Basic definitions for organic chemistry

Scope Organic chemistry is a vast subject so is split it into small sections for study. This is 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 or triple covalent bonds.

Q.1

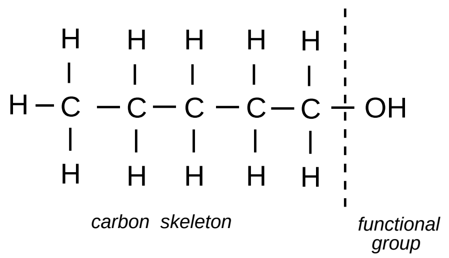
- *Why does carbon form so many catenated compounds ?*
- *Why does silicon undergo catenation to a lesser extent than carbon ?*

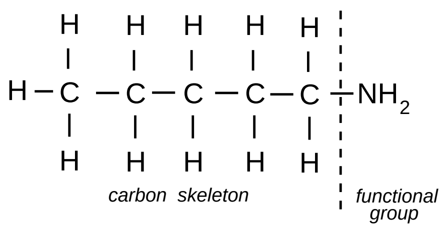
Homologous Series A series of organic compounds having the **same functional group** and **each member differs from the previous by CH_2** .

- all share the same general formula
- formulae differ from their neighbours 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.

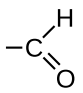
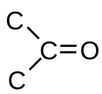
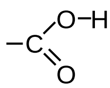
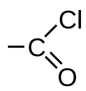
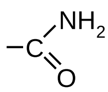
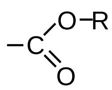
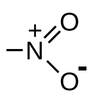
Functional Group A group of atoms responsible for the characteristic reactions of a compound.

- can consist of
  - one atom **— Br**
  - a group of atoms **— OH**
  - multiple bonds between carbon atoms **C = C**
- each functional group has its own distinctive properties





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 − X (X= Cl, Br, I)	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
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

Q.2 *Draw out* ***legitimate*** *structures for each formula and classify the compounds according to the functional group present. NB Carbon atoms will have four covalent bonds surrounding them, oxygen atoms 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

Use of different formulae in organic chemistry

General — the simplest algebraic formula for a 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 element in a molecule

C_4H_{10} for butane

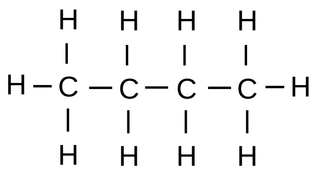
Empirical — shows the simplest whole number ratio of atoms of each element in a molecule

C_2H_5 for butane

Structural — the minimal detail that shows the arrangement of atoms in a molecule

$CH_3CH_2CH_2CH_3$ butane
$CH_3CHOHCH_3$ propan-2-ol

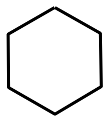
Displayed — shows the relative positioning of atoms and the number of bonds between them



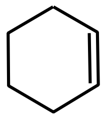
butane

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

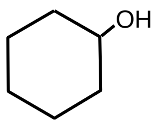
- each covalent bond is shown by a line
- a carbon atom is at the join of lines
- functional groups are shown
- the number of hydrogen atoms on each carbon atom is the difference between the number of lines and 4



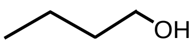
cyclohexane



cyclohexene

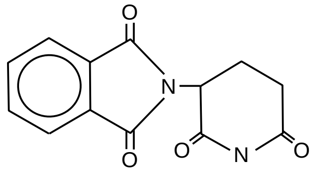


cyclohexanol



butan-1-ol

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



Nomenclature in organic chemistry

Systems A naming system must tell you everything about a structure without 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*
	acetic acid	acetum = vinegar (Lat.)	ethanoic acid (CH_3COOH)

Systematic (IUPAC) Nomenclature

STEM Shows the number of carbon atoms in longest chain bearing the functional group + (if necessary) a prefix showing the position and identity of any 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 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 The **ending** tells you **which functional group** is present

Nomenclature If any functional groups are present, add relevant ending to the basic stem. 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

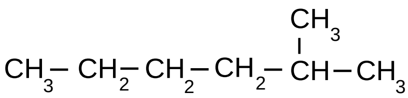
Stem

- 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
- 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

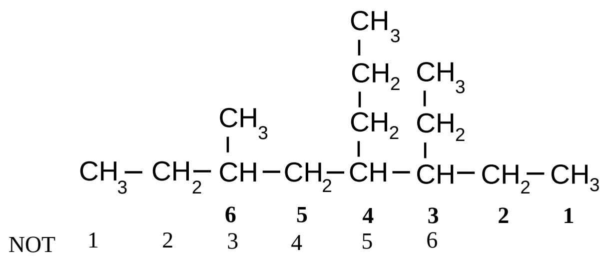


If there is more than one side-chain the following rules apply:-

- 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 etc
- numbers are separated from names by a HYPHEN ***2-methylheptane***
- numbers are separated from numbers by a COMMA ***2,3-dimethylbutane***

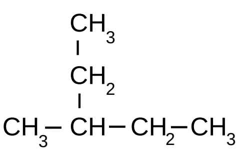
Example

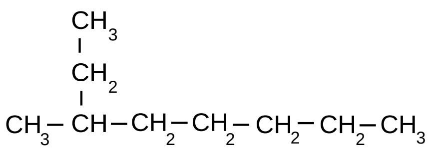
- *longest chain 8 (it is an octane)*
- *3,4,6 are the numbers NOT 3,5,6*
- *order is ethyl, methyl, propyl*

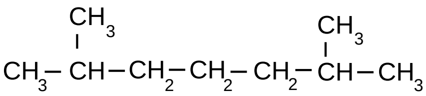


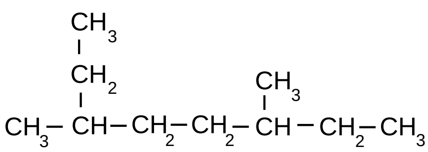
3-ethyl-6-methyl-4-propyloctane

Q.3 *Name these alkanes*









ALKENES / ALCOHOLS

Length In alkenes and alcohols the principal chain is not always the longest chain.

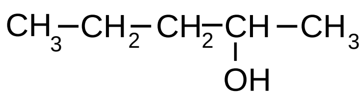
Alkenes It **must contain the C=C bond**. The name ends in -ENE

Alcohols It **must contain the OH group**. The name ends in -OL

Position *Alkenes* Indicated by the lower numbered carbon atom on one end of the double bond. Count from one end to give lowest number.

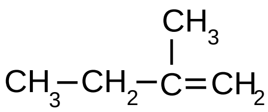
$CH_3-CH=CH-CH_2-CH_3$ is *pent-2-ene* (NOT *pent-3-ene*)

Alcohols Count from one end to give lowest number.

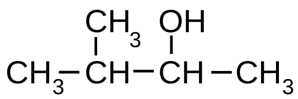


is *pentan-2-ol* (NOT *pentan-4-ol*)

Side-chain Position is based on the number allocated to the C=C bond or OH group.



2-methylbut-1-ene

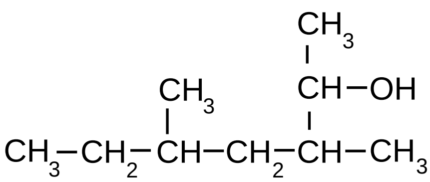


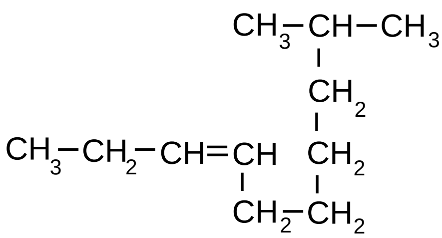
3-methylbutan-2-ol

Q.4 *Draw structures for . . .*

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

Q.5 *Name these compounds.*





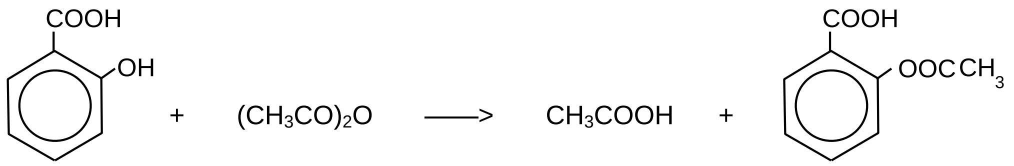
PERCENTAGE YIELD

Yield • the mass of a product obtained in reaction

Percentage yield • the mass of product obtained expressed as a percentage of what you ought to get assuming complete conversion

Example 1 *What mass of salicylic acid will make 5g of aspirin (assuming 100% conversion)?*

Aspirin can be made by the reaction between salicylic acid and ethanoic anhydride. If one mole of each of the reactants is used the masses involved are...



M_r = 138 M_r = 102 M_r = 60 M_r = 180

In order to make 180g of aspirin you will need a minimum of 138g of salicylic acid.

If you only want 5g of aspirin you will need to scale the masses accordingly...

molar scale	*138g*	*102g*	*60g*	*180g*
divide by 180	*138g/180*	*102g/180*	*60g/180*	*1g*
multiply by 5	*5 x 138g/180*	*5 x 102g/180*	*5 x 60g/180*	*5g*

3.833g salicylic acid *will produce* ***5g of aspirin***

Example 2 *When an experiment was carried out using 3.833g of salicylic acid, only 3.75g of aspirin was produced. What is the percentage yield of aspirin?*

If there is a 100% yield then... 3.833g salicylic acid ——> 5g of aspirin

If 3.75g of aspirin is made, the percentage yield = 3.75g / 5g x 100 = ***75%***

Q.6 *The equation for the synthesis of N-ethyl ethanamide from ethylamine and ethanoyl chloride is*

$$CH_3COCl + C_2H_5NH_2 \longrightarrow CH_3CONHC_2H_5 + HCl$$

- *What mass of ethanoyl chloride is required to make 3g of N-ethyl ethanamide?*
- *If only 1.8g are produced, what is the percentage yield?*

Q.7 *Ethyl ethanoate can be synthesised from ethanoyl chloride and ethanol.*

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$$

- *What mass of ethanoyl chloride will react with 2.3g of ethanol?*
- *If only 1g of ethyl ethanoate is produced, what is the percentage yield from 2.3g of ethanol?*

ATOM ECONOMY

Background
- in most reactions you only want to make one of the resulting products
- atom economy is a measure of how much of the products are useful

ATOM ECONOMY = MOLECULAR MASS OF DESIRED PRODUCT / SUM OF MOLECULAR MASSES OF ALL PRODUCTS x 100

Example 1 *Calculate the atom economy for the formation of 1,2-dichloroethane, $C_2H_4Cl_2$*

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

	C_2H_4	Cl_2	$C_2H_4Cl_2$
M_r	28	71	99

$$\text{atom economy} = \frac{\text{molecular mass of } C_2H_4Cl_2}{\text{molecular mass of all products}} \times 100 = \frac{99 \times 100}{99} = \mathbf{100\%}$$

Example 2 *Calculate the atom economy for the formation of nitrobenzene, $C_6H_5NO_2$*

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

	C_6H_6	HNO_3	$C_6H_5NO_2$	H_2O
M_r	78	63	123	18

$$\text{atom economy} = \frac{\text{molecular mass of } C_6H_5NO_2}{\text{molecular mass of all products}} \times 100 = \frac{123 \times 100}{141} = \mathbf{87.2\%}$$

Notes
- **addition** reactions will have **100% atom** economy
- **substitution** reactions will have **less than 100% atom** economy
- **elimination** reactions will have **less than 100% atom** economy
- **high atom economy = fewer waste materials**
- reactions may have a high yield but a low atom economy

Q.8 *Calculate the atom economy of the following reactions (required product is in **bold**);*

- $CH_3COCl + C_2H_5NH_2 \longrightarrow \mathbf{CH_3CONHC_2H_5} + HCl$
- $C_2H_5Cl + NaOH \longrightarrow \mathbf{C_2H_5OH} + NaCl$
- $C_2H_5Cl + NaOH \longrightarrow \mathbf{C_2H_4} + H_2O + NaCl$

Elucidation of the structures of organic compounds - a brief summary

Introduction Traditionally, working out the identity was a long-winded process but, with the use of modern analytical instruments, the process is much quicker.

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

Elemental composition The presence of carbon and hydrogen can be proved by letting the compound undergo combustion. Carbon is converted to carbon dioxide and hydrogen to water. Other elements can also be identified.

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.

- 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 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 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.

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
- 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**.