Basic definitions for organic chemistry

Scope Organic chemistry is a vast subject so it is easier to split it into small sections for study. This is usually done by studying compounds which behave in a similar way because they have a particular atom, or group of atoms, (FUNCTIONAL GROUP) in their structure.

Catenation The **ability to form bonds between atoms of the same element**. Carbon catenates to form chains and rings, with single, double and/or triple covalent bonds.

Q.1

- *Why does carbon form so many catenated compounds ?*

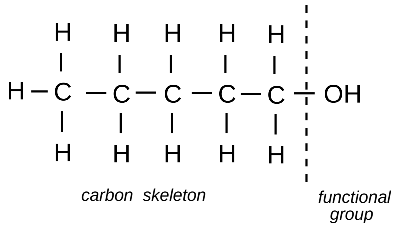
- *Why does silicon undergo catenation to a lesser extent than carbon ?*

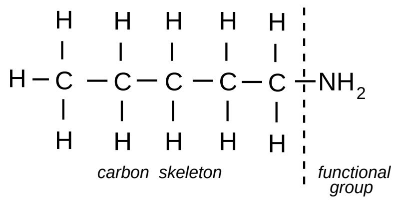
Homologous Series A series of compounds of similar structure in which each member differs from the next by a common repeating unit, CH_2 . The members of the series are called homologues.

- All share the same general formula.
- Formula of a homologue differs from its neighbour by CH_2. *(e.g. CH_4, C_2H_6, . . . etc)*
- Contain the same functional group(s).
- Have similar chemical properties.
- Show a gradual change in physical properties as molar mass increases.
- Can usually be prepared by similar methods.

Functional Groups

- Can consist of one atom, a group of atoms or multiple bonds between carbon atoms.
- Each functional group has its own distinctive properties which means that the properties of a compound are governed by the functional group(s) in it.

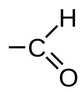
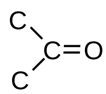
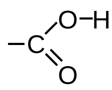
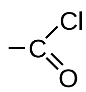
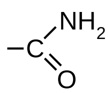
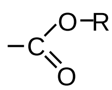
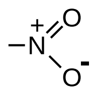
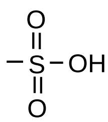




Q.2 *The following list contains some molecular formulae. Draw out as many legitimate structures for each and classify each compound made according to the functional group present. Remember that carbon atoms will have four covalent bonds surrounding them, oxygen atoms will have two, nitrogen atoms three and hydrogen atoms and halogen atoms just one.*

C_2H_6 C_4H_{10} C_4H_8 C_2H_6O C_3H_6O C_2H_7N $C_2H_4O_2$ C_2H_3N

Some common functional groups

GROUP	ENDING	GEN. FORMULA / STRUCTURE		EXAMPLE	
ALKANE	- ane	RH	C − C	C_2H_6	ethane
ALKENE	- ene		C = C	C_2H_4	ethene
ALKYNE	- yne		C ≡ C	C_2H_2	ethyne
HALOALKANE	halo -	RX	C − Cl	C_2H_5Cl	chloroethane
ALCOHOL	- ol	ROH	−O−H	C_2H_5OH	ethanol
ALDEHYDE	-al	RCHO		CH_3CHO	ethanal
KETONE	- one	RCOR		CH_3COCH_3	propanone
CARBOXYLIC ACID	- oic acid	RCOOH		CH_3COOH	ethanoic acid
ACYL CHLORIDE	- oyl chloride	RCOCl		CH_3COCl	ethanoyl chloride
AMIDE	- amide	$RCONH_2$		CH_3CONH_2	ethanamide
ESTER	- yl - oate	RCOOR		CH_3COOCH_3	methyl ethanoate
NITRILE	- nitrile	RCN	−C ≡ N	CH_3CN	ethanenitrile
AMINE	- amine	RNH_2	C − NH_2	CH_3NH_2	methylamine
NITRO	- nitro	RNO_2		CH_3NO_2	nitromethane
SULPHONIC ACID	- sulphonic acid	RSO_3H		$C_6H_5SO_3H$	benzene sulphonic acid
ETHER	- oxy - ane	ROR	R-O-R	$C_2H_5OC_2H_5$	ethoxyethane

The symbol R represents groups of carbon and hydrogen atoms in the rest of the molecule

Use of different formulae in organic chemistry

General represents any member of a homologous series

C_nH_{2n+2} for an alkane
C_nH_{2n} for an alkene

Molecular shows the exact number of atoms of each type

C_4H_{10} for butane

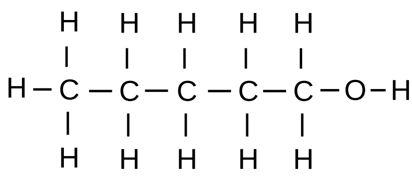
Empirical shows the simplest whole number ratio of atoms

C_2H_5 for butane

Structural the minimal detail, using conventional groups, for an unambiguous structure

$CH_3CH_2CH_2CH_3$ for butane

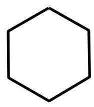
Displayed shows the relative placing of atoms and the number of bonds between them



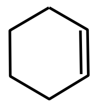
pentan-1-ol

Skeletal used to show a simplified organic formula by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups.

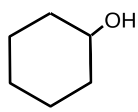
- each covalent bond is shown by a line
- a carbon atom is at the join of lines
- functional groups are shown
- the number of hydrogen atoms on each carbon atom is the difference between the number of lines and 4



cyclohexane

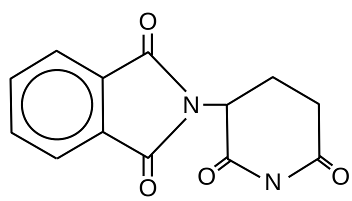


cyclohexene



cyclohexanol

Skeletal formulae tend to be used with larger organic molecules - e.g. *thalidomide*



Q.3 *State the molecular formula and empirical formula of...*

cyclohexane	*MF =*	*EF =*
cyclohexene	*MF =*	*EF =*
cyclohexanol	*MF =*	*EF =*
thalidomide	*MF =*	*EF =*

Nomenclature in organic chemistry

Systems Ideally one needs a naming system that tells you everything about a structure without any ambiguity. There are two types of naming system commonly found in organic chemistry;

Trivial : based on some property or historical aspect;
the name tells you little about the structure

Systematic : based on an agreed set of rules (I.U.P.A.C);
exact structure can be found from the name (and vice-versa).

Series	*trivial name*	*systematic name*	*example(s)*
	paraffin	alkane	methane, butane
	olefin	alkene	ethene, butene
	fatty acid	alkanoic (carboxylic) acid	ethanoic acid

Compounds	*trivial name*	*derivation*	*systematic name*
	methane	methu = wine (Gk.)	methane (CH_4)
	butane	butyrum = butter (Lat.)	butane (C_4H_{10})
	acetic acid	acetum = vinegar (Lat.)	ethanoic acid (CH_3COOH)

Systematic (I.U.P.A.C.) Nomenclature

A systematic name has **two main parts.**

STEM number of carbon atoms in longest chain bearing the functional group + (if necessary) a prefix showing the position and identity of any side-chain substituents.

Nomenclature Apart from the first four, which retain trivial names, the number of carbons atoms is indicated by a prefix derived from the Greek numbering system.

- The list of alkanes demonstrate the use of prefixes.
- The ending -ane is the same as they are all alkanes.

Prefix	*C atoms*	*Alkane*
meth-	1	methane
eth-	2	ethane
prop-	3	propane
but-	4	butane
pent-	5	pentane
hex-	6	hexane
hept-	7	heptane
oct-	8	octane
non-	9	nonane
dec-	10	decane

SUFFIX An ending that tells you which functional group is present

Nomenclature See if any functional groups are present. Add relevant ending to the basic stem. In many cases the position of the functional group must be given to avoid any ambiguity.

In many cases the chain of carbon atoms is branched so one must include the ...

Substituents Many compounds have substituents (additional atoms, or groups of atoms) attached to the chain. Their position is numbered according to a set of rules.

NOMENCLATURE - GENERAL RULES

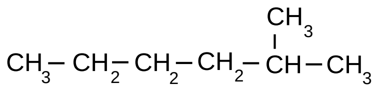
Stem

- look for the longest chain of carbon atoms containing the functional group.
- the carbon atoms must be in a continuous row.
- use prefixes as shown on previous page
- the ending tells you what type of carbon structure you have; alkanes end in **ANE**

Side-chain

- carbon based substituents are named before the chain name.
- they have the prefix -yl added to the basic stem (e.g. CH_3 is methyl).
- Number the principal chain from one end so that the side chain is attached to a carbon atom with the **lowest possible number**.

e.g. 2-methylhexane

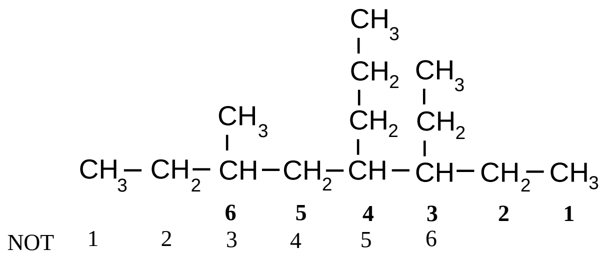


If there is more than one side-chain the following rules apply:-

- Side-chain names appear in alphabetical order i.e. butyl, ethyl, methyl, propyl.
- Number the principal chain from one end to give the lowest numbers.
- Each side-chain is given its own number.
- If identical side-chains appear more than once, prefix with di, tri, tetra, penta, hexa.
- Numbers are separated from names by a HYPHEN *e.g.* 2-methylheptane
- Numbers are separated from numbers by a COMMA *e.g.* 2,3-dimethylbutane

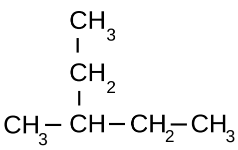
Example

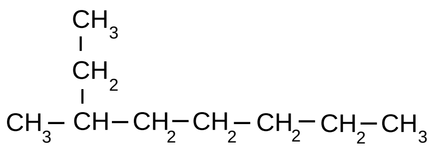
- *longest chain 8 (it is an octane)*
- *3,4,6 are the numbers NOT 3,5,6*
- *order is ethyl, methyl, propyl*

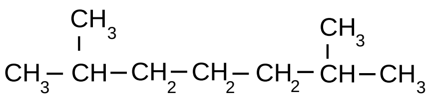


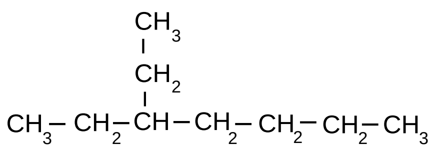
3-ethyl-6-methyl-4-propyloctane

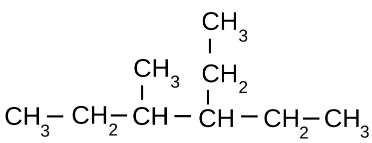
Q.4 *Name these alkanes*

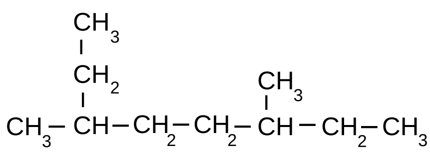












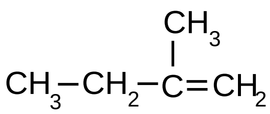
ALKENES

Length In alkenes the principal chain is not always the longest chain. It **must contain the double bond**. The name ends in -ENE

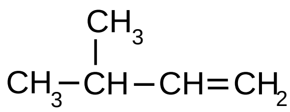
Position Indicated by the lower numbered carbon atom on one end of the double bond. Count from one end as with alkanes.

$CH_3{-}CH{=}CH{-}CH_2{-}CH_3$ is pent-2-ene (NOT pent-3-ene)

Side-chain Similar to alkanes but position is based on the number allocated to the double bond.



2-methylbut-1-ene



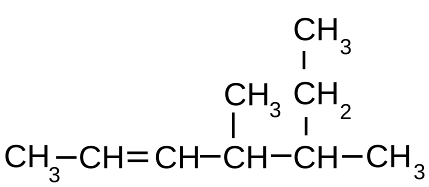
3-methylbut-1-ene

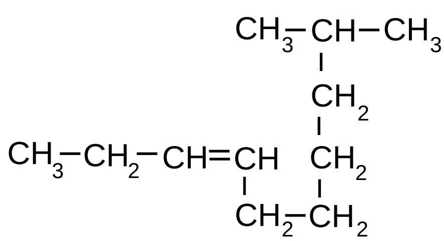
ALKYNES Similar rules to alkenes but end in -YNE

Q.5 *Draw structures for . . .*

- *4-methylhex-2-ene*
- *3,3-dimethyloct-1-ene*
- *4-ethyl-3-methylhex-1-ene*

Q.6 *Name these compounds.*





Elucidation of the structures of organic compounds - a brief summary

Introduction Organic chemistry is so vast that the identification (characterisation) of a compound can be quite involved. The characterisation takes place in a series of stages *(see below)*. In earlier times relatively large amounts of substance were required to elucidate the structure but, with the advance in technology and the increased use of electronic instrumentation, only very small amounts are now required.

ELEMENTAL COMPOSITION → **PERCENTAGE COMPOSITION** → **EMPIRICAL FORMULA**
↓
MOLECULAR MASS → **MOLECULAR FORMULA** → **STRUCTURAL FORMULA**

Elemental composition One assumes that organic compounds contain carbon and hydrogen but it can be proved by letting the compound undergo combustion. Carbon is converted to carbon dioxide and hydrogen to water.

Percentage composition The percentage composition by mass is found by dividing the mass of an element present by the mass of the compound present, then multiplying by 100. Elemental mass of C and H can be found by allowing the substance to undergo complete combustion. From this one can find...

- mass of carbon = 12/44 of the mass of CO_2 produced
- mass of hydrogen = 2/18 of the mass of H_2O produced

Empirical formula This gives the simplest ratio of elements present in the substance. It can be calculated by dividing the mass or percentage mass of each element present by its molar mass and finding the simplest ratio between the answers. Empirical formula is converted to the molecular formula using molecular mass.

Molecular mass Molecular mass determination was traditionally carried out using a variety of techniques such as ...

- volumetric analysis or
- molar volume methods such as the Dumas, Victor-Meyer or gas syringe experiments.

Nowadays **mass spectrometry** is used. The position of the last m/z signal is due to the molecular ion and gives the molecular mass. The fragmentation pattern also gives information about the compound.

Molecular formula The molecular formula is an exact multiple of the empirical formula. Comparing the molecular mass with the empirical mass allows one to find the true formula.

e.g. *if the empirical formula is CH (relative mass = 13) and the molecular mass is 78 the molecular formula will be 78/13 or 6 times the empirical formula i.e.* C_6H_6 .

Structural formula Because of the complexity of organic molecules, there can be more than one structure for a given molecular formula. To work out the structure, one can carry out different tests...

Chemical Use chemical reactions to identify the functional group(s) present.

Spectroscopy *e.g.* IR detects bond types due to absorbance of i.r. radiation
NMR gives information about the position and relative numbers of hydrogen atoms present in a molecule

Confirmation By comparison of **spectra** and **melting point or boiling point**.