An introduction to AS Level organic chemistry

Functional groups and naming, types of formula, reaction types and mechanisms, curly arrows, sp, sp2 and sp3 shapes, and structural and stereoisomerism including cis/trans isomerism and chiral centres.

13.1 Formulas, functional groups and the naming of organic compounds

A **hydrocarbon** contains only carbon and hydrogen. **Alkanes** are simple hydrocarbons with **no functional group**. A **functional group** is the atom or group of atoms that decides the chemical properties of a compound.

Types of formula

- **General formula:** for example alkanes C_nH_{2n+2}, alkenes C_nH_{2n}, alcohols $C_nH_{2n+1}OH$.
- **Structural formula:** shows the arrangement of the atoms, for example $CH_3CH_2CH_2OH$.
- **Displayed formula:** shows every atom and every bond.
- **Skeletal formula:** shows the carbon skeleton as lines, with functional groups written in; carbon atoms are at the ends and bends, and hydrogen atoms on carbon are not drawn.

You should be able to deduce the **molecular** and **empirical** formula from any of these.

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Functional groups

Class	Functional group	Suffix / prefix	Example
Alkane	C–C	-ane	ethane
Alkene	C=C	-ene	propene
Halogenoalkane	–F, –Cl, –Br, –I	chloro-, bromo-	1-bromopropane
Alcohol	–OH	-ol	ethanol
Aldehyde	–CHO	-al	ethanal
Ketone	C=O between carbons	-one	propanone
Carboxylic acid	–COOH	-oic acid	ethanoic acid
Ester	–COO–	-yl …-oate	ethyl ethanoate
Amine	$-NH_2$	-amine	ethylamine
Nitrile	–C≡N	-nitrile	ethanenitrile

Naming (up to six carbon atoms)

Name the **longest chain** containing the functional group, number it so the functional group has the **lowest number**, name branches as alkyl groups in alphabetical order (methyl, ethyl) with numbers, and use di-, tri- for repeated groups: 2,3-dimethylbutane. Esters are named from the alcohol (alkyl) then the acid (-oate): $CH_3COOCH_2CH_3$ is ethyl ethanoate.

Reading a structure without losing atoms

For a skeletal formula, count every unlabelled line end and vertex as carbon, then add enough hydrogen atoms for each carbon to have four bonds. Heteroatoms such as O, N and halogens are written explicitly. A line ending at an O label is a bond to oxygen, not an additional hidden carbon. A double bond counts twice towards valency but still joins only two atoms.

Worked example: $CH_3CH(CH_3)CH_2OH$ has four carbons, ten hydrogens and one oxygen, so its molecular formula is $C_4H_{10}O$. Choose the longest chain containing the OH carbon: three carbons, numbered from the OH end, giving **2-methylpropan-1-ol**. The longest visible horizontal line in a drawing is not always the correct parent chain.

General formulas require stated restrictions. C_nH_{2n} applies to an acyclic hydrocarbon with one double bond, but also to a cycloalkane with one ring. Therefore a molecular formula alone does not prove the

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presence of C=C. An alcohol formula such as $C_nH_{2n+1}OH$ assumes a saturated, acyclic, monohydric alcohol.

Naming groups and choosing the parent

Number to give the principal functional group its required low locant, then identify substituent positions. In aldehydes and carboxylic acids the characteristic carbon belongs to the chain; in nitriles the nitrile carbon also counts. Esters need two independently identified fragments: the group bonded to oxygen supplies the alkyl name, and the carbonyl-containing fragment supplies the alkanoate name.

Worked example: $CH_3CH_2COOCH_3$ is methyl propanoate, not propyl methanoate. The acid fragment has three carbons including the carbonyl carbon; the oxygen-linked methyl fragment comes from methanol. A displayed or structural formula is the safest check when an unfamiliar name is supplied.

> **TRY IT**
>
> Give the molecular formula and name of $CH_3CH(Br)CH_2CH_3$.

Answer: C_4H_9Br, 2-bromobutane. Numbering from the nearer end gives bromine locant 2 rather than 3. There are four carbons, and bromine has replaced one hydrogen of butane.

13.2 Characteristic organic reactions

Terminology

- **Homologous series:** a family with the same functional group and general formula, each member differing by CH_2, with similar chemical properties and gradually changing physical properties.
- **Saturated:** only single bonds. **Unsaturated:** contains multiple bonds.
- **Homolytic fission:** a bond breaks with one electron going to each atom, forming two **free radicals**. **Heterolytic fission:** both electrons go to one atom, forming a cation and an anion.
- **Free radical** reactions have **initiation, propagation** and **termination** steps.
- A **nucleophile** is an electron-pair donor (attacks a $\delta+$ carbon, such as OH^-, CN^-, NH_3). An **electrophile** is an electron-pair acceptor (such as H^+, $Br^{\delta+}$).
- Reaction types: **addition**, **substitution**, **elimination** (loss of a small molecule), **hydrolysis** (reaction with water), **condensation** (two molecules join with loss of a small molecule such as water), **oxidation** and **reduction**. In organic equations $[O]$ stands for oxygen from an oxidising agent and $[H]$ for hydrogen from a reducing agent.

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Mechanisms at AS Level

Free-radical substitution, electrophilic addition, nucleophilic substitution and nucleophilic addition.

> **Curly arrows show the movement of an electron pair. The arrow starts at a bond or a lone pair (not at an atom) and points to where the pair ends up. A half-headed (fish-hook) arrow shows one electron in homolytic fission.**

Classify the change before choosing a mechanism

Addition joins species across a multiple bond, substitution replaces an atom or group, and elimination forms a multiple bond while removing a small molecule. Hydrolysis uses water to break a bond; it is not a synonym for dissolving a substance. Organic oxidation often increases bonding to oxygen or decreases bonding to hydrogen, while reduction commonly does the reverse. Track the functional group rather than relying on a reagent name alone.

Worked comparison: bromoethane to ethanol replaces Br with OH and is substitution. Ethanol to ethene removes water and is elimination. Ethene to ethanol adds the elements of water across C=C and is addition. The two ethanol/ethene directions need different reaction conditions, despite reversing the overall formula change.

Drawing electron movement properly

An electron-pair arrow starts at an identifiable electron source: a lone pair, a negative-charge-bearing atom with an appropriate pair, or a bond. It ends at the atom receiving the pair or at the position of a new bond. A bond-breaking arrow starts on that bond and points to the atom taking the pair. Draw partial charges on a polar starting bond and full charges on ionic intermediates where required.

A nucleophile need not be negative: ammonia is neutral but has a donating lone pair. An electrophile need not be a complete positive ion: the partially positive carbon of a carbonyl group can accept a pair. The labels describe electron-pair behaviour, not simply electric attraction between two full charges.

> **TRY IT**
>
> For $OH^- + CH_3Br \rightarrow CH_3OH + Br^-$, where do the two electron-pair arrows begin and end?

Answer: One starts at an oxygen lone pair and points to carbon. The other starts at the C–Br bond and points to bromine. Starting the first arrow at the negative sign floating beside the ion, or pointing the second towards carbon, does not correctly show pair movement.

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13.3 Shapes of organic molecules; σ and π bonds

Molecules can be **straight-chained**, **branched** or **cyclic**.

Hybridisation	Shape and angle	σ and π bonds	Example
sp^3	tetrahedral, 109.5°	four σ	C in ethane
sp^2	trigonal planar, 120°	three σ and one π	C in ethene
sp	linear, 180°	two σ and two π	C in ethyne, C in $HC{\equiv}N$

In ethene all the atoms lie in one **plane**: the π bond is formed by sideways overlap of p orbitals above and below that plane.

Local geometry and restricted rotation

Assign geometry at the particular atom, not to the entire molecule as a single label. In ethanal, the carbonyl carbon is approximately trigonal planar, while the methyl carbon is tetrahedral. In a nitrile, the nitrile carbon and nitrogen lie along a near-linear C–C≡N axis. A molecule with both kinds of carbon has different local angles.

Sigma overlap lies along the bond axis. Pi overlap requires parallel p orbitals, so turning one end of C=C relative to the other disrupts it. This restriction provides the physical basis for geometrical isomerism. Rotation around an ordinary C–C single bond usually gives conformations of the same compound rather than different structural isomers.

> **TRY IT**
>
> Explain why a flat drawing of ethane does not mean all six hydrogens and both carbons lie in one plane.

Answer: Each carbon is tetrahedral, approximately 109.5°. A two-dimensional drawing is a representation; use wedges and dashed bonds where the spatial arrangement must be explicit.

13.4 Isomerism: structural isomerism and stereoisomerism

Isomers have the same molecular formula but different structures.

Structural isomerism

- **Chain:** different carbon skeletons (butane and 2-methylpropane).
- **Positional:** the same skeleton, the functional group in a different place (propan-1-ol and propan-2-ol).

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- **Functional group:** different functional groups (ethanol and methoxymethane).

Stereoisomerism

Same structural formula, different arrangement in space.

- **Geometrical (cis/trans) isomerism** arises in alkenes because the π bond **restricts rotation** about C=C. Each carbon of the double bond must carry two **different** groups. **Cis:** the same groups on the same side; **trans:** on opposite sides. (E/Z is also acceptable.) Cyclic compounds can show it too.
- **Optical isomerism** arises from a **chiral centre**: a carbon bonded to **four different groups**. The two non-superimposable mirror images are **enantiomers**. A molecule may have more than one chiral centre.

> **TRY IT**
>
> How many isomers have the formula C_4H_9Br? Which is chiral?

There are four **structural** isomers: 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. **2-bromobutane** is chiral, as C-2 has H, Br, CH_3 and C_2H_5. Counting its two enantiomers separately gives five distinct isomers in total.

Enumerating isomers systematically

Start with each possible carbon skeleton, then move the functional group to genuinely different positions. Check symmetry: numbering a straight chain from the opposite end may reproduce a structure already listed. Finally consider stereoisomers of each structural formula. This sequence prevents mixing a rotated drawing with a new connectivity.

Worked example: $C_4H_{10}O$ alcohols have a straight four-carbon skeleton or a branched three-carbon parent. Unique OH positions give butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol. Ethers are additional functional-group isomers if the question asks for all compounds of that molecular formula rather than specifically alcohols. Read the scope carefully.

For alkene stereoisomerism, check both double-bond carbons. Propene fails because the terminal carbon has two hydrogens; but-2-ene passes because each carbon has H and methyl. A substituted alkene with no identical groups across the bond may require E/Z terminology rather than cis/trans. For optical isomerism, compare the **whole attached groups**, not just the first atom: two carbon-containing substituents can still differ.

> **TRY IT**
>
> Which can show geometrical isomerism: but-1-ene, but-2-ene or 2-methylpropene?

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Answer: But-2-ene only. Each carbon of its double bond has two different groups. The other two have a double-bond carbon bearing two hydrogens.

Chapter check: translate between formula representations, identify functional groups before naming, and distinguish different connectivity from different spatial arrangement. Use these foundations in every subsequent reaction chapter.

References and further reading

Scope follows section 13 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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