UNIT 3

ORGANIC MOLECULES

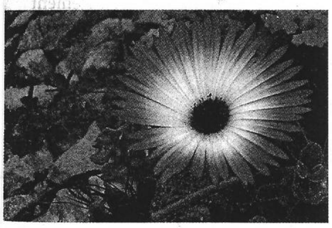
KEY CONCEPTS
- rmulae
- nctional groups
- PAC names
- merism
- ydrocarbons
- mologous series
- ubstitution
- ddition
- limination

When you have completed this unit, you should be able to:
- understand the different ways of writing formulae
- recognise functional groups in organic compounds
- use the IUPAC system for naming organic compounds
- identify and name structural isomers
- know, identify and name all the homologous series of organic compounds
- identify and write balanced equations for the reactions of organic compounds.

Organic chemistry is a specific field of study within the subject of chemistry. It involves the structure, properties, composition, reactions and preparations of the chemical compounds of carbon and hydrogen, which may also contain other elements, such as nitrogen, oxygen, halogens, phosphorus and sulphur.

Carbon has an atomic number of 6 and is a non-metal in group IV of the periodic table. It has a valency of four and forms covalent bonds. Carbon is a unique element because its atoms combine directly with one another through single, double or triple bonds to form long molecular chains and rings, which may also contain other elements. The straight chains and rings can again combine with one another to form even more complex structures.

The unique properties of multicarbon compounds result in an enormous variety of organic compounds and lead to a wide range of applications. They form the basis or are important constituents of many industries (paints, plastics, food, explosives, drugs, petrochemicals, and many others). Organic compounds also form the basis of all life processes.

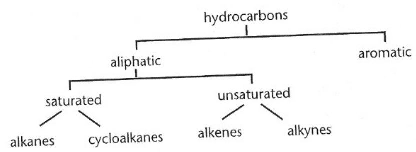


The chemistry of the flower differs from the surrounding soil because it is based on the elements carbon and hydrogen.

In the 1700s, chemists thought that organic molecules contained a 'vital force' which was part of living organisms and that these chemicals could not be reproduced in laboratories. In about 1816, Michel Chevreul started his study of soaps made from various fats and an alkali. He separated the different acids that produced the soap and recognised that these were all individual compounds. He demonstrated that it was possible to make chemical changes in fats and produce new organic compounds without using life processes.

The event that completely destroyed the myth of 'vitalism' occurred in 1828 when Friedrich Wöhler first manufactured urea, a constituent of urine. In his report he stated that he made urea entirely without the assistance of a kidney. Although the vitalistic theory is no longer accepted, organic chemistry is, for practical reasons, still studied as a separate section of chemistry.

Organic compounds are generally classified as **aliphatic** or **aromatic**. Aromatic compounds contain one or more rings consisting of five or six carbon atoms. When the rings contain six carbons they are known as arenes or benzene rings. They have distinctive, usually pleasant smells. All other organic compounds are aliphatic. When carbon compounds contain only carbon and hydrogen atoms, they are known as **hydrocarbons**. We classify hydrocarbons as follows:



When carbon compounds contain other elements as well, a range of organic compound families are formed. A summary of these families of compounds can be found on pages 212–213.

Types of formulae

Chemists use different types of formulae to indicate organic molecules. We will describe them here.

Molecular formulae

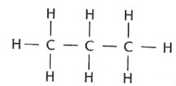
A molecular formula shows the number of atoms of each element present in the molecule, e.g. the molecular formula of propane is C_3H_8.

General formulae

A group of similar organic compounds, known as a homologous series, has a general formula. All members of a specific homologous series have the same general formula. Propane belongs to the homologous series called the alkanes and has the general formula C_nH_{2n+2} where n is the number of carbon atoms present.

Structural formulae

The structural formula shows all the atoms and bonds in a molecule. The structural formula of propane is:



Three carbon atoms form a short chain. The carbon atoms at the ends are bonded to three hydrogen atoms each and the carbon in the middle is bonded to two hydrogen atoms. Remember, each carbon atom always makes four bonds.

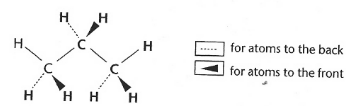
Condensed structural formulae are often used. Here the carbon-hydrogen and carbon-carbon single bonds are not shown, e.g. the condensed structural formula for propane can be written as: $CH_3CH_2CH_3$

Skeletal formulae

This shows the carbon skeleton only. Hydrogen atoms are omitted and the carbon atoms are not labelled. Skeletal formulae are used to show the structures of larger molecules and cyclic hydrocarbons. The skeletal formula of propane is:

Three-dimensional formulae

A three-dimensional formula gives the best representation of the shape of a molecule. Heavy wedged lines show bonds that are directed out of the plane of the page, normal lines are in the same plane as the page, and the dotted lines are directed backwards behind the plane of the page. The three-dimensional formula for propane is:



Functional groups

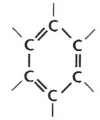
We have already classified elements according to their positions in the periodic table and noticed that elements belonging to the same group have similar properties. The alkali metals are soft, shiny metals that react violently with oxygen to form basic oxides that dissolve well in water to form strong alkaline solutions. Likewise, the members of the halogens and the noble gases also have distinctly similar properties. In the same way, organic molecules can be classified into separate families according to their chemical and physical properties, each with their own characteristic set of reactions. A family of organic molecules is called a **homologous series**.

The distinctive group of atoms attached to a carbon chain that all the members of the homologous series have in common is called the **functional group**. Functional groups are groups of atoms in a molecule with a specific arrangement that are responsible for the characteristic chemical reactions of that molecule. A functional group will undergo the same chemical reaction regardless of the size of the molecule it is part of.

> In a homologous series, all the molecules have the same functional group, but different lengths of carbon chains.

The simplest homologous series is the alkanes. All members of the alkanes contain carbon and hydrogen atoms. The carbon atoms are bonded to each other with single bonds to form a chain that can be straight or branched. The first member of the series is methane, which has only one carbon atom and four hydrogen atoms. The second member is ethane with two carbon and six hydrogen atoms. The functional group of the homologous series is the single bond between the carbon atoms.

The table shows the functional groups that you will learn about in this course:

Homologous series	Structure of functional group	Name of example	Condensed structural formula of example	Name ending
alkanes	—C—C—	ethane	CH_3CH_3	-ane
alkenes	>C=C<	ethene	$CH_2{=}CH_2$	-ene
alkynes	—C≡C—	ethyne	$CH{\equiv}CH$	-yne
haloalkanes	—X where X is F, Cl, Br or I	chloromethane	CH_3Cl	
alcohols	—O—H	ethanol	CH_3CH_2OH	-ol
ethers	—C—O—C—	dimethyl ether	CH_3OCH_3	-ether
ketones	—C—C(=O)—C—	propanone	CH_3COCH_3	-one
aldehydes	—C—C(=O)—H	ethanal	CH_3CHO	-al
carboxylic acids	—C—C(=O)—O—H	ethanoic acid	CH_3COOH	-oic acid
esters	—C—C(=O)—O—C—	ethyl ethanoate	$CH_3COOC_2H_5$	-oate
amines	—N(H)—H	methylamine	CH_3NH_2	-amine
amides	—C—C(=O)—N—	ethanamide	CH_3CONH_2	-amide
arenes (aromatic)		benzene	C_6H_6	

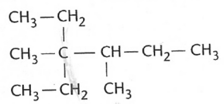
Naming organic compounds

Organic molecules can be very complicated and varied and it is important to use a consistent and systematic way to name these compounds. We use the IUPAC system – pronounced 'eye you pack' – to name organic compounds. (IUPAC stands for International Union of Pure and Applied Chemistry.) The IUPAC system uses three parts to name a compound: the parent, prefix and suffix. The name describes precisely which elements and groups make up a compound and how they are arranged in the compound. The parent name specifies the size of the molecule by stating the number of carbon atoms in the longest chain; the suffix identifies the family or homologous series it belongs to; and the prefix lists all the functional groups attached to the parent and their positions.

prefix	parent	suffix
where and what functional groups	number of carbon atoms	homologous series

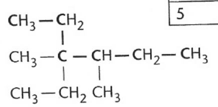
Basic rules for naming hydrocarbons

Note: To explain the rules we will use the following example:

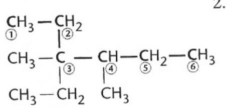


1. Find the longest continuous carbon chain in the molecule and use the name of that chain as the parent name. The following prefixes are used to show the number of carbon atoms in the chain:

Number of carbon atoms	Parent name	Number of carbon atoms	Parent name
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-



The example has six C-atoms and is a hex-.



2. Now number the parent chain beginning at the end closest to the first branch point. The total of the numbers of the branches must be the smallest possible. In the example we number the parent carbons in such a way that the branches are attached to C3, C3 and C4, and not to C3, C4 and C4.

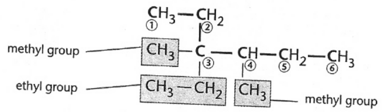
3. Identify and number the substituents.

Alkyl groups

If a hydrogen atom is removed from an alkane, the partial structure that remains is called an alkyl group. They are named by replacing the -ane ending of the parent alkane with an -yl ending. For example, CH_3– becomes a methyl group and CH_3CH_2– an ethyl group. Propane can give rise to two alkyl groups: propyl ($CH_3CH_2CH_2$–) and isopropyl ($CH_3\overset{|}{C}HCH_3$), in which the attachment is to the middle carbon atom. The position of these alkyl groups is indicated by the number of the carbon atom it is attached to.

Alkyl groups attached to stem:

Group	Name	Group	Name
$-CH_3$	methyl	$-CH_2CH_2CH_3$	propyl
$-CH_2CH_3$	ethyl	$CH_3\overset{|}{C}HCH_3$	isopropyl

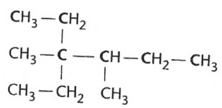


The example contains two methyl groups and one ethyl group.

Other substituents

One or more halides can also attach to a parent chain. Then we use the prefixes fluoro-, chloro-, bromo- or iodo-.

4. If more than one identical functional group is attached to the parent the name is prefixed by di- (two), tri- (three), tetra- (four), and so on. For example, 2,2,3-trimethyl- indicates that there are three methyl groups attached to the stem, two on the second carbon and one on the third carbon, and 1,2-dichloro- indicates that a chlorine atom is attached to carbon one and another to carbon two. If two or more different side chains or substituents are present, refer to them in alphabetical order. Do not use the prefixes for alphabetisation.



Full name: 3-ethyl-3,4-dimethylhexane

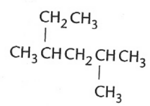
5. For hydrocarbons that contain double bonds (alkene family) or triple bonds (alkyne family), we use the suffixes -ene and -yne respectively. The chain containing the double or triple bond is always the parent chain. Begin numbering at the end closest to the double/triple bond. The position of the double or triple bond is indicated by the lower number of the two carbon atoms involved. For example:

$CH_3CH{=}CHCH_3$ (2-butene) $\quad$ $CH{\equiv}CCH_2CH_3$ (1-butyne)

6. The names of the members of the other homologous series and the suffixes are indicated in the table on pages 212–213.

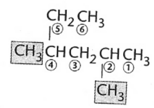
Example 1

Give the IUPAC name for the compound on the right:



Solution:

The molecule has a chain of six carbons with two methyl groups attached to it. Numbering from the end closest to the first methyl group gives 2,4-dimethylhexane.



Homologous series

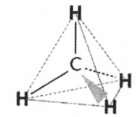
We will now systematically look at some of the most important homologous series of organic compounds.

Hydrocarbons: alkanes

Alkanes are non-polar molecules containing only carbon and hydrogen atoms. They are hydrocarbons with single bonds between the carbon atoms. No further atoms can be added to the molecules of these compounds, making them **saturated** hydrocarbons. This makes the alkanes quite unreactive. Although the chemical properties of all the alkanes are very similar, their physical properties vary. The table shows the melting points and boiling points of some of the alkanes. As the length of the molecules increases, the opportunities for Van der Waals forces to form weak bonds between the molecules also increase. The effect is that the boiling points increase with molecular mass.

Alkane	Molecular formula	Melting point (°C)	Boiling point (°C)	Phase at room temperature
methane	CH_4	−183	−162	gas
ethane	C_2H_6	−183	−89	gas
propane	C_3H_8	−190	−42	gas
butane	C_4H_{10}	−138	0	gas
pentane	C_5H_{12}	−130	36	liquid
hexane	C_6H_{14}	−95	69	liquid
heptane	C_7H_{16}	−91	99	liquid
octane	C_8H_{18}	−57	126	liquid
nonane	C_9H_{20}	−54	151	liquid
decane	$C_{10}H_{22}$	−30	174	liquid
undecane	$C_{11}H_{24}$	−25	196	liquid
dodecane	$C_{12}H_{26}$	−10	216	liquid
eicosane	$C_{20}H_{42}$	37	344	solid
triacontane	$C_{30}H_{62}$	66	450	solid

From the table we can see that the simplest alkane is methane. The valence orbitals of one carbon atom hybridise to form four equal sp^3 hybrid orbitals that bond with four hydrogen atoms to form the tetrahedral methane molecule.



The tetrahedral methane molecule

The prefix of the alkane name is derived from the number of carbon atoms it contains, and all the names end in -ane, the suffix for the alkanes. Each consecutive member of the homologous series has an added $-CH_2-$ group. Another way of writing the long-chained alkanes is by showing the number of $-CH_2-$ groups, e.g. decane can be written as $CH_3(CH_2)_8CH_3$.

DID YOU KNOW?

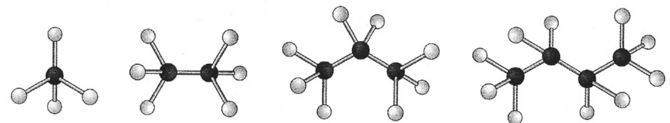
Long before the IUPAC system was devised to name organic compounds, many compounds in common use already had names. Many of these *trivial* or *common* names are still used today. The trivial names of the alkanes use the prefixes *n*-, *iso*- and *neo*-. The three isomers of pentane are then called *n*-pentane for the straight chain, *iso*pentane for the branched isomer with one methyl group, and *neo*pentane for the branched isomer containing two methyl groups.

$CH_3CH_2CH_2CH_2CH_3$ — *n*-pentane

$CH_3CH(CH_3)CH_2CH_3$ — *isopentane*

$CH_3C(CH_3)_2CH_3$ — *neopentane*

All the formulae for these molecules fit the general formula C_nH_{2n+2} where n is the number of carbon atoms present. The first four members of the alkanes are:

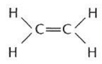

methane ethane propane butane

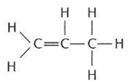
Alkanes
- contain only single bonds
- are saturated hydrocarbons
- have the general formula C_nH_{2n+2}

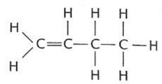
Hydrocarbons: alkenes

As in the case of alkanes, alkenes are hydrocarbons that contain only carbon and hydrogen atoms. However, the alkenes contain at least one double bond between two carbon atoms. This makes them unsaturated, because during a reaction the double bond can break to allow more atoms to be added onto the molecule. Alkenes with only one double bond have the general formula C_nH_{2n}. The simplest alkene must contain two carbon atoms to allow for the C=C double bond, and is called ethene (common name ethylene). Ethene is the most important commercial organic chemical and is used to make the plastic polythene (polyethylene), 1,2-ethanediol (ethylene glycol) and many other products. Propene is polymerised to make polypropene (polypropylene) and other plastics. The table shows the formulae and boiling points of the first four alkenes. Again the boiling points increase with molecular mass.

Alkene	Molecular formula	Boiling point (°C)	Phase at room temperature
ethene	C_2H_2	–104	gas
propene	C_3H_6	–47	gas
butene	C_4H_8	–6	gas
pentene	C_5H_{10}	30	liquid


ethene

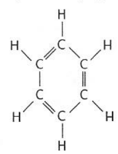

propene


1-butene

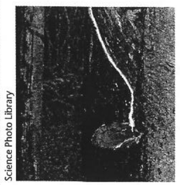
When a molecule contains more than one double bond separated by single bonds, a **conjugated diene** is formed. An example of a diene is 1,3-butadiene. Benzene is a cyclic conjugated molecule.

$CH_2{=}CH{-}CH{=}CH_2$

1,3-butadiene

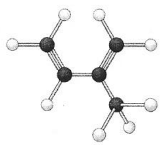

benzene

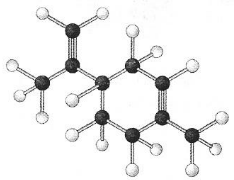
DID YOU KNOW?


Science Photo Library

Rubber trees are tapped for their latex that forms natural rubber. The latex is a polymer of the diene, isoprene.

The natural oil limonene is present in the rind of lemons and oranges. It is derived from two isoprene units.

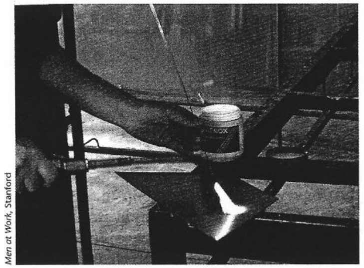

isoprene (2-methyl-1,3-butadiene)


limonene, derived from two isoprene units

Alkenes	• contain at least one C=C double bond between two carbon atoms in the chain • are unsaturated hydrocarbons • have the general formula CnH_2n.

The terms 'saturated' and 'unsaturated' are often used in connection with oils and fats. Saturated fats have single bonds only and tend to have higher melting points that make them harder at room temperature. Oils and soft margarines contain many double bonds between the carbon atoms in the chains and are referred to as polyunsaturated. An increase in the number of double bonds increases the melting point. Many polyunsaturated oils and fatty acids are essential in a healthy diet.

Hydrocarbons: alkynes


Men at Work, Stanford

Welding with an oxyacetylene torch

Alkynes form the third family of hydrocarbons and contain a C≡C triple bond. The simplest member is ethyne, C_2H_2, a highly reactive colourless gas also known by its common name acetylene. The combustion of ethyne in oxygen releases a lot of heat and gives an extremely hot flame (about 3 000 °C). It is used in the oxyacetylene torch to weld metals. Ethyne can be prepared by the reaction between calcium carbide and water.

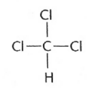
$$CaC_2(s) + 2H_2O(\ell) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

Alkynes are unsaturated and can undergo the same reactions as the alkenes.

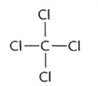
Alkynes	• contain at least one C≡C triple bond between two carbon atoms in the chain • are unsaturated hydrocarbons • have the general formula C_nH_{2n-2}

Alkyl halides

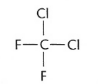
Alkyl halides include haloalkanes and haloalkenes. They contain at least one halogen atom. Simple haloalkanes with one halogen atom attached to the carbon chain have the general formula $C_nH_{2n+1}X$ where X is a halogen atom F, Cl, Br or I. Haloalkanes are generally volatile liquids that do not mix with water.



trichloromethane (chloroform)



tetrachloromethane (carbon tetrachloride)



dichlorodifluoromethane (CFC)

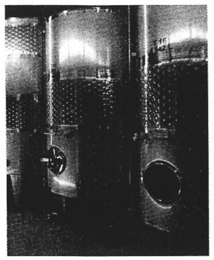
Haloalkenes contain double bonds and can be polymerised to form useful polymers. Poly(chloroethene), also known as PVC and poly(tetrafluoroethene), abbreviated as PTFE, are used in many domestic products. You will learn more about these products in Module 6.

CFCs such as dichlorodifluoromethane and trichlorofluoromethane have been used as refrigerants, aerosol propellants and blowing agents to produce foamed polymers. As we learned in Grade 11, CFCs are blamed for the hole in the ozone layer. They are very stable molecules that can move to the upper layers of the atmosphere to break down ozone molecules. Other well-known haloalkanes include trichloromethane (chloroform), used as an anaesthetic in the late 19th and early 20th centuries, and tetrachloromethane (carbon tetrachloride), used as a dry-cleaning solvent up to the early 1950s.

Haloalkanes
- R—X, where R is an organic group
- contain at least one halogen atom, i.e. F, Cl, Br or I
- have the general formula $C_nH_{2n+1}X$, where X is the halogen.

Alcohols

This homologous series consists mostly of polar molecules that contain one or more hydroxyl (–OH) groups. The general formula for the series is $C_nH_{2n+1}OH$. The simplest member of the group, methanol, contains one carbon atom and is commonly known as methyl alcohol. Methanol is also called wood alcohol because it was once prepared by heating wood in the absence of air. Methanol is toxic to humans, causing blindness in low doses and death in larger amounts.



Fermentation tanks in a wine cellar

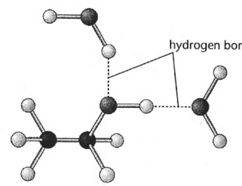
Ethanol has two carbon atoms and is commonly known as ethyl alcohol. It is the product of the fermentation process of fruits and other plant material. Yeast cells are single-cell fungi that can be found everywhere. They ferment the sugar in fruit to gain energy and form carbon dioxide and ethanol as waste products.

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow[\text{in yeast}]{\text{enzymes}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + \underset{\text{carbon dioxide}}{2CO_2(g)}$$

Beer and wine are made through this process. Beer is made from fermenting barley, hops and other ingredients to get distinctive flavours. Wine is made by fermenting grape juice. Beer contains about 4% ethanol and wine between 8% and 14% ethanol by volume.

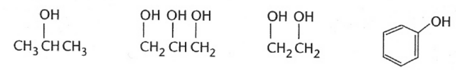
In industry ethanol is made by the hydration of ethene. We will discuss the reactions of ethene in the next section. Ethanol is widely used as a solvent in paints, glues, perfumes, aftershave and many other household products. It is also used as a raw material for making other organic chemicals.

Both methanol and ethanol are miscible with water in all proportions. Hydrogen bonds exist between molecules in water and in methanol or ethanol. The hydrogen bonds between the water molecules and between the alcohol molecules are interchangeable with no significant change in energy. When ethanol is mixed with water, hydrogen bonds form between the water molecules and ethanol molecules. The strong hydrogen bonds result in alcohols having higher melting and boiling points than hydrocarbons of similar size.



Other important alcohols include 2-propanol (isopropyl alcohol or rubbing alcohol), 1,2-ethanediol (ethylene glycol) and 1,2,3-propanetriol (glycerol). Rubbing alcohol is used in the nursing profession to clean skin before injections, ethylene glycol is the main constituent of antifreeze used in motor vehicle engines, and glycerol is used as a moisturising agent in many foods and cosmetics.

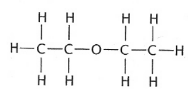
Phenols are compounds that have a hydroxyl group bonded directly to a benzene ring, C_6H_5OH. Phenol is an important industrial chemical.



2-propanol (rubbing alcohol) — 1,2,3-propanetriol (glycerol) — 1,2-ethanediol (ethylene glycol) — phenol

Alcohols
- R—OH where R is an organic group
- contain at least one –OH group
- form hydrogen bonds between molecules
- have the general formula $C_nH_{2n+1}OH$

Ethers



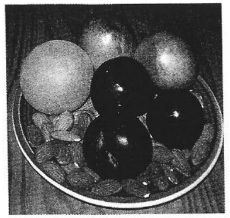
diethyl ether

Ethers are compounds that have two organic groups bonded to the same oxygen atom. Diethyl ether (ethoxyethane), the most common member of the ether family, was used for many years as an anaesthetic in medicine, but has now been replaced by safer non-flammable alternatives.

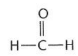
Ethers • R—O—R', where R and R' are the same or different organic groups.

Aldehydes and ketones

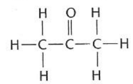
Both these homologous series contain the carbonyl functional group C=O. In an aldehyde, a hydrogen atom is bonded to the carbonyl group (pronounced car-bo-neel). We write it as –CHO. In a ketone, the carbon atom in the carbonyl group is bonded to a carbon on both sides. Aldehyde names end in the suffix -al and ketones end in -one. The simplest aldehyde is methanal, also known as formaldehyde ($H_2C=O$). Formalin is a saturated solution of formaldehyde in water and is used as a biological preservative. The simplest ketone is propanone (acetone). This is a pleasant-smelling liquid used mainly as a solvent for organic compounds and an active ingredient in nail polish removers. Aldehydes and ketones contribute to the distinctive smells of foods and plants. The simplest aromatic aldehyde is benzaldehyde, C_6H_5CHO. It smells like almonds and is used to make almond essence. It also contributes to the flavours of many fruits such as almonds, cherries, apricots, plums and peaches.



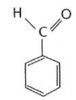
Benzaldehyde contributes to the distinctive flavour of almonds, plums and peaches.



methanal (formaldehyde)



propanone (acetone)



benzaldehyde

Aldehydes • R—C(=O)—H where R is an organic group.

Ketones • R—C(=O)—R' where R and R' are organic groups.

Carboxylic acids

Organic acids belong to the homologous series of the carboxylic acids and all contain the carboxylic acid functional group –COOH. Many natural products are carboxylic acids or are derived from them. The first four members of the series are shown in the table.

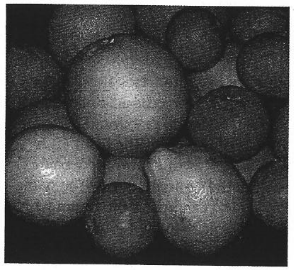
Structural formula	IUPAC name	Common name
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

The first two members of the series are liquids at room temperature. Methanoic acid can be found in stinging nettles and ants, and ethanoic acid is the sour component of vinegar. Butanoic acid gives the unpleasant smell to rancid butter. The acidity of lemons is caused by citric acid. The simplest aromatic carboxylic acid, benzoic acid, is used as a flavouring and preservative in fizzy drinks, such as lemonade.

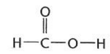
Vegetable oils and animal fats are the esters of carboxylic acids and the alcohol 1,2,3-propanetriol (glycerol). Carboxylic acids that are obtained from oils and fats are called fatty acids. Stearic acid, a component of animal fat, is used in soap-making. Its IUPAC name is octadecanoic acid, $CH_3(CH_2)_{16}COOH$. We will look at soaps in Module 6.

DID YOU KNOW?

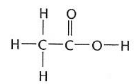
The aroma of oranges contains 30 different esters, 10 carboxylic acids, 34 alcohols, 34 aldehydes and ketones, and 36 hydrocarbons!



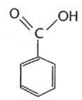
Citrus fruit contains citric acid.



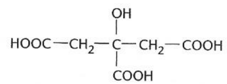
methanoic acid (formic acid)



ethanoic acid (acetic acid)



benzoic acid



citric acid

Organic acids are weak acids with low K_a values and which ionise partially in water. In an aqueous solution of 1 mol dm^{-3} ethanoic acid, only 1% of the molecules will be ionised.

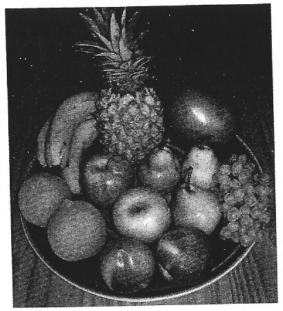
$$\underset{\text{ethanoic acid}}{CH_3COOH(\ell)} + H_2O(\ell) \rightleftharpoons \underset{\text{oxonium or hydronium ion}}{H_3O^+(aq)} + \underset{\text{ethanoate ion}}{CH_3COO^-(aq)}$$

Carboxylic acids
- R—C(=O)—O—H where R is an organic group
- ionise to form weak acids
- have the general formula $C_nH_{2n+1}COOH$

Esters

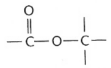
The homologous series of the esters form a group of pleasant smelling compounds. They are largely responsible for the flavours and scents of fruits and flowers. Esters are used as food flavourings and in perfumes, and used as solvents and adhesives. Nail varnish and whiteboard marker pens use ethyl ethanoate as solvent.
The smells of esters:

Ester	Smell or flavour
Ethyl-2-methyl butanoate	apple
3-methylbutyl ethanoate	pear
Butyl butanoate	pineapple
Octyl ethanoate	orange
Methylpropyl methanoate	raspberry
Pentyl butanoate	strawberry

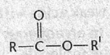


The distinctive flavours of these fruits can be attributed to esters.

The ester functional group is:



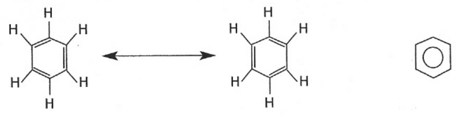
Esters contain the carbonyl functional group C=O and are formed when a carboxylic acid reacts with an alcohol in an esterification reaction. The name of the ester consists of two parts: the first part is derived from the parent alcohol and the second part is derived from the carboxylic acid. The name has the suffix -oate. An example is methanol which reacts with propanoic acid and the ester methyl propanoate is formed.

Esters
-  where R is an H or organic group and R' an organic group
- have pleasant smells
- form from alcohols and carboxylic acids in an esterification reaction.

Aromatic hydrocarbons: the arenes

Arenes contain one or more benzene rings. Benzene is the simplest arene and consists of six carbon atoms connected in a ring containing three double bonds and six hydrogen atoms.

Although Michael Faraday discovered benzene in 1826, it took a further 40 years for chemists to work out its structure. Finally, in 1865, August Kekulé deduced that the benzene molecule could be represented best by a ring structure.



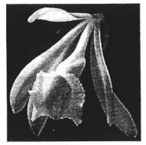
(a) (b) (c)

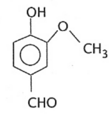
We use structure (c) in structural formulae.

Although benzene has the same empirical formula as ethyne (CH) and a high degree of unsaturation, it is much less reactive and relatively inert. Benzene is a raw material in the manufacture of compounds as varied as medicines, dyes and explosives.

DID YOU KNOW?

Vanilla oil can be extracted from the pods of the vanilla orchid. It contains the chemical vanillin. Today, vanillin can be synthetically produced to make vanilla essence. Vanilla essence is used in cakes, biscuits and icecream.





vanillin

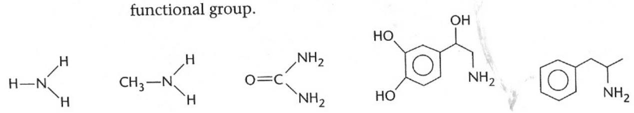
Arenes
- contain a benzene ring
- are more stable than alkenes
- sometimes have aromatic smells.

Nitrogen compounds

Nitrogen-containing compounds are essential to life and a number of functional groups contain nitrogen atoms. We will briefly look at the amines and amides.

Amines

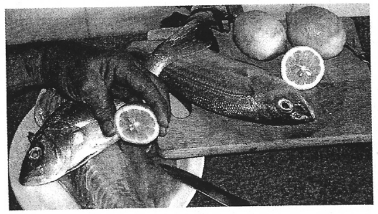
The amino functional group is $-NH_2$. They are organic bases derived from ammonia, and have one or more of the hydrogen atoms replaced by an organic substitute. Amines range from simple molecules to giant biological macromolecules. The smell given off by rotting animal flesh is caused by amines such as putrescine, $NH_2(CH_2)_4NH_2$, and cadaverine, $CH_2(CH_2)_5NH_2$. Urea, present in urine, is also an amine. Other interesting amines include amphetamine, a medicine used as a stimulant to mimic the effect of noradrenaline. Noradrenaline is a neurotransmitter that prepares animals to respond rapidly in danger. Medicines, such as morphine (a painkiller) and tetracycline (an antibiotic), also contain the amino functional group.



ammonia, methylamine, urea, noradrenaline, amphetamine

DID YOU KNOW?

Like ammonia, amines are weak bases. The smell of rotting fish is caused by trimethylamine, $(CH_3)_3N$. When acidic lemon juice is added to fish to mask fish smells, a simple acid-base neutralisation reaction takes place.

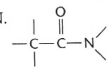


An acid-base reaction between trimethylamine and lemon juice neutralises the fish smell.

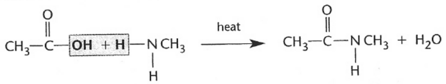
Amines
- $R-NH_2$ where R is an organic group
- are bases.

Amides

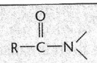
Amides contain the carbonyl group bonded to N. The amide functional group is:



The amide functional group is also called a peptide linkage because it links together amino acids to produce proteins. Without amides there would be no life. Synthetic polymers, such as nylon, also have amide groups. Amides can be prepared by reacting ammonia or an amine with a carboxylic acid.



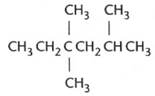
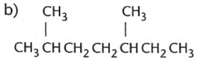
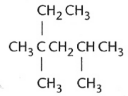
ethanoic acid, methylamine, methylethanamide

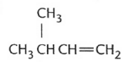
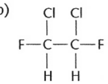
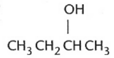
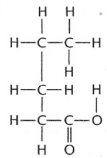
Amides
-  where R is an organic group
- are formed through elimination reaction between an amine and a carboxylic acid.

WORK ALONE

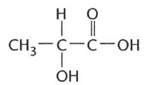
Activity 16: Applying IUPAC rules and functional groups

LO1: AS2, AS3; LO2: AS1, AS2

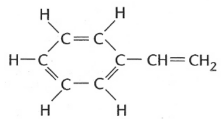
1. a) 
   b) 
   c) 
   i) Which of the molecules shown in the diagram are identical?
   ii) Give the IUPAC names of these molecules.
2. Draw the isomers of C_5H_{10} as condensed structures and give their IUPAC names.
3. What are the IUPAC names of the following molecules?

a) 
b) 
c) 
d) 

4. Draw the full structures of the following compounds:
   a) 2,2,4-trimethylpentane
   b) 2-methyl-2-butene
   c) propyne.
5. List the functional groups in each of the following molecules:



lactic acid found in sour milk



styrene, used to make polystyrene

6. Explain the following terms used in organic chemistry and give examples of each:
   a) general formula
   b) homologous series
   c) functional group.

7. There is a marked difference between the boiling points of the first four members of the alkanes in comparison to the first four members of the alcohols.
   a) Name the types of intermolecular forces between alkane molecules and the forces between alcohol molecules.
   b) Explain the trend in boiling points in the alkanes in terms of these intermolecular forces.
   c) Ethanol is miscible with water, but ethane is not. Explain this difference in terms of intermolecular forces.

Chemical properties of organic substances

Organic compounds can undergo a wide range of chemical reactions. In Grade 11 we studied acid-base and reduction-oxidation (redox) reactions. Organic compounds can also take part in these reactions. For example, ethanoic acid can react with a sodium hydroxide solution in an acid-base reaction to form a salt and water:

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} + \underset{\text{sodium hydroxide}}{NaOH(aq)} \longrightarrow \underset{\text{sodium ethanoate}}{CH_3COONa(aq)} + \underset{\text{water}}{H_2O(\ell)}$$

Examples of redox reactions are ethanol that can be oxidised to ethanoic acid, and the combustion reactions of alkanes. When wine is left exposed to air, it goes 'off' and develops an unpleasant taste. Ethanol in the wine is oxidised to ethanal and finally to ethanoic acid by bacteria in the wine:

$$\underset{\text{ethanol}}{CH_3CH_2OH(aq)} + \underset{\text{oxygen}}{O_2(g)} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + \underset{\text{water}}{H_2O(\ell)}$$

The combustion reactions of organic compounds are used to provide heat, drive motor vehicle engines and drive turbines to generate electricity. Organic compounds such as the alkanes, alkenes, alkynes and alcohols burn in an excess of air to form carbon dioxide, water vapour and large amounts of heat:

$$\underset{\text{ethane}}{2C_2H_6(g)} + \underset{\text{oxygen}}{7O_2(g)} \longrightarrow \underset{\text{carbon dioxide}}{4CO_2(g)} + \underset{\text{water}}{6H_2O(g)} + \text{heat}$$

There are several other types of reaction, and we will look at substitution, addition and elimination. Unit 4 of this module deals with polymerisation reactions. They are classified as addition or condensation reactions. To understand condensation polymerisation we also need to have a brief look at esterification reactions. These are substitution, addition, elimination and esterification.

Substitution

Substitution involves replacing an atom or group of atoms by another atom or group of atoms. Two families that can undergo substitution are the alkanes and haloalkanes.

Alkanes are regarded as inert compounds because they consist of non-polar molecules and do not react with the polar molecules in water, acids, alkalis and many oxidising and reducing agents. However, they can react with non-polar molecules, e.g. the halogens, in the presence of ultraviolet light in a substitution reaction. Halogen atoms then substitute hydrogen atoms on the alkane to form a haloalkane. When methane is mixed with chlorine and left in sunlight, chloromethane and hydrogen chloride is formed. This is a photochemical reaction because sunlight is required.

$$\underset{\text{methane}}{CH_4(g)} + \underset{\text{chlorine gas}}{Cl_2(g)} \xrightarrow{\text{sunlight}} \underset{\text{chloromethane}}{CH_3Cl(g)} + \underset{\text{hydrogen chloride gas}}{HCl(g)}$$

By controlling the relative amounts of reactants and reaction time, more substitutions are possible to form dichloromethane, trichloromethane and tetrachloromethane.

DID YOU KNOW?

The substitution reaction mechanism involves several steps. During the *initiation step* the chlorine molecule absorbs light energy to break the bond between the atoms. Two chlorine radicals form.

$$Cl{-}Cl(g) \xrightarrow{\text{UV light}} Cl\cdot(g) + Cl\cdot(g)$$

A chlorine radical reacts with a methane molecule to form hydrogen chloride and a methyl radical. The methyl radical now reacts with a chlorine molecule to form chloromethane and a new chlorine radical. These two steps continue to form a chain reaction and are known as the *propagation steps* of the reaction.

$$Cl\cdot(g) + H{-}CH_3(g) \longrightarrow Cl{-}H(g) + CH_3\cdot(g)$$

$$CH_3\cdot(g) + Cl{-}Cl(g) \longrightarrow CH_3Cl(g) + Cl\cdot(g)$$

When all the reactants are depleted, the reaction stops. Two possible *termination steps* to remove the radicals and interrupt the chain reaction are:

$$Cl\cdot(g) + Cl\cdot(g) \longrightarrow Cl_2(g)$$

$$CH_3\cdot(g) + CH_3\cdot(g) \longrightarrow CH_3CH_3(g)$$

As the reaction is a substitution involving radicals, it is known as a radical substitution.

A similar radical reaction mechanism is responsible for the depletion of the ozone layer, which we investigated in Grade 11.

Haloalkanes can undergo nucleophilic substitution when reacted with a strong alkali, water or ammonia. The halogen is replaced by another group, for example OH^- or NH_2^-. Bromoethane dissolved

Note: A nucleophile can donate a pair of electrons during a reaction. During nucleophilic substitution, one nucleophile replaces another that is attached to a saturated carbon atom.

in ethanol will react with a strong alkali, NaOH or KOH, to form ethanol. The same reaction happens without the alkali, but at a slower rate. This reaction is also called a hydrolysis (reaction with water). If a bromoethane/ethanol mix is heated under pressure with ammonia, ethylamine forms.

With KOH:

CH_3CH_2Br (in alcohol) + KOH $\longrightarrow$ CH_3CH_2OH + KBr

With water:

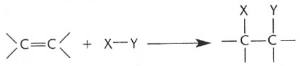
CH_3CH_2Br (in alcohol) + H_2O $\longrightarrow$ CH_3CH_2OH + HBr

With ammonia:

CH_3CH_2Br (in alcohol) + NH_3 $\longrightarrow$ $CH_3CH_2NH_2$ + HBr

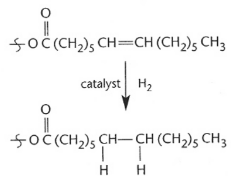
Addition

Addition reactions involve two molecules joining together to form a single new molecule. *Alkenes* and *alkynes* can undergo addition reactions. During the reactions the double or triple bond is broken and new atoms are added onto the molecules to form more saturated products. These reactions take place much faster than substitution reactions, and the difference in reaction speed can be used to distinguish between saturated and unsaturated hydrocarbons. The addition always occurs on the two carbons of the double or triple bond. Addition reactions are widely used during polymerisation.



Addition of hydrogen

In this reaction the unsaturated alkene is converted to a saturated alkane. Hydrogen gas and the alkene are passed over a finely divided Ni, Pt or Pd catalyst. The double bond in the alkene is broken and the hydrogen atoms bond to the carbon atoms of the double bond. This reaction is used to make margarine from vegetable oil in the process called **hydrogenation**.

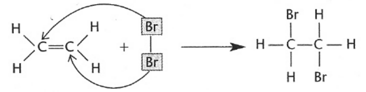


partial structure of vegetable oil

partial structure of saturated margarine

Addition of halogens

When an alkene is bubbled through a bromine solution, the bromine solution is rapidly discoloured from orange-brown to colourless without the addition of sunlight. We can use this reaction to test for an alkene. Chlorine and iodine produce similar reactions. The addition of a halogen to an alkene is called **halogenation**.



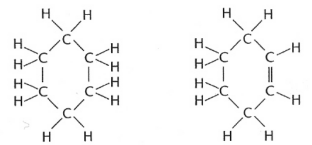
ethene bromine solution 1,2-dibromoethane

WORK IN GROUPS/ALONE

Activity 17: Investigating addition and substitution reactions of alkanes and alkenes

LO1: AS1, AS2, AS3

In the following reactions, the cyclohexane's behaviour is typical of an alkane and the cyclohexene's behaviour is typical of an alkene.



cyclohexane cyclohexene

You will need

- cyclohexane
- cyclohexene
- test tubes with stoppers and test tube stand
- bromine/CCl_4 solution

1. Using this apparatus, design an experiment to show the differences between alkanes and alkenes. Write down your method point by point.
2. Now conduct your experiment and record your observations.
3. Using structural formulae, give balanced equations for all the reactions that take place.
4. Name the type of reaction in each case.
5. Suggest a simple method to distinguish between an unknown alkane and alkene.

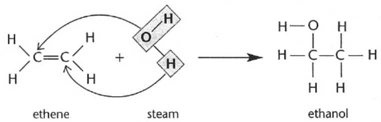
Addition of hydrogen halides

Hydrogen halides, such as hydrogen chloride, can add on to an alkene. For example, when ethene is mixed with hydrogen chloride gas, chloroethane forms.

$$\underset{\text{ethene}}{CH_2{=}CH_2(g)} + \underset{\text{hydrogen chloride}}{HCl(g)} \longrightarrow \underset{\text{chloroethane}}{CH_3CH_2Cl(\ell)}$$

Addition of steam

Alcohols can be industrially prepared by adding steam onto alkenes during a hydration reaction. The gaseous alkene and steam are passed over a phosphoric acid catalyst at a temperature of 300 °C and a pressure of 6 MPa. The addition of steam to ethene produces ethanol.



Elimination

Elimination involves the removal of a molecule from a larger one. Passing ethanol vapour over a hot catalyst may reverse the addition of ethene to steam. A water molecule is eliminated.

$$\underset{\text{ethanol}}{CH_3CH_2OH(g)} \longrightarrow \underset{\text{ethene}}{CH_2{=}CH_2(g)} + \underset{\text{water}}{H_2O(g)}$$

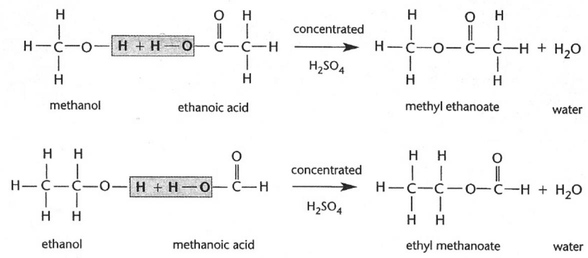
Elimination reactions take place when saturated hydrocarbons are cracked to produce more unsaturated products. Ethene is used in industry as a raw material to produce polyethylene. Ethane is cracked in the presence of a Pt catalyst at a temperature of about 800 °C to produce ethene and hydrogen gas.

$$\underset{\text{ethane}}{C_2H_6(g)} \xrightarrow[800\,°C]{Pt} \underset{\text{ethene}}{CH_2{=}CH_2(g)} + \underset{\text{hydrogen gas}}{H_2(g)}$$

Large straight-chain alkanes can be cracked to produce shorter-chained alkenes and branched alkanes that are more suitable for use in petrol.

Esterification

Carboxylic acids react with alcohols to form esters. The dehydrating property of concentrated sulphuric acid is used to catalyse the reaction. During the reaction the OH–bond in the alcohol is broken.



We can see that both esters in the previous examples have the molecular formula $C_3H_6O_2$. Methyl ethanoate and ethyl methanoate are therefore structural isomers.

WORK IN GROUPS

Activity 18: Preparing an ester

LO1: AS1, AS2, AS3

Note: Many organic compounds are flammable and should not be left near an open flame.

You will need

- large test tubes
- Bunsen burner
- water bath
- beaker with water
- ethanol
- ethanoic acid (glacial acetic acid)
- concentrated sulphuric acid
- fragments of porcelain or boiling stones

1. Pour 3 ml ethanol, 1 ml concentrated sulphuric acid and 4 ml ethanoic acid into a test tube. Add the boiling stones.
2. Heat in the water bath for a few minutes. The temperature of the water bath should not exceed 85 °C. The reaction is completed when the froth disappears.
3. Pour the contents onto water in a beaker. Smell the ester that should float on the water.
4. Using structural formulae, write a balanced equation for the reaction.
5. Why is sulphuric acid added to the reaction mixture?
6. Other esters that can be synthesised are shown in the table.

Note: To smell a chemical safely, wave your hand across the beaker towards your nose and sniff cautiously.

Alcohol	Carboxylic acid	Ester	Flavour
ethanol	methanoic acid		rum
	ethanoic acid	pentyl ethanoate	banana
butanol	butanoic acid		pineapple
ethanol		ethyl butanoate	apricot

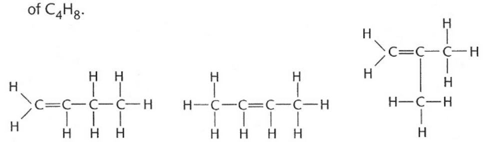
Now complete the table by filling in the missing names. Your teacher can demonstrate the formation of these esters if the alcohols and carboxylic acids are available.

WORK ALONE

Activity 19: Applying organic reactions

LO1: AS3, AS4; LO2: AS1, AS2

1. Propane gas is mixed with chlorine gas. The mixture is left in the sun for a while.
   a) Write a balanced equation for the reaction by using structural formulae.
   b) Name the type of reaction that took place.
   c) What will happen if the reaction mixture is not placed in the sun?
2. 1-bromopropane is dissolved in ethanol. The solution is allowed to react with (i) sodium hydroxide and (ii) ammonia.
   a) Write balanced equations (use condensed structural formulae) for the reactions that occur in (i) and (ii).
   b) What is this type of reaction called?
   c) Give the names of the organic products that form.
3. The following diagrams show the structures of the three isomers of C_4H_8.



A B C

   a) To which homologous series do the three isomers belong?
   b) Compound A reacts with bromine.
      i) Draw the full structural formula of the product and give its IUPAC name.
      ii) What type of reaction has taken place?
      iii) What do you observe during the reaction?
   c) Compound B is mixed with hydrogen gas and passed over a Pd-catalyst.
      i) Draw the full structural formula of the product and give its IUPAC name.
      ii) What is this type of reaction called?
      iii) How is this reaction used in industry?
   d) Compound C is reacted with steam in the presence of phosphoric acid.
      i) Name the type of reaction that occurs.
      ii) Draw the full structural formulae of the two different products that can form, and give their IUPAC names.
4. Heptane can undergo an elimination reaction to produce an alkene with three carbon atoms and a branched four-carbon alkane.
   a) Write a balanced equation using structural formulae for this reaction.
   b) Give the IUPAC names of all the organic molecules involved in the reaction.
5. Consider the compound ethyl propanoate.
   a) To which homologous series does this compound belong?
   b) Name the most distinctive characteristic of this homologous series.
   c) Give the functional group of this series.
   d) Name the carboxylic acid and the alcohol which reacted to form ethyl propanoate.
   e) Using structural formulae, write a balanced equation for the formation of ethyl propanoate.
   f) Why is concentrated sulphuric acid added to the reaction mixture?