# 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 next 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.

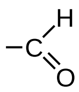
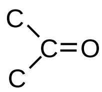
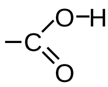
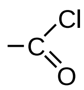
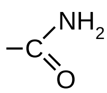
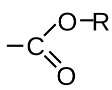
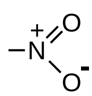
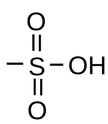
**Functional Group** A group of atoms responsible for the characteristic reactions of a compound.

- 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

**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** — 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

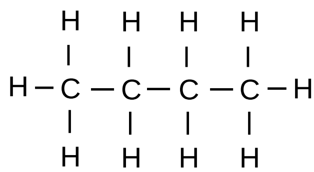
$C_2H_5$ for butane

**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

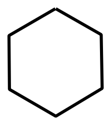
**Displayed** — shows the relative positioning of atoms and the number of bonds between them

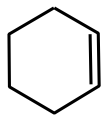


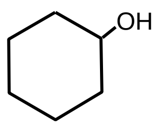
butane

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

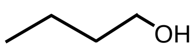
- each covalent bond is shown by a line
- a carbon atom is at the join of lines
- functional groups are shown
- the number of hydrogen atoms on each carbon atom is the difference between the number of lines and 4


cyclohexane


cyclohexene

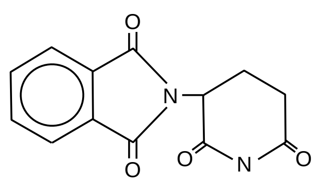


cyclohexanol



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 ...

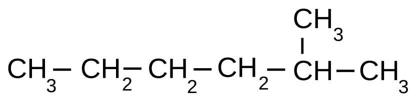
**Substituents** Many compounds have substituents (additional atoms, or groups of atoms) attached to the chain. Their position is numbered according to a set of rules.

## 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*

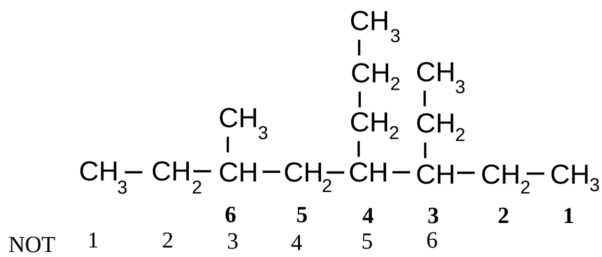


**If there is more than one side-chain the following rules apply:-**

- 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***

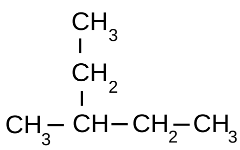
*Example*

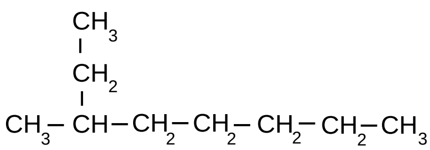
- *longest chain 8 (it is an octane)*
- *3,4,6 are the numbers NOT 3,5,6*
- *order is ethyl, methyl, propyl*

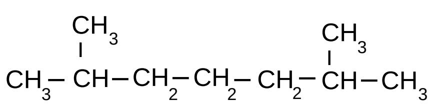


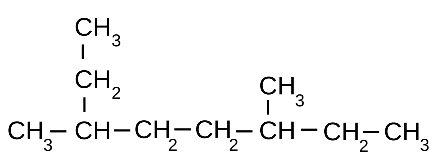
***3-ethyl-6-methyl-4-propyloctane***

**Q.3** *Name these alkanes*









## ALKENES / ALCOHOLS

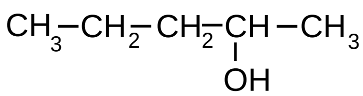
***Length*** In alkenes and alcohols the principal chain is not always the longest chain.

*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.

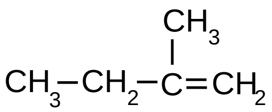
$CH_3-CH=CH-CH_2-CH_3$ is *pent-2-ene* ( NOT *pent-3-ene* )

*Alcohols* Count from one end to give lowest number.

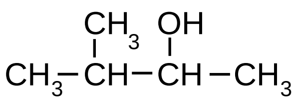



is *pentan-2-ol* ( NOT *pentan-4-ol* )

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




*2-methylbut-1-ene*

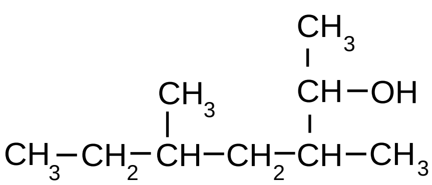


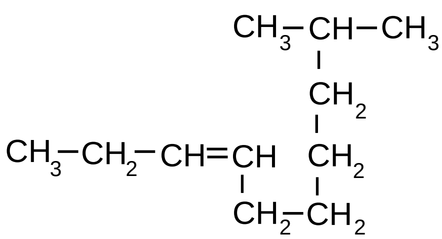

*3-methylbutan-2-ol*

**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.*



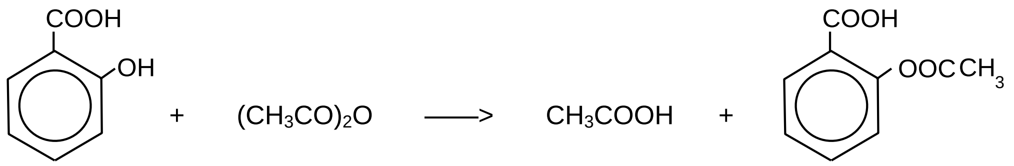
## PERCENTAGE YIELD

**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 = $\frac{\text{MOLECULAR MASS OF DESIRED PRODUCT}}{\text{SUM OF MOLECULAR MASSES OF ALL PRODUCTS}}$ 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**
↓
**MOLECULAR MASS** → **MOLECULAR FORMULA** → **STRUCTURAL FORMULA**

**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*

| | | |
|---|---|---|
| *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**.