The structure is able to allow ‘delocalised’ electrons to pass along the chain (recall the delocalised electrons in benzene). With the correct treatment, poly(ethyne) can be used to make conducting membranes for high performance loudspeakers.

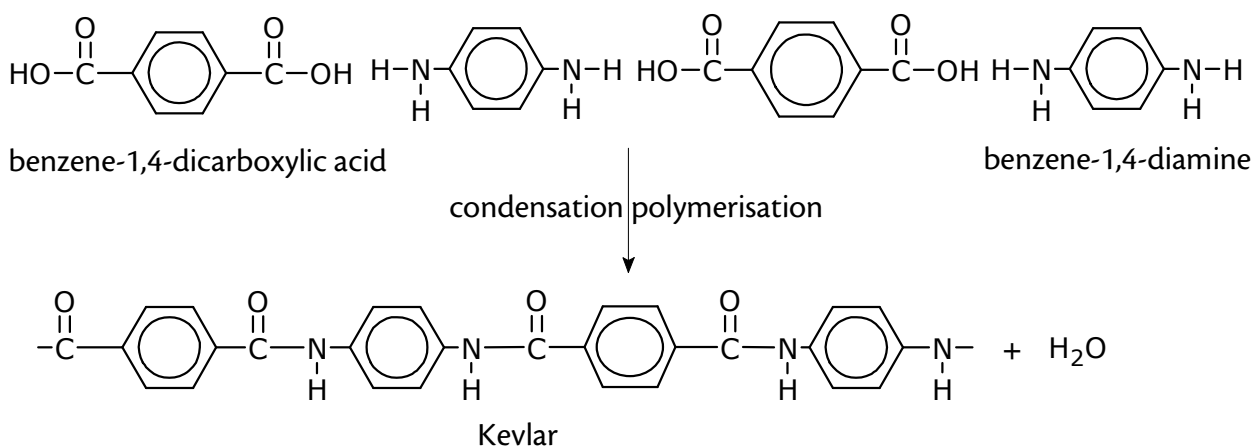
**Poly(vinyl carbazole)** has the special property of photoconductivity – it can conduct better when light is shone on it. This is used in photocopying machines. It is an addition polymer with the following structure:



Try drawing the repeating unit and the monomer structure for this.

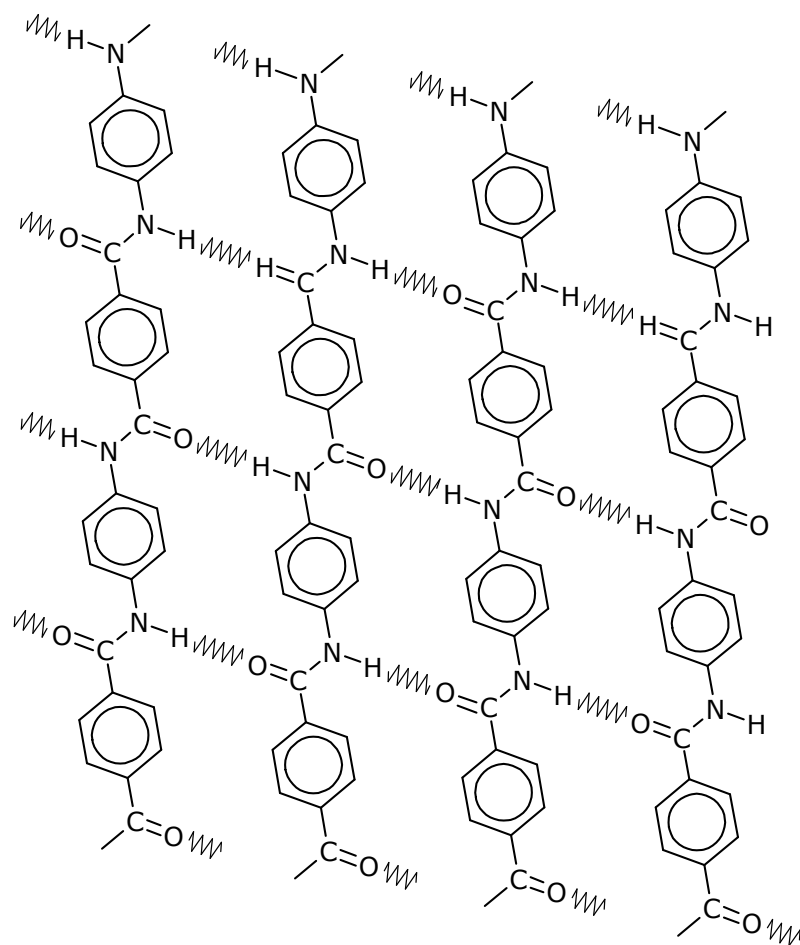
### A Bulletproof Polymer

The following two structures are able to make a very special polyamide – Kevlar



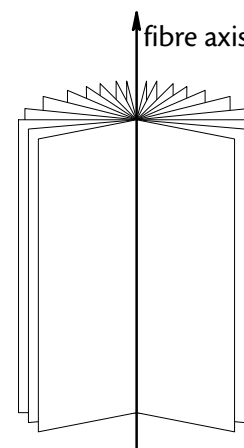
This polymer is special in that the chains of alternating aromatic rings align themselves in a flat formation which makes it possible to hydrogen bond in a very regular and closely packed formation as shown:

## Hydrogen-bonded molecular sheet



~~~~~ represents hydrogen bonding

## Stacked sheets



The sheets of molecules can then pack around the axis along their length so we have a material which has great strength due to the extensive bonding. Kevlar is used to make very strong ropes and cords for car tyres – it is much stronger than steel yet considerably lighter. When stiffened, it can be used to make wings on aircraft and it is also used to make bulletproof vests, safety jackets for fencers, and body protectors for motorcyclists and horse riders.

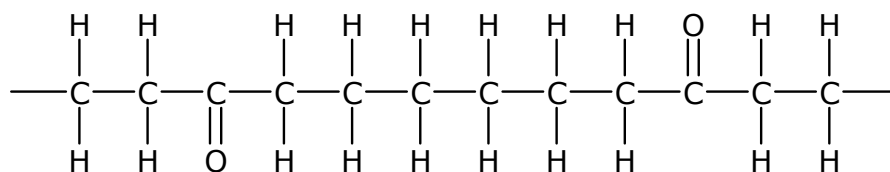
## Degradable Polymers

The polymers already mentioned are all very stable and pose a huge environmental problem – they do not break down and are therefore a big disposal problem. If simply dumped in landfill sites in large quantities, they will just stay there without breaking down. Natural materials like wood and paper do break down and become part of the natural processes again. A great deal of research has been necessary to try to combat this increasing problem, including methods of recycling plastics and also the production of 'degradable polymers', which do break down and are less likely to cause environmental damage.



### A Photodegradable Polymer

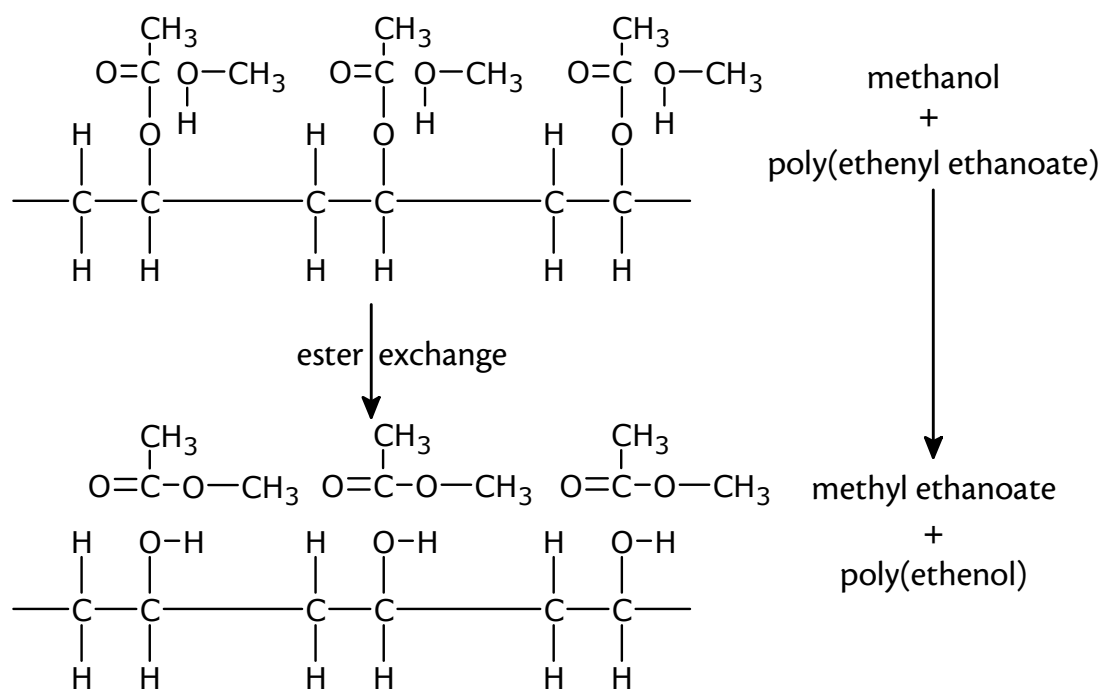
If poly(ethene) is made in such a way that carbonyl groups can be introduced into the chain, we have a polymer which can break down on exposure to light.



The presence of the carbonyl groups in these chains allows the absorption of strong sunlight. The energy trapped by this is able to be used to break carbon-carbon bonds near the carbonyl group and this eventually breaks the molecules into smaller chunks which can 'biodegrade'. This type of material is already being used as the can rings around six pack drinks and is likely to become more used in carrier bags, packaging material and as protective films around young plants.

### A Water Soluble Polymer

The polymer poly(ethenyl ethanoate) was mentioned earlier. This polymer can be reacted with methanol in a reaction called 'ester exchange', in which the ester groups along the chain are replaced as can be seen in the reaction scheme:



The poly(ethenol) produced from this is water soluble if the number of -OH groups along the chain is controlled. The following table shows how the solubility is altered by controlling the number of ester groups which are exchanged:

| % -OH Groups | Solubility in water  |
|--------------|----------------------|
| 100-99       | insoluble            |
| 99-97        | soluble (hot water)  |
| 96-90        | soluble (warm water) |

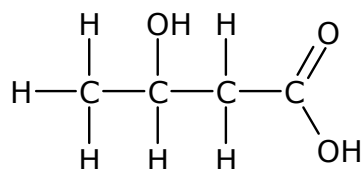
Pure poly(ethenol) is insoluble in water because the -OH groups are involved in a great deal of internal hydrogen bonding so water is unable to interfere with the structure. If,

however, the internal hydrogen bonding is broken up by having the ester groups at regular sites along the chain, then water is able to break in to the structure and dissolve it.

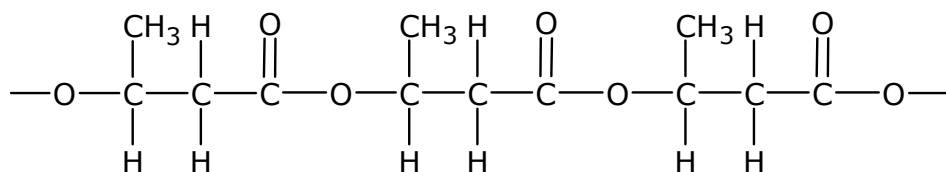
This polymer is used to make laundry bags for hospitals – the laundry is put in to the washing machines enclosed in the bags and the bag quickly dissolves away, exposing the laundry to the washing liquid. It is also used for soluble stitches in surgery, and to make protective coatings for cars, which can be hosed off.

### Biodegradable polymers (biopol)

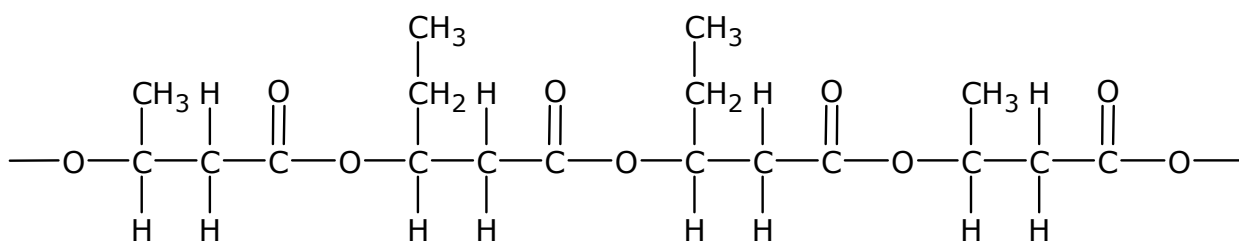
Biodegradable polymers are a group of natural condensation polymers which can be broken down by micro-organisms in the environment. The trade name biopol is one such polymer. The structure is based on the polymerisation of 3-hydroxybutanoic acid to make poly(3-hydroxybutanoate) or PHB for short. This polymer was in fact discovered about 70 years ago when it was discovered that certain bacteria actually synthesise it and use it as an energy store. It is made commercially by using bacteria in a fermenting mixture. The basic monomer has the following structure:



The linking of the monomers is through the carboxyl group and the hydroxyl group to make ester linkages so it is a polyester.



A modified form of this is actually made to suit the commercial requirements, where propanoic acid is added to the fermenting mixture and some side reactions result in monomers which polymerise to make the following structure:



It was hoped that Biopol could be used in medical fields (surgical stitches and for holding broken bones while they healed) as well as a few other applications. However, high production costs have halted the commercial production in the meantime.