

Introduction to organic chemistry: formulae, nomenclature, reactions and isomerism

These notes cover the introductory organic chemistry topic of the Cambridge International AS Level Chemistry (9701) syllabus: how organic molecules are represented, how they are named, the language used to describe how bonds break and which species attack them, the types of reaction you will meet, and the different kinds of isomerism. Every later organic topic (alkanes, alkenes, halogenoalkanes, alcohols, carbonyls, carboxylic acids) depends on this one, so learn the definitions in the boxes exactly.

1. Formulae of organic compounds

1.1 Why carbon forms so many compounds

Carbon has four outer electrons and forms four covalent bonds. Carbon to carbon bonds are strong, so carbon atoms can join into long chains, branched chains and rings. Carbon also bonds strongly to hydrogen, oxygen, nitrogen and the halogens. This is why there are millions of organic compounds.

1.2 Types of formula

Empirical formula: the simplest whole number ratio of the atoms of each element present in one molecule or formula unit of the compound.

Molecular formula: the actual number of atoms of each element present in one molecule of the compound.

General formula: an algebraic formula that applies to every member of a homologous series, for example C_nH_{2n+2} for the alkanes.

Structural formula: the minimal detail that shows the arrangement of atoms in a molecule, written without drawing bonds, for example $CH_3CH_2CH_2OH$.

Displayed formula: a formula that shows the relative positioning of all the atoms in a molecule and all the bonds between them.

Skeletal formula: a simplified formula drawn by removing hydrogen atoms from alkyl chains and carbon atoms, leaving just the carbon skeleton as lines, with functional groups shown.

Worked comparison for propan-1-ol.

Type	Propan-1-ol
Molecular	C_3H_8O
Empirical	C_3H_8O (already the simplest ratio)
General (alcohols)	$C_nH_{2n+1}OH$
Structural	$CH_3CH_2CH_2OH$
Displayed	Every bond drawn: three carbons in a row, each C with its H atoms drawn with single lines, and the last carbon bonded to O, which is bonded to H (the O to H bond must be drawn)



Skeletal	A zigzag of three lines: the first two lines join the three carbon positions, and the third line runs from the end carbon to OH, written at its end
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How to draw a skeletal formula. Each line end and each corner of a zigzag represents a carbon atom. Hydrogen atoms bonded to carbon are not shown; each carbon is assumed to have enough H atoms to make four bonds. Atoms other than C and H (O, N, Cl, Br) are always written in, along with any H attached to them (OH, NH₂). A double bond is drawn as two parallel lines. A benzene ring is drawn as a hexagon with a circle inside, or with alternating double bonds.

Worked example: from skeletal to molecular formula. A skeletal formula shows a zigzag of four line segments (five carbon positions) with a double line between the second and third carbon. Carbons: 5. Each end carbon has 1 bond in the skeleton, so 3 H each. Carbon 2 has one single and one double bond (3 bonds), so 1 H. Carbon 3 has a double and a single bond, so 1 H. Carbon 4 has two single bonds, so 2 H.

Total H = 3 + 1 + 1 + 2 + 3 = 10. Molecular formula C₅H₁₀; name pent-2-ene.

Worked example: empirical formula from percentage composition. A hydrocarbon contains 85.7% carbon by mass. Find its empirical formula. (A_r: C = 12.0, H = 1.0)

Hydrogen = 100 – 85.7 = 14.3%.

Moles: C = 85.7 ÷ 12.0 = 7.14; H = 14.3 ÷ 1.0 = 14.3.

Ratio: divide by 7.14 to give C = 1.00, H = 2.00. Empirical formula CH₂.

If M_r = 56, n = 56 ÷ 14 = 4, so the molecular formula is C₄H₈.

2. Homologous series and functional groups

2.1 Homologous series

Homologous series: a family of compounds with the same functional group, the same general formula, and similar chemical properties, in which each member differs from the next by a CH₂ group and physical properties show a gradual trend.

Functional group: an atom or group of atoms in a molecule that is responsible for the characteristic chemical reactions of that molecule.

As chain length increases in a homologous series, boiling point rises because the molecules have more electrons and larger surface area, so instantaneous dipole to induced dipole forces (London dispersion forces) are stronger. Chemical properties stay similar because the functional group is the same.

2.2 Hydrocarbons

Hydrocarbon: a compound containing carbon and hydrogen only.

Saturated: containing only single carbon to carbon bonds.

Unsaturated: containing at least one carbon to carbon multiple bond (C=C or C≡C).

Aliphatic compounds contain straight or branched chains, or non-aromatic rings. **Alicyclic** compounds are aliphatic compounds arranged in rings, for example cyclohexane. **Aromatic** (arene)

compounds contain a benzene ring.

2.3 Functional groups you must recognise at AS Level

Homologous series	Functional group	Prefix or suffix	Example
Alkane	C to C single bonds only	-ane	propane, $\text{CH}_3\text{CH}_2\text{CH}_3$
Alkene	$\text{C}=\text{C}$	-ene	propene, $\text{CH}_3\text{CH}=\text{CH}_2$
Arene	benzene ring	phenyl- or -benzene	methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$
Halogenoalkane	$\text{C}-\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	fluoro-, chloro-, bromo-, iodo-	bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$
Alcohol	$-\text{OH}$	-ol	ethanol, $\text{CH}_3\text{CH}_2\text{OH}$
Aldehyde	$-\text{CHO}$	-al	ethanal, CH_3CHO
Ketone	$\text{C}=\text{O}$ between two carbons	-one	propanone, CH_3COCH_3
Carboxylic acid	$-\text{COOH}$	-oic acid	ethanoic acid, CH_3COOH
Ester	$-\text{COO}-$	-yl ...-oate	methyl ethanoate, $\text{CH}_3\text{COOCH}_3$
Amine (primary)	$-\text{NH}_2$	-amine	ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$
Nitrile	$-\text{C}\equiv\text{N}$	-nitrile	propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$
Acyl chloride	$-\text{COCl}$	-oyl chloride	ethanoyl chloride, CH_3COCl

Note: in a nitrile the carbon of $\text{C}\equiv\text{N}$ is counted in the chain, so $\text{CH}_3\text{CH}_2\text{CN}$ has three carbons and is propanenitrile.

2.4 Classifying alcohols and halogenoalkanes

Primary (1°): the carbon bonded to the functional group is bonded to one other carbon atom (or none, as in methanol).

Secondary (2°): the carbon bonded to the functional group is bonded to two other carbon atoms.

Tertiary (3°): the carbon bonded to the functional group is bonded to three other carbon atoms.

Examples: butan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, is primary; butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, is secondary; 2-methylpropan-2-ol, $(\text{CH}_3)_3\text{COH}$, is tertiary. The same idea applies to halogenoalkanes: 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, is tertiary.

3. IUPAC nomenclature

3.1 Stems

The stem tells you the number of carbon atoms in the longest chain that contains the functional group.

Carbons	1	2	3	4
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Stem	meth	eth	prop	but
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Carbons	5	6	7	8
Stem	pent	hex	hept	oct

Carbons	9	10
Stem	non	dec

Alkyl side chains take the same stem with -yl: methyl (CH_3-), ethyl (C_2H_5-), propyl (C_3H_7-).

3.2 Rules for naming

1. Find the **longest continuous carbon chain** that contains the main functional group. This gives the stem. (Chains can bend in a drawing; follow the bonds, not the straight line on the page.)
2. Identify the **main functional group**, which gives the suffix (-ol, -al, -one, -oic acid, -ene).
3. **Number the chain** from the end that gives the main functional group the lowest number. If there is no suffix group (or a tie), number to give the substituents the lowest numbers at the first point of difference.
4. Name **substituents** as prefixes (methyl, ethyl, chloro, bromo) with their position numbers.
5. Use **di-**, **tri-**, **tetra-** for repeated identical substituents, giving each one a number: 2,2-dimethyl.
6. Put prefixes in **alphabetical order**, ignoring di-, tri-: so 2-bromo-3-methyl, not 3-methyl-2-bromo.
7. Punctuation: **commas** between numbers, **hyphens** between numbers and letters, and no space between prefix and stem.

Aldehydes and carboxylic acids are always at carbon 1, so no number is needed (propanal, butanoic acid). In propanone and butanone the ketone position is fixed, so the number is usually left out, but pentan-2-one and pentan-3-one need it.

Worked example. Name $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$.

Longest chain: 5 carbons, so pentane.

Substituents: a methyl and a chloro. Numbering from the left: methyl on C2, chloro on C3, set {2,3}. Numbering from the right: chloro on C3, methyl on C4, set {3,4}. First point of difference: 2 is lower than 3, so number from the left.

Alphabetical order: chloro before methyl.

Name: **3-chloro-2-methylpentane**.

Worked example. Name $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{OH}$.

Longest chain containing the OH and the $\text{C}=\text{C}$: 4 carbons. The main group is OH, so number from the CH_2OH end: OH on C1, methyl on C2, $\text{C}=\text{C}$ between C3 and C4.

Name: **2-methylbut-3-en-1-ol**. (The -e of "ene" is dropped before a vowel suffix, so "en-1-ol".)

3.3 Naming esters

An ester is named from the alcohol part (as an alkyl group) and the acid part (as -oate). The alkyl group from the alcohol comes first as a separate word.

Worked example. $\text{CH}_3\text{CH}_2\text{COOCH}_3$ is made from propanoic acid and methanol. The acid part ($\text{CH}_3\text{CH}_2\text{COO}-$, three carbons including the $\text{C}=\text{O}$ carbon) is propanoate; the alcohol part ($-\text{CH}_3$) is methyl. Name: **methyl propanoate**.

3.4 Naming drills

Cover the right-hand column and name each compound, then check.

Structural formula	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	butane
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$	methylpropane (2-methylpropane)
$(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$	2,2-dimethylbutane
$\text{CH}_3\text{CH}=\text{CHCH}_3$	but-2-ene
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_3$	methylpropene (2-methylpropene)
$\text{CH}_3\text{CHBrCH}_3$	2-bromopropane
$\text{CH}_2\text{ClCH}_2\text{Cl}$	1,2-dichloroethane
$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	butan-2-ol
$\text{HOCH}_2\text{CH}_2\text{OH}$	ethane-1,2-diol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	butanal
$\text{CH}_3\text{COCH}_2\text{CH}_3$	butanone
$\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$	2-methylpropanoic acid
$\text{HCOOCH}_2\text{CH}_3$	ethyl methanoate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	butanenitrile
$\text{CH}_3\text{CHClCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	2-chloro-3-methylpentane
$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine (ethanamine)

Exam tip. The most common naming errors are: choosing a chain that is not the longest (a chain drawn with a bend), numbering from the wrong end, forgetting to repeat numbers with di- (write 2,2-dimethyl, not 2-dimethyl), and putting prefixes in numerical rather than alphabetical order.

4. Bond fission and reactive species

4.1 Homolytic and heterolytic fission

Homolytic fission: the breaking of a covalent bond in which each atom takes one electron from the shared pair, forming two free radicals.

Heterolytic fission: the breaking of a covalent bond in which one atom takes both electrons from the shared pair, forming a positive ion and a negative ion.

Homolytic fission: $\text{Cl}-\text{Cl} \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$. It happens with non-polar bonds and needs energy, often from ultraviolet light or high temperature.

Heterolytic fission: $(\text{CH}_3)_3\text{C}-\text{Br} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. It happens most easily with polar bonds; the more electronegative atom takes both electrons.

Curly arrows. A full curly arrow (double-headed) shows the movement of a pair of electrons, from a lone pair or a bond, to where the new bond forms or to the atom that receives the pair. A half-headed (fish-hook) arrow shows the movement of a single electron, as in homolytic fission. In a mechanism the arrow must start at a bond or a lone pair, never at an atom's symbol alone.

4.2 Free radicals

Free radical: a species with one or more unpaired electrons.

Free radicals are very reactive because the unpaired electron readily pairs up with another electron. They are shown with a dot: $\text{Cl}\cdot$, $\text{CH}_3\cdot$. Free radical reactions occur in three stages: **initiation** (radicals formed, often by UV light), **propagation** (a radical reacts to form a product and a new radical, so the chain continues), and **termination** (two radicals join, removing radicals).

4.3 Nucleophiles and electrophiles

Nucleophile: a species that can donate a pair of electrons to form a new covalent bond (an electron pair donor).

Electrophile: a species that can accept a pair of electrons to form a new covalent bond (an electron pair acceptor).

Nucleophiles have a lone pair of electrons and are often negatively charged or have a δ^- atom: OH^- , CN^- , NH_3 , H_2O . They are attracted to electron-deficient carbon atoms, such as the δ^+ carbon in a C–Br bond.

Electrophiles are electron deficient: positive ions or species with a δ^+ atom, such as H^+ , NO_2^+ , and a Br_2 molecule that becomes polarised ($\text{Br}^{\delta+}-\text{Br}^{\delta-}$) as it approaches the electron-rich $\text{C}=\text{C}$ bond of an alkene. They are attracted to regions of high electron density, such as $\text{C}=\text{C}$ double bonds.

4.4 Carbocations and inductive effect

A **carbocation** is an ion with a positively charged carbon atom, formed by heterolytic fission or by an electrophile adding to an alkene. Carbocations are classed as primary, secondary or tertiary by the number of alkyl groups attached to the positive carbon. Alkyl groups have a positive inductive effect: they push electron density towards the positive carbon, spreading out the charge. So stability increases in the order primary < secondary < tertiary. This explains which product is the major one when an unsymmetrical alkene adds HBr (Markovnikov addition: the more stable carbocation intermediate is formed).

5. Types of organic reaction

5.1 The reaction types to learn

Addition: a reaction in which two molecules join to form one product molecule (typical of alkenes).

Substitution: a reaction in which one atom or group of atoms is replaced by another atom or group.

Elimination: a reaction in which a small molecule (such as H_2O or HBr) is removed from a larger molecule, usually forming a $\text{C}=\text{C}$ bond.

Hydrolysis: a reaction in which a compound is broken down by reaction with water (often catalysed by acid or alkali).

Condensation: a reaction in which two molecules join together with the loss of a small molecule such as water.

Oxidation: in organic chemistry, addition of oxygen or removal of hydrogen, shown in equations as $[\text{O}]$.

Reduction: addition of hydrogen or removal of oxygen, shown in equations as $[\text{H}]$.

5.2 Combining reaction type with attacking species

Mechanism names combine the attacking species with the type of reaction.

Mechanism	Example	Equation
Free radical substitution	methane + chlorine in UV light	$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$
Electrophilic addition	ethene + bromine	$\text{CH}_2=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br}$
Nucleophilic substitution	bromoethane + aqueous hydroxide ions, heated	$\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Br}^-$
Nucleophilic addition	ethanal + hydrogen cyanide (with CN^- catalyst)	$\text{CH}_3\text{CHO} + \text{HCN} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$
Elimination	bromoethane + ethanolic hydroxide ions, heated	$\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{Br}^-$

Worked example: classify the reaction. Ethanol is heated with excess hot concentrated sulfuric acid (or passed over hot aluminium oxide) to make ethene: $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$. One molecule becomes two smaller ones, water is removed and a $\text{C}=\text{C}$ bond forms. This is **elimination** (specifically dehydration).

Exam tip. The solvent decides between substitution and elimination for a halogenoalkane with hydroxide: **aqueous** NaOH gives an alcohol (substitution); **ethanolic** NaOH gives an alkene (elimination). Always state the solvent and "heat under reflux".

6. Isomerism

Isomers: compounds with the same molecular formula but different arrangements of atoms.

Structural isomers: compounds with the same molecular formula but different structural formulae.

Stereoisomers: compounds with the same molecular formula and the same structural formula but a different arrangement of atoms in space.

6.1 Structural isomerism

There are three kinds.

- **Chain isomerism:** different arrangement of the carbon skeleton (straight or branched). C_4H_{10} : butane, $CH_3CH_2CH_2CH_3$, and methylpropane, $CH_3CH(CH_3)CH_3$.
- **Position isomerism:** the same functional group at a different position on the same carbon skeleton. C_3H_7OH : propan-1-ol and propan-2-ol. C_4H_8 : but-1-ene and but-2-ene.
- **Functional group isomerism:** different functional groups. C_3H_6O : propanal (aldehyde) and propanone (ketone). C_2H_6O : ethanol (alcohol) and methoxymethane, CH_3OCH_3 (ether). $C_3H_6O_2$: propanoic acid and methyl ethanoate. Alkenes and cycloalkanes with the same formula, such as propene and cyclopropane (C_3H_6), are also isomers of different series.

Worked example: isomers of C_5H_{12} . Work systematically by shortening the longest chain.

Longest chain 5: pentane, $CH_3CH_2CH_2CH_2CH_3$.

Longest chain 4 with one methyl: 2-methylbutane, $CH_3CH(CH_3)CH_2CH_3$. (A methyl on C1 just lengthens the chain, and "3-methylbutane" is the same molecule numbered from the other end.)

Longest chain 3 with two methyls: 2,2-dimethylpropane, $C(CH_3)_4$.

There are **three** structural isomers. Branching lowers the boiling point because branched molecules have less surface contact, so London forces are weaker.

6.2 Stereoisomerism: geometrical (cis-trans) isomerism

Rotation about a $C=C$ double bond is restricted because the π bond would have to break. If **each** carbon of the $C=C$ has **two different** atoms or groups attached, two arrangements are possible.

- **cis isomer:** the two identical (or matching) groups are on the same side of the double bond.
- **trans isomer:** the two identical groups are on opposite sides.

Example: but-2-ene, $CH_3CH=CHCH_3$. In cis-but-2-ene both CH_3 groups are on the same side; in trans-but-2-ene they are on opposite sides. Draw both with the $C=C$ horizontal and bond angles of about 120° around each carbon.

But-1-ene, $CH_2=CHCH_2CH_3$, has **no** cis-trans isomers because the first carbon carries two identical H atoms. Likewise 2-methylpropene has none, because one carbon carries two CH_3 groups.

Condition for cis-trans isomerism (learn): a $C=C$ double bond, with two different groups attached to each carbon atom of the double bond.

Cis and trans isomers have the same chemical reactions in most cases but can have different physical properties such as melting point and boiling point, because the shape of the molecule changes how closely molecules pack and the overall dipole.

Restricted rotation also occurs in rings, but the Cambridge AS requirement centres on $C=C$ bonds.

6.3 Stereoisomerism: optical isomerism

Chiral centre: a carbon atom with four different atoms or groups attached to it.

Optical isomers (enantiomers): stereoisomers that are non-superimposable mirror images of each other.

A molecule with one chiral centre exists as two optical isomers. They are drawn in three dimensions, with the chiral carbon at the centre of a tetrahedron (bond angle about 109.5°): two bonds in the plane of the paper drawn as lines, one coming towards you as a solid wedge, one going away as a dashed (hashed) wedge. The second isomer is drawn as the mirror image.

Enantiomers have identical physical properties (melting point, boiling point, density) and identical chemical properties with most reagents. They differ in the direction they **rotate plane-polarised light**: one rotates it clockwise, the other anticlockwise, by the same angle. They can also behave differently with other chiral molecules, which is why one enantiomer of a drug may be effective and the other inactive or harmful.

Racemic mixture: a mixture containing equal amounts of the two enantiomers. It has no effect on plane-polarised light because the rotations cancel.

Worked example: finding chiral centres. Does butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, have a chiral centre?

Look at C2. Its four groups are: H, OH, CH_3 and CH_2CH_3 . All four are different, so C2 is a chiral centre and butan-2-ol has two optical isomers.

Propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$: C2 carries H, OH and two identical CH_3 groups, so it is **not** chiral.

Tips for spotting chiral centres: a CH_3 , CH_2 or $\text{C}=\text{O}$ carbon, or a carbon in a $\text{C}=\text{C}$ bond, can never be a chiral centre (it cannot have four different groups). Look for carbons with one H and three different groups, or with no H and four different groups. A common exam context is 2-hydroxypropanoic acid (lactic acid), $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, whose C2 carries H, OH, CH_3 and COOH .

6.4 Counting isomers that combine types

Worked example. How many isomers (including stereoisomers) are there for alkenes of formula C_4H_8 ?

Structural isomers that are alkenes: but-1-ene, but-2-ene and methylpropene.

But-2-ene has cis and trans forms; the other two do not.

Total alkene isomers = $1 + 2 + 1 = 4$. (If the question asks for all isomers of C_4H_8 , cyclobutane and methylcyclopropane must be added, giving 6.)

Quick check

1. Define the terms *homologous series* and *functional group*. [3]
2. For 2-methylpropan-1-ol give (a) the molecular formula, (b) the structural formula, (c) the empirical formula, and (d) describe its skeletal formula. [4]
3. A compound contains 54.5% C, 9.1% H and 36.4% O by mass, and has $M_r = 88$. Calculate its empirical and molecular formulae. (A_r : C = 12.0, H = 1.0, O = 16.0) [4]
4. Name the following: (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, (b) $\text{CH}_3\text{CHBrCHBrCH}_3$, (c) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$, (d) $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$. [4]
5. Draw (describe) the structural formula of (a) 3-methylbut-1-ene, (b) 2,3-dimethylpentan-2-ol, (c) 1,1,2-trichloroethane. [3]

6. A student named a compound "2-ethylpropane". Explain why this name is wrong and give the correct name. [2]
7. Classify each alcohol as primary, secondary or tertiary: (a) propan-2-ol, (b) 2-methylbutan-2-ol, (c) 2-methylpropan-1-ol. [3]
8. Explain the difference between homolytic and heterolytic fission, using the C–Cl bond in chloromethane as an example of each. [4]
9. Define *nucleophile* and *electrophile*. Classify each of the following as nucleophile, electrophile or free radical: CN^- , H^+ , $\text{Br}^\bullet$, NH_3 , NO_2^+ . [5]
10. Classify each reaction as addition, substitution, elimination, hydrolysis, oxidation or condensation: (a) $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$; (b) $\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr}$; (c) $\text{CH}_3\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$; (d) $\text{CH}_3\text{CHBrCH}_3 + \text{OH}^- \text{ (ethanolic)} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O} + \text{Br}^-$. [4]
11. Explain why a tertiary carbocation is more stable than a primary carbocation. [2]
12. Name and give the structural formulae of the four structural isomers of $\text{C}_4\text{H}_9\text{Br}$. [4]
13. Explain why pent-2-ene shows cis-trans isomerism but pent-1-ene does not. [3]
14. Identify the chiral centre in 2-hydroxypropanoic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, explain how its two optical isomers differ in their physical properties, and describe how you would draw them. [4]
15. Compound X, $\text{C}_4\text{H}_{10}\text{O}$, is an alcohol that has a chiral centre. Identify X, explain your reasoning, and name one functional group isomer of X. [4]

1. A homologous series is a family of compounds with the same functional group and general formula, similar chemical properties, each member differing from the next by CH_2 , with a gradual trend in physical properties. A functional group is an atom or group of atoms responsible for the characteristic chemical reactions of a molecule.
2. (a) $\text{C}_4\text{H}_{10}\text{O}$. (b) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$. (c) $\text{C}_4\text{H}_{10}\text{O}$, since 4 : 10 : 1 has no common factor. (d) Two lines meeting at C2 (from C3 to C2 to C1), a third line from C2 for the methyl branch, and a line from C1 ending in OH. No C or H labels are drawn on the carbon chain.
3. Moles: $\text{C} = 54.5 \div 12.0 = 4.54$; $\text{H} = 9.1 \div 1.0 = 9.1$; $\text{O} = 36.4 \div 16.0 = 2.275$. Divide by the smallest (2.275): $\text{C} = 2.00$, $\text{H} = 4.00$, $\text{O} = 1.00$. Empirical formula $\text{C}_2\text{H}_4\text{O}$, mass of empirical unit = $24.0 + 4.0 + 16.0 = 44.0$. $n = 88 \div 44 = 2$. Molecular formula $\text{C}_4\text{H}_8\text{O}_2$.
4. (a) Longest chain 5 carbons with a methyl on C3 (same from either end): 3-methylpentane. (b) Four carbons, Br on C2 and C3: 2,3-dibromobutane. (c) Five carbons with $\text{C}=\text{O}$ on C3: pentan-3-one. (d) Acid part $\text{CH}_3\text{CH}_2\text{COO}^-$ has three carbons (propanoate), alcohol part $-\text{CH}_2\text{CH}_3$ is ethyl: ethyl propanoate.
5. (a) $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_3$: four-carbon chain, double bond from C1 to C2, methyl on C3. (b) $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$: five-carbon chain, C2 carries OH and a methyl, C3 carries a methyl. (c) $\text{CHCl}_2\text{CH}_2\text{Cl}$: two carbons, two Cl on C1 and one Cl on C2.
6. The longest chain has not been chosen. The structure is $\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_3$, and following the bonds through the ethyl group gives a four-carbon chain with a methyl on C2. The correct name is 2-methylbutane (often written methylbutane).
7. (a) Secondary: the C bearing OH is bonded to two carbons. (b) Tertiary: the C bearing OH (C2) is bonded to three carbons (C1, C3 and the methyl). (c) Primary: the C bearing OH (C1) is bonded to only one carbon.

- 8.** In homolytic fission each atom takes one electron from the shared pair, forming two free radicals: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\cdot + \text{Cl}\cdot$. In heterolytic fission one atom takes both electrons, forming ions. Chlorine is more electronegative than carbon, so it takes the pair: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$. Homolytic fission is shown with half-headed arrows (one electron each); heterolytic with a full curly arrow from the bond to Cl.
- 9.** A nucleophile is an electron pair donor; an electrophile is an electron pair acceptor. CN^- : nucleophile (lone pair on C, negative charge). H^+ : electrophile (positive, can accept a pair). $\text{Br}\cdot$: free radical (unpaired electron). NH_3 : nucleophile (lone pair on N). NO_2^+ : electrophile (positive ion).
- 10.** (a) Addition: two molecules form one product (hydration of ethene). (b) Substitution: an H atom is replaced by Br (free radical substitution, in UV light). (c) Oxidation: hydrogen is removed from ethanol to form ethanal. (d) Elimination: HBr is removed (as H_2O and Br^- with OH^-) and a $\text{C}=\text{C}$ forms.
- 11.** Alkyl groups have a positive inductive effect: they donate (push) electron density towards the positively charged carbon. A tertiary carbocation has three alkyl groups, a primary only one, so in the tertiary ion the positive charge is spread out (reduced) more, making it more stable.
- 12.** 1-bromobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$; 2-bromobutane, $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$; 1-bromo-2-methylpropane, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$; 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$. The first two are position isomers of each other, and chain isomers of the last two.
- 13.** Pent-2-ene is $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$. Rotation about the $\text{C}=\text{C}$ bond is restricted, and each carbon of the double bond has two different groups (C2 has H and CH_3 ; C3 has H and C_2H_5), so cis and trans forms exist. Pent-1-ene is $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$: C1 carries two identical H atoms, so swapping groups gives the same molecule and there are no cis-trans isomers.
- 14.** The chiral centre is C2, which carries four different groups: H, OH, CH_3 and COOH . The two enantiomers have identical melting points, boiling points and densities, but rotate plane-polarised light by equal angles in opposite directions. To draw them: place C2 at the centre, draw two bonds in the plane of the paper as plain lines, one bond towards the viewer as a solid wedge and one away as a hashed wedge, and attach the four groups; then draw the second molecule as the mirror image across a dashed vertical line.
- 15.** The alcohols of formula $\text{C}_4\text{H}_{10}\text{O}$ are butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol. Check each for a carbon with four different groups. Butan-1-ol: C1 has two H atoms, not chiral. Butan-2-ol: C2 carries H, OH, CH_3 and C_2H_5 , all different, so it is chiral. 2-methylpropan-1-ol: C2 carries two CH_3 groups, not chiral. 2-methylpropan-2-ol: C2 carries three CH_3 groups, not chiral. So X is butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$. A functional group isomer is an ether with the same formula, for example ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (or methoxypropane, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$).