

An introduction to AS Level organic chemistry

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Read first: Atoms, molecules and stoichiometry, Chemical bonding

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What you need to know

By the end of this topic you should be able to:

1. Formulas, functional groups and names (13.1)

- (a) Say what a **hydrocarbon** is: a compound of carbon and hydrogen atoms only.
- (b) Know that **alkanes** are the simplest hydrocarbons and have **no functional group**.
- (c) Know that the other classes in the syllabus each have a **functional group**, and that this group decides how the compound behaves, physically and chemically. The classes are: alkenes, halogenoalkanes (primary, secondary, tertiary), alcohols (primary, secondary, tertiary), aldehydes, ketones, carboxylic acids, esters, primary amines and nitriles.
- (d) Read and write the **general, structural, displayed and skeletal** formulas of these classes.
- (e) **Name** simple non-ring (aliphatic) molecules containing these groups with up to six carbon atoms (an ester can have up to six on each side), and draw a molecule from its name. Esters and nitriles are only asked with straight chains.
- (f) Work out the **molecular** and **empirical** formula of a compound from its structural, displayed or skeletal formula.

2. The words for reactions (13.2)

- (a) Use these terms correctly: homologous series; saturated and unsaturated; homolytic and heterolytic fission; free radical, initiation, propagation, termination; nucleophile, electrophile, nucleophilic, electrophilic; addition, substitution, elimination, hydrolysis, condensation; oxidation and reduction, including writing [O] for one oxygen atom from an oxidising agent and [H] for one hydrogen atom from a reducing agent.
- (b) Use the names of the four mechanisms: free-radical substitution, electrophilic addition, nucleophilic substitution and nucleophilic addition, and draw curly arrows that start at a bond or a lone pair.

3. Shapes, σ and π bonds (13.3)

- (a) Describe a molecule as straight-chained, branched or cyclic.
- (b) Describe and explain the shape and bond angles around sp , sp^2 and sp^3 atoms.
- (c) Describe how the σ and π bonds are arranged around these atoms.

- (d) Use the word **planar** for atoms that all lie in one flat plane, as in ethene.

4. Isomerism (13.4)

- (a) Describe **structural isomerism** and its three kinds: chain, positional and functional group.
- (b) Describe **stereoisomerism** and its two kinds: geometrical (cis/trans) and optical. (E/Z names are accepted but not needed.)
- (c) Describe cis/trans isomerism in alkenes and explain that it comes from restricted rotation caused by the π bond.
- (d) Explain what a **chiral centre** is and that one chiral centre gives two optical isomers (enantiomers). A molecule can have more than one chiral centre; meso compounds and the word "diastereoisomer" are not needed.
- (e) Find the chiral centres and any cis/trans isomerism in a given structure, including ring compounds.
- (f) Work out the possible isomers of a given molecular formula.

Understand it

Hydrocarbons and functional groups

Organic chemistry is the chemistry of carbon compounds. Carbon forms four covalent bonds and bonds strongly to other carbon atoms, so it builds chains, branches and rings of almost any size.

A **hydrocarbon** contains only carbon and hydrogen. **Alkanes** such as propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, contain only C–C and C–H single bonds. They are **saturated** (no multiple bonds between carbon atoms) and have no functional group, which is why they react so little.

A **functional group** is the atom or group of atoms that gives a class of compounds its reactions: the C=C in alkenes, the –OH in alcohols, and so on. Molecules with the same functional group react in the same way whatever the length of their carbon chain. A molecule with a C=C or $\text{C}\equiv\text{C}$ bond is **unsaturated**.

A **homologous series** is a family of compounds with the **same general formula** and the **same functional group**, so they have **similar chemical properties**. Each member differs from the next by CH_2 , and physical properties such as boiling point change gradually along the series.

Homologous series	Functional group	General formula	Three-carbon example
alkane	none	$\text{C}_n\text{H}_{2n+2}$	propane, $\text{CH}_3\text{CH}_2\text{CH}_3$
alkene	C=C	C_nH_{2n}	propene, $\text{CH}_2=\text{CHCH}_3$
halogenoalkane	C–X (X = F, Cl, Br, I)	$\text{C}_n\text{H}_{2n+1}\text{X}$	1-chloropropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
alcohol	–OH (hydroxyl)	$\text{C}_n\text{H}_{2n+1}\text{OH}$	propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
aldehyde	–CHO (carbonyl at the end of the chain)	$\text{C}_n\text{H}_{2n}\text{O}$	propanal, $\text{CH}_3\text{CH}_2\text{CHO}$

Homologous series	Functional group	General formula	Three-carbon example
ketone	C=O inside the chain (carbonyl)	$C_nH_{2n}O$	propanone, CH_3COCH_3
carboxylic acid	$-COOH$ (carboxyl)	$C_nH_{2n}O_2$	propanoic acid, CH_3CH_2COOH
ester	$-COO-$	$C_nH_{2n}O_2$	methyl ethanoate, CH_3COOCH_3
amine (primary)	$-NH_2$	$C_nH_{2n+1}NH_2$	propylamine, $CH_3CH_2CH_2NH_2$
nitrile	$-C\equiv N$	$C_nH_{2n+1}CN$	propanenitrile, CH_3CH_2CN

(For aldehydes, ketones, acids and esters, n counts every carbon; for the others the formula is written around the alkyl group C_nH_{2n+1} .) Notice that aldehydes and ketones share a general formula, and so do acids and esters: these pairs can be isomers of each other.

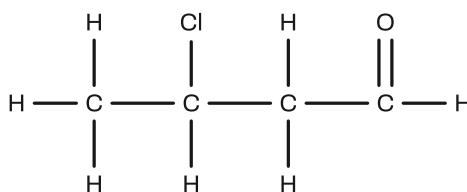
The syllabus writes **R** for an alkyl group (and sometimes H), and **X** for a halogen atom.

Primary, secondary, tertiary. For an alcohol or halogenoalkane, look at the carbon carrying the $-OH$ or $-X$ and count the carbon atoms joined to it: one (or none, as in methanol) is **primary**, two is **secondary**, three is **tertiary**. Propan-1-ol is primary, propan-2-ol is secondary and 2-methylpropan-2-ol is tertiary.

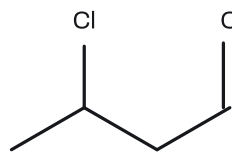
Six kinds of formula

Formula	What it shows	3-chlorobutanal
general	the pattern for a whole series	$C_nH_{2n}O$ family (with one H swapped for Cl)
structural	each carbon with what is attached to it, written in a line, with no ambiguity	$CH_3CHClCH_2CHO$
displayed	every atom and every bond (including O–H)	see the figure
skeletal	carbon chain as zigzag lines; C atoms and the H atoms on carbon are left out; every other atom is written	see the figure
molecular	the actual number of each atom	C_4H_7ClO
empirical	the simplest whole-number ratio of atoms	C_4H_7ClO (it cannot be divided down)

3-chlorobutanal, $\text{CH}_3\text{CHClCH}_2\text{CHO}$ (structural formula)



displayed formula



skeletal formula

Reading a skeletal formula. Every corner and every line end is a carbon atom, unless another atom is written there. Each carbon makes four bonds, so fill in hydrogens: a line end with one bond is CH_3 , a corner with two bonds is CH_2 , a carbon with three bonds is CH , one with four bonds has no H. A double line counts as two bonds. H atoms on O and N are written in ($-\text{OH}$, $-\text{NH}_2$).

Empirical formula. Divide the molecular formula by the largest number that goes into every subscript: but-2-ene C_4H_8 gives CH_2 ; ethanoic acid $\text{C}_2\text{H}_4\text{O}_2$ gives CH_2O .

Naming

1. **Find the longest carbon chain that contains the functional group.** Its length gives the stem: meth (1), eth (2), prop (3), but (4), pent (5), hex (6).
2. **Add the ending for the main group:** -ane (alkane), -ene, -ol, -al, -one, -oic acid, -nitrile. Halogens are prefixes: chloro-, bromo-. If there is a second group, the lower-priority one becomes a prefix, for example hydroxy- for an $-\text{OH}$ in a molecule that also has a $\text{C}=\text{O}$ group.
3. **Number the chain from the end that gives the main group the lowest number**, then the side chains and prefixes. Aldehydes, acids and nitriles always have their group on carbon 1, so no number is needed. In a nitrile the carbon of $\text{C}\equiv\text{N}$ counts in the chain: $\text{CH}_3\text{CH}_2\text{CN}$ is propanenitrile.
4. **Put the prefixes in alphabetical order**, with di- or tri- when a group appears two or three times (2,3-dichloropentane). Commas go between numbers and hyphens between numbers and words.
5. **Esters** are named from the alcohol part first, then the acid part: $\text{CH}_3\text{CH}_2\text{COOCH}_3$ comes from methanol and propanoic acid, so it is **methyl propanoate**.
6. **Amines** in the syllabus are named from the alkyl group: propylamine.

How organic reactions are described

Breaking a covalent bond can happen two ways:

- **homolytic fission:** each atom keeps one of the two bonding electrons, making two **free radicals** (species with an unpaired electron), for example $\text{Br}_2 \rightarrow 2\text{Br}\bullet$ in ultraviolet light;
- **heterolytic fission:** one atom takes both electrons, making a positive and a negative ion.

A **nucleophile** donates a lone pair of electrons to an electron-poor ($\delta+$) carbon; examples are OH^- , CN^- and NH_3 . An **electrophile** accepts a pair of electrons from an electron-rich region such as a $\text{C}=\text{C}$ bond; examples are H^+ , $\text{Br}^{\delta+}$ in a polarised Br_2 molecule, and carbocations. "Nucleophilic" and "electrophilic" describe the attacking species in a mechanism.

Types of reaction:

Type	What happens
addition	two molecules join to make one product (typical of $\text{C}=\text{C}$ and $\text{C}=\text{O}$)
substitution	one atom or group is swapped for another
elimination	a small molecule (such as H_2O or HBr) is removed from one molecule, leaving a $\text{C}=\text{C}$
hydrolysis	a bond is broken by reaction with water (often with acid or alkali)
condensation	two molecules join and a small molecule, usually water, is lost
oxidation	gain of oxygen or loss of hydrogen; written with $[\text{O}]$
reduction	gain of hydrogen or loss of oxygen; written with $[\text{H}]$

For example, oxidising propan-1-ol to propanal: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$. Balance the atoms as usual; $[\text{O}]$ and $[\text{H}]$ count as one atom each.

The four AS mechanisms combine a reagent type with a reaction type:

Mechanism	Typical example (met in later topics)
free-radical substitution	alkane + Cl_2 in UV light; steps are initiation, propagation, termination
electrophilic addition	alkene + Br_2 or HBr
nucleophilic substitution	halogenoalkane + OH^- or CN^-
nucleophilic addition	aldehyde or ketone + HCN

In a free-radical chain, **initiation** makes radicals, **propagation** steps use one radical and make another, and **termination** joins two radicals so the chain stops. In mechanism diagrams a **curly arrow** shows a pair of electrons moving; it must start at a bond or a lone pair and point to where the pair ends up.

Shapes: sp^3 , sp^2 and sp carbon

A carbon atom mixes (hybridises) its outer s and p orbitals in one of three ways, depending on how many other atoms it bonds to:

Carbon with	Hybridisation	σ bonds	Unhybridised p orbitals	Shape and angle
four single bonds	sp^3	4	0	tetrahedral, 109.5°

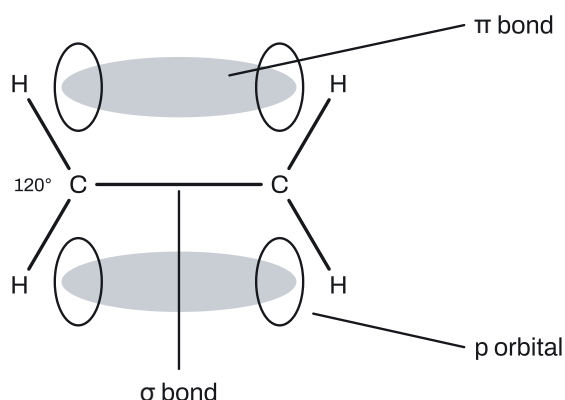
Carbon with	Hybridisation	σ bonds	Unhybridised p orbitals	Shape and angle
one double bond	sp^2	3	1 (used in the π bond)	trigonal planar, 120°
one triple bond (or two double bonds)	sp	2	2 (used in two π bonds)	linear, 180°

The hybrid orbitals point as far apart as possible, which is why the angles are 109.5° , 120° and 180° .

Hybridisation belongs to atoms, not bonds.

A **σ bond** forms by **head-on** overlap of orbitals along the line between the two nuclei. A **π bond** forms by **sideways** overlap of two p orbitals, above and below that line. So:

- a single bond is 1 σ ;
- a double bond is 1 σ + 1 π ;
- a triple bond is 1 σ + 2 π .



Because the p orbitals must line up for sideways overlap, the two carbons of a $C=C$ and the four atoms joined to them all lie in one plane: ethene is **planar**. Methanal and benzene are planar too. A molecule with an sp^3 carbon that carries two or more other atoms, such as ethane or a cyclohexane ring, is **not** planar. Other atoms follow the same idea: the N in a nitrile $C\equiv N$ is sp , and an O in a $C=O$ bond forms one σ and one π bond.

Counting σ bonds quickly. In a molecule with A atoms and R rings, the number of σ bonds is $A - 1 + R$ (ethene: $6 - 1 = 5$; cyclohexane, C_6H_{12} : $18 - 1 + 1 = 18$). Then count π bonds from the double and triple bonds. Remember that every C–H and O–H bond is a σ bond.

Isomerism

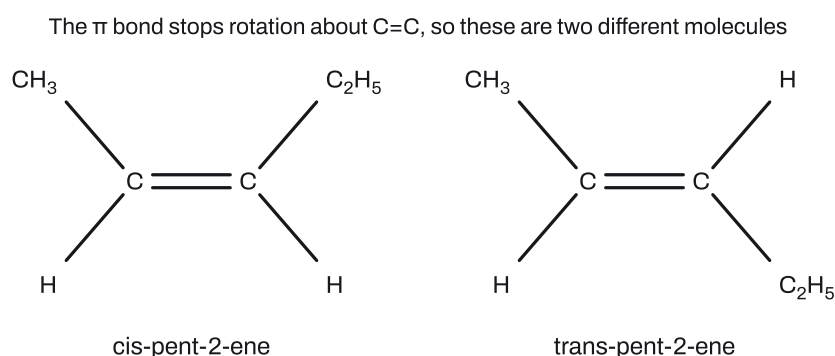
Isomers have the same molecular formula but are different compounds.

Structural isomers have the same molecular formula but a **different structural formula** (atoms joined in a different order). There are three kinds:

- **chain:** a different carbon skeleton, for example pentane, 2-methylbutane and 2,2-dimethylpropane (C_5H_{12});
- **positional:** the same functional group on a different carbon, for example propan-1-ol and propan-2-ol;
- **functional group:** a different functional group, for example butanal and butanone (C_4H_8O), or an acid and an ester.

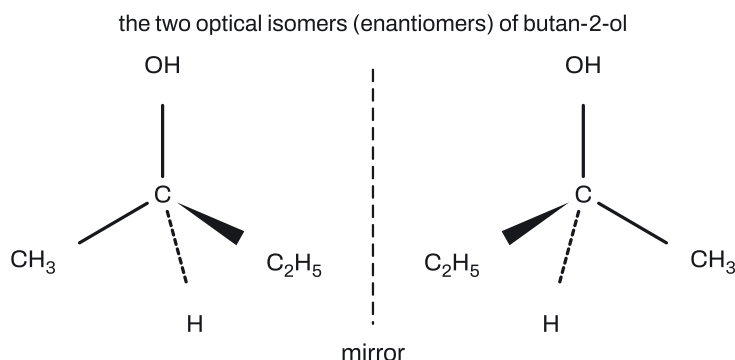
Stereoisomers have the same molecular **and** structural formula but a **different arrangement of their atoms in space**. There are two kinds.

Geometrical (cis/trans) isomerism. A $C=C$ bond cannot rotate, because turning one end would twist the p orbitals apart and break the π bond. So groups fixed on the same side stay on the same side. Two isomers exist when **each** carbon of the $C=C$ carries **two different** atoms or groups. In the **cis** isomer the matching groups are on the same side; in the **trans** isomer they are on opposite sides.



Pent-1-ene, $CH_2=CHCH_2CH_2CH_3$, has no cis/trans isomers because its end carbon carries two identical H atoms. A $C=C$ inside a ring of six or fewer atoms, as in cyclohexene, can only be arranged one way, so it gives no cis/trans isomers.

Optical isomerism. A **chiral centre** is a carbon atom bonded to **four different atoms or groups**. Such a molecule has two forms that are **mirror images** of each other and **cannot be superimposed**, like your left and right hands. These are the two **optical isomers** (enantiomers). Draw them in 3D: two bonds in the plane of the paper, one wedge (towards you) and one dashed (away from you), then reflect the whole drawing.



To test a carbon, list its four groups **all the way along each chain**. In 3-methylhexane, $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$, carbon 3 carries H, CH_3 , C_2H_5 and C_3H_7 : four different groups, so it is chiral. In 3-methylpentane the same carbon carries two C_2H_5 groups, so it is not. A carbon with two H atoms,

or with a double bond, can never be a chiral centre. In rings, go round the ring both ways: the carbon is chiral if the two paths are different.

Counting stereoisomers. Each chiral centre and each C=C that shows cis/trans isomerism doubles the number of arrangements. With n such features, the number of stereoisomers is 2^n (multiply, never add: three features give $2 \times 2 \times 2 = 8$, not 6). If the molecule is symmetrical, some combinations turn out to be the same molecule, so check.

Key facts and formulas

"Given" means it is printed on the Periodic Table in the exam paper. "Learn it" means you must remember it; the Data Booklet does not list organic formulas, names or shapes.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, Cl 35.5, Br 79.9	Given
General formulas: alkane C_nH_{2n+2} ; alkene C_nH_{2n} ; halogenoalkane $C_nH_{2n+1}X$; alcohol $C_nH_{2n+1}OH$; aldehyde and ketone $C_nH_{2n}O$; acid and ester $C_nH_{2n}O_2$; amine $C_nH_{2n+1}NH_2$; nitrile $C_nH_{2n+1}CN$	Learn it
Stems: meth 1, eth 2, prop 3, but 4, pent 5, hex 6; endings -ane, -ene, -ol, -al, -one, -oic acid, -nitrile, alkyl alkanoate, alkylamine	Learn it
sp^3 : tetrahedral, 109.5° ; sp^2 : trigonal planar, 120° ; sp : linear, 180°	Learn it
Single bond = 1σ ; double = $1 \sigma + 1 \pi$; triple = $1 \sigma + 2 \pi$	Learn it
σ bonds in a molecule = $A - 1 + R$ (A atoms, R rings)	Learn it
Stereoisomers = 2^n , n = chiral centres + C=C bonds showing cis/trans	Learn it
[O] = one O atom from an oxidising agent; [H] = one H atom from a reducing agent	Learn it
Primary / secondary / tertiary: 1 / 2 / 3 carbons joined to the carbon carrying -OH or -X	Learn it

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (119 questions, 2021–2025), the types came up this often. 44 of the 119 questions mix more than one type, so the counts add up to more than 119.

Question type	Questions
Identify or count chiral centres	26
Count σ and π bonds, state hybridisation, predict shape, planarity or bond angles	26
Deduce a molecular or empirical formula from a structure	22
Decide which stereoisomerism a compound shows, or count its stereoisomers	20
Name a reaction type, mechanism, bond fission, reagent role or reactive species	18
Draw structural isomers or name the type of structural isomerism	17
Count all the isomers of a molecular formula	15
Explain or define stereoisomerism and what causes it	14
Name a compound, or give its formula from a name	12
Identify functional groups, classify, use general formulas	11
Draw stereoisomers (cis/trans or 3D optical isomers)	10
Define a basic term	7

1. Identify or count chiral centres (26 questions)

Usually a multiple-choice question with a large skeletal formula (a steroid, a drug, a natural product).

1. **Skip every carbon that cannot be chiral:** CH_3 and CH_2 carbons, and any carbon in a $\text{C}=\text{C}$, $\text{C}=\text{O}$ or $\text{C}\equiv\text{N}$.
2. **For each remaining carbon** (CH or a carbon with no H), write down its four groups, remembering the hidden H in skeletal formulas.
3. **Compare the groups by following each branch outwards** until they differ. In a ring, go both ways round. If two branches are identical all the way, the carbon is not chiral.
4. Count, and mark each chiral centre with an asterisk (*) if asked.

Variations you will meet:

- **A name instead of a structure.** Draw it first, then test each carbon.
- **"After reaction with hydrogen"** ($\text{C}=\text{C}$ becomes $\text{C}-\text{C}$): redraw the product first, because new chiral centres can appear and ring or chain carbons change.
- **"Smallest alkane with a chiral centre":** you need a carbon with H, CH_3 , C_2H_5 and C_3H_7 attached, which is 3-methylhexane.
- **Molecular formula and chiral count together:** do both checks separately; a wrong H count loses the mark even when the chiral count is right.
- **A central CH with two identical halves** (a symmetrical molecule) is not chiral.

2. Count σ and π bonds, state hybridisation, predict shape, planarity or bond angles (26 questions)

1. **Draw the full displayed formula**, including every C–H and O–H.
2. **σ bonds**: count every bond once (or use $A - 1 + R$). **π bonds**: one per double bond, two per triple bond.
3. **Hybridisation of each carbon**: four single bonds sp^3 , one double bond sp^2 , a triple bond sp .
4. **Bond angle** around an atom: 109.5° (sp^3), 120° (sp^2), 180° (sp).

Variations you will meet:

- **Planarity**. A molecule is planar only if every atom lies in one plane: all sp^2 and sp centres with nothing sticking out. One CH_2 or CH_3 group in a ring or chain makes it non-planar.
- **Draw the π bond**. Draw a p orbital (two lobes) above and below each carbon, overlapping **sideways**, and label the overlap " π bond". Say the σ bond comes from head-on overlap.
- **What two molecules have in common**, for example ethane and ethene both contain σ bonds, but only ethene has a π bond and 120° angles.
- **Counting hybrid orbitals**: an sp^3 carbon has four sp^3 orbitals, an sp^2 carbon has three sp^2 orbitals, an sp carbon two sp orbitals.
- **Outer electrons on carbon in CH_3 species**: a carbocation CH_3^+ has 6 (an electrophile), a radical $\text{CH}_3^\bullet$ has 7, a carbanion CH_3^- has 8 (a nucleophile).

3. Deduce a molecular or empirical formula from a structure (22 questions)

1. **Count carbons**: every corner and line end without a letter.
2. **Count hydrogens carbon by carbon**: $4 - (\text{number of bonds drawn to that carbon})$, counting double bonds as two. Add the H atoms written on O and N.
3. **Count the other atoms** (O, N, halogens) from the letters.
4. **Empirical formula**: divide every number by the highest common factor.

Check: a non-ring molecule with only single bonds has the alkane pattern $\text{C}_n\text{H}_{2n+2}$ (O atoms don't change this); every ring or double bond ($\text{C}=\text{C}$ or $\text{C}=\text{O}$) takes away 2 H, a triple bond 4 H. 3-Methylcyclohex-2-en-1-one has 7 carbons, 1 ring, a $\text{C}=\text{C}$ and a $\text{C}=\text{O}$: $16 - 2 - 2 - 2 = 10$ H, so it is $\text{C}_7\text{H}_{10}\text{O}$.

Variations you will meet: the formula of a **product** (write the product's structure first, for example an ester loses H_2O when it forms); **choose which structure** has a given formula; give the **empirical** formula when the molecular one is bigger (a symmetrical molecule often cancels down).

4. Decide which stereoisomerism a compound shows, or count its stereoisomers (20 questions)

1. **Draw or read the structure**, including H atoms.
2. **Check every $\text{C}=\text{C}$** not inside a small ring: does each carbon carry two different groups? If yes, it shows cis/trans isomerism.

3. **Check every sp^3 carbon** for four different groups: each is a chiral centre and gives optical isomerism.

4. **Name the type** (geometrical, optical, both or neither), or **count** stereoisomers as 2^n .

Variations you will meet: pick the one compound out of four names that shows stereoisomerism (draw all four quickly; a $=CH_2$ end or a C with two identical groups rules a $C=C$ out); decide what kind of isomers two given structures are (same structural formula but cis/trans swapped means geometrical); "which compound has the most stereoisomers" (count n for each); molecules with two $C=C$ bonds (test each separately; watch symmetry).

5. Name a reaction type, mechanism, bond fission, reagent role or reactive species (18 questions)

1. **Look at what changes:** two molecules into one is addition; a swap is substitution; a $C=C$ forms and a small molecule leaves is elimination; water breaks a bond is hydrolysis; two join and water leaves is condensation (esters form this way); O gained or H lost is oxidation.

2. **For a mechanism name, add the attacking species:** a radical gives free-radical substitution; an electrophile attacking $C=C$ gives electrophilic addition; a nucleophile replacing a halogen gives nucleophilic substitution; a nucleophile adding to $C=O$ gives nucleophilic addition.

3. **Bond fission:** radicals are made by homolytic fission; ions by heterolytic fission.

4. **Reagent role:** acidified $KMnO_4$ or $K_2Cr_2O_7$ is an oxidising agent; $NaBH_4$ is a reducing agent; CN^- and OH^- are nucleophiles.

Variations you will meet: name the step in a free-radical chain (initiation, propagation, termination); write an equation for homolytic fission ($Cl_2 \rightarrow 2Cl\bullet$, or breaking a $C-Br$ bond into two radicals); write a redox equation with $[O]$ or $[H]$; explain why a reaction is addition (only one product forms).

6. Draw structural isomers or name the type of structural isomerism (17 questions)

1. **Keep the molecular formula** of the original; count atoms in every structure you draw.

2. **Change one thing at a time:** the carbon skeleton (chain), the position of the group (positional), or the group itself (functional group).

3. **Check each new structure is really new.** Turn it round and renumber: $CH_3CH_2CH_2CH_2Cl$ drawn backwards is the same compound.

4. Draw in the form asked (skeletal, displayed or structural). Any unambiguous formula is usually accepted when no form is specified.

Variations you will meet: cyclic isomers of a ring compound (a smaller ring with a side chain, or the same ring with substituents in different places); recognise the type between two named compounds; pick "which pair are isomers" (check the molecular formulas match, and that they are not the same molecule written two ways).

7. Count all the isomers of a molecular formula (15 questions)

1. **Read the question carefully:** structural only, or structural **and** stereoisomers; open-chain only, or rings too; one class only (esters, alcohols, secondary alcohols)?

2. **List systematically:** longest chain first, then one branch, then two branches; move the functional group along each skeleton.
3. **Cross off repeats.**
4. **If stereoisomers count,** add one extra for each isomer with a chiral centre or a cis/trans C=C (two for a structure with two such features, and so on: use 2^n per structure).

Variations you will meet: esters (split the carbons between the acid side and the alcohol side: methanoates, ethanoates, propanoates ...); halogenoalkanes of one class (primary only); the formula has to be worked out first from data (percentage by mass, moles of Br₂ that add on, or a gas volume), then the isomers counted.

8. Explain or define stereoisomerism and what causes it (14 questions)

- **Stereoisomers:** same molecular formula **and** same structural formula, **different arrangement of atoms in space.**
- **Geometrical isomerism:** restricted (no) rotation about the C=C, because of the π bond, **and** two different groups on **each** carbon of the C=C. "Why does this one not show it?" means pointing to the carbon with two identical groups.
- **Optical isomerism:** a chiral centre, a carbon **bonded to** four different atoms or groups, giving two non-superimposable mirror images.
- **What optical isomers share:** molecular, empirical and structural formula and functional groups; only the 3D arrangement differs.

9. Name a compound, or give its formula from a name (12 questions)

1. Find the main functional group and the longest chain containing it.
2. Number from the end nearer the main group; add substituent prefixes in alphabetical order.
3. For an ester, split at the -COO-: the part joined to the single-bonded O is the alkyl (from the alcohol), named first.
4. **From a name to a formula:** draw the stem chain, number it, then put each group on its numbered carbon and fill with H.

Variations you will meet: name an alkene with cis/trans (cis-but-2-ene); name the alcohol and acid that make a given ester; name compounds with two groups (2-hydroxypropanoic acid style); give a displayed formula (every bond, including O-H).

10. Identify functional groups, classify, use general formulas (11 questions)

1. **Name every group you can see:** C=C alkene; -OH alcohol (but -COOH is carboxylic acid, not alcohol); C=O at the chain end aldehyde, inside the chain ketone; -COO- between two carbons ester; -NH₂ amine; -C $\equiv$ N nitrile.
2. **Classify** an alcohol or halogenoalkane by counting carbons on the C-O or C-X carbon.
3. **General formula questions:** write each class's general formula for the same n and compare, or check which classes fit a given empirical formula by trying $n = 1, 2, 3 \dots$

Variations you will meet: which carbons can be oxidised (primary and secondary alcohols can, tertiary cannot); which class has the highest H to C ratio (compare C_nH_{2n+2} -type formulas with C_nH_{2n} -type).

11. Draw stereoisomers (cis/trans or 3D optical isomers) (10 questions)

- **Cis/trans:** draw the $C=C$ with the four groups at about 120° , then swap the two groups on **one** carbon. Don't draw two groups that are the same on one carbon, and don't redraw the same isomer upside down.
- **Optical isomers:** draw the chiral carbon with two bonds in the plane, one wedge and one dash, in a clear tetrahedral shape, then draw its exact reflection in a mirror line. Each group must be joined by the right atom ($-OH$ by its O, $-CN$ by its C).

12. Define a basic term (7 questions)

- **Structural isomers:** same molecular formula (**M1**), different structural formula (**M2**).
- **Empirical formula:** the simplest whole-number ratio of the atoms of each element in a compound.
- **Homologous series:** same general formula (or members differ by CH_2) (**M1**) and similar chemical properties (**M2**).
- **Hydrocarbon:** a compound of carbon and hydrogen **only**.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

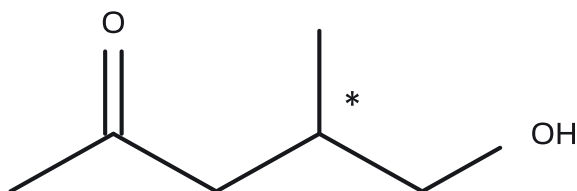
- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Compound P has the structural formula $CH_3COCH_2CH(CH_3)CH_2OH$.

- (a) Draw the skeletal formula of P. [**1**]
- (b) Give the molecular formula and the empirical formula of P. [**2**]
- (c) Name the two functional groups in P, and state whether the alcohol group is primary, secondary or tertiary. [**2**]
- (d) Give the systematic name of P. [**1**]
- (e) State the number of chiral centres in P and the number of σ and π bonds in one molecule of P. [**2**]

(a) A zigzag of five carbons, with a C=O on carbon 2, a methyl line on carbon 4 and OH at the end. **B1**



the chiral centre is marked *

(b) Carbons: $1 + 1 + 1 + 1 + 1 + 1 = 6$. Hydrogens: $3 + 0 + 2 + 1 + 3 + 2 + 1 = 12$. Oxygens: 2.
Molecular formula $C_6H_{12}O_2$. **B1**

All three numbers divide by 2: empirical formula C_3H_6O . **B1**

(c) Ketone (C=O inside the chain) and alcohol (hydroxyl). **B1** The –OH carbon is joined to one other carbon, so it is a **primary** alcohol. **B1**

(d) The longest chain holding both groups has five carbons. Numbering from the left puts the ketone (the main group) on carbon 2, the methyl on carbon 4 and the OH on carbon 5: **5-hydroxy-4-methylpentan-2-one**. **B1**

(e) Only carbon 4 is a CH with four different groups: H, CH_3 , CH_2OH and CH_2COCH_3 . One chiral centre. **B1**

P has $6 + 12 + 2 = 20$ atoms and no rings, so $20 - 1 = 19$ σ bonds; the C=O adds one π bond: 19 σ bonds and 1 π bond. **B1**

Example 2

Several compounds have the molecular formula C_3H_5Cl .

(a) Draw the structural formulas and give the names of the three non-cyclic structural isomers of C_3H_5Cl . **[3]**

(b) State the type of structural isomerism shown by your answers to (a). **[1]**

(c) Only one of the isomers in (a) shows stereoisomerism. Explain why, and draw its stereoisomers. **[3]**

(d) Including cyclic compounds and stereoisomers, how many isomers of C_3H_5Cl are there? **[1]**

(a) One C=C is needed (C_3H_6 is an alkene with one H replaced). Move the Cl along the chain:

- $CH_2=CHCH_2Cl$, 3-chloropropene **B1**
- $CH_2=CClCH_3$, 2-chloropropene **B1**
- $CH_3CH=CHCl$, 1-chloropropene **B1**

(b) The same group on different carbons: **positional** isomerism. **B1**

(c) In 1-chloropropene each carbon of the C=C carries two different groups (H and CH₃; H and Cl) **B1**, and there is no rotation about the C=C because of the π bond **B1**. In the other two, one carbon of the C=C carries two H atoms.

The two isomers: cis-1-chloropropene, with CH₃ and Cl on the same side of the C=C, and trans-1-chloropropene, with them on opposite sides, each drawn with 120° angles as in the pent-2-ene figure. **B1**

(d) Chlorocyclopropane is the only ring isomer, and it is not chiral. Total: 3-chloropropene, 2-chloropropene, cis- and trans-1-chloropropene and chlorocyclopropane, which is **5** isomers. **B1**

Example 3

Pent-3-enenitrile, CH₃CH=CHCH₂CN, is made when 1-bromobut-2-ene, BrCH₂CH=CHCH₃, is heated with KCN in ethanol.

(a) Name the type of reaction and the mechanism, and state the role of the CN[−] ion. **[2]**

(b) Give the hybridisation of each carbon atom in pent-3-enenitrile (carbon 1 is the carbon of the C≡N), and the bond angle around carbon 1. **[2]**

(c) Give the numbers of σ and π bonds in one molecule. **[2]**

(d) Pent-3-enenitrile reacts with bromine. Name the mechanism, and state the number of chiral centres in the product CH₃CHBrCHBrCH₂CN. **[2]**

(e) Heating pent-3-enenitrile with HCl(aq) forms pent-3-enoic acid. Name this type of reaction. **[1]**

(a) Br is replaced by CN: **substitution**, by the mechanism **nucleophilic substitution**. **B1** CN[−] donates a lone pair to the δ⁺ carbon of C–Br: it is a **nucleophile**. **B1**

(b) C1 *sp* (it is in C≡N), C2 *sp*³, C3 *sp*², C4 *sp*², C5 *sp*³. **B1** Around C1 the angle is 180° (linear). **B1**

(c) Formula C₅H₇N: 13 atoms, no ring, so 13 − 1 = 12 σ bonds. **B1** One π in C=C and two in C≡N: 3 π bonds. That is 12 σ bonds and 3 π bonds. **B1**

(d) Bromine attacks the electron-rich C=C: **electrophilic addition**. **B1** In the product, 3,4-dibromopentanenitrile, C3 carries H, Br, CH₂CN and CHBrCH₃; C4 carries H, Br, CH₃ and CHBrCH₂CN. Both are chiral: **2** chiral centres. **B1**

(e) The C≡N is broken by water (acid catalysed): **hydrolysis**. **B1** (C₅H₇N + 2H₂O + HCl → C₅H₈O₂ + NH₄Cl.)

Example 4

Compound Q is CH₃CH=CHCH(CH₃)CH(OH)CH=CHCH₃.

(a) Give the molecular formula of Q. **[1]**

(b) Identify the chiral centres in Q, giving the four groups on each. **[2]**

(c) Explain why both C=C bonds in Q give rise to geometrical isomerism. **[2]**

(d) Deduce the total number of stereoisomers with the structural formula of Q. **[1]**

(e) Q is warmed with acidified potassium dichromate(VI), which oxidises its secondary alcohol group to a ketone. The C=C bonds do not react. Deduce the number of stereoisomers of the product. **[2]**

Number the chain from the left: C1 to C8, with a methyl on C4 and OH on C5.

(a) Carbons: 8 in the chain + 1 methyl = 9. Hydrogens: 3 + 1 + 1 + 1 + 3 + 1 + 1 + 1 + 3 on carbon, plus 1 on O = 16. Formula $C_9H_{16}O$. **B1**

(b) C4: H, CH_3 , $CH=CHCH_3$ and $CH(OH)CH=CHCH_3$. C5: H, OH, $CH=CHCH_3$ and $CH(CH_3)CH=CHCH_3$. Both have four different groups, so **two** chiral centres, C4 and C5. **B1 B1**

(c) The π bond stops rotation about each C=C. **B1** At each C=C, both carbons carry two different groups: C2 has H and CH_3 , C3 has H and the rest of the chain; the same is true at C6 and C7. **B1**

(d) Four stereo features (2 chiral centres + 2 cis/trans C=C): $2^4 = 16$ stereoisomers. **B1**

(e) The product is $CH_3CH=CHCH(CH_3)COCH=CHCH_3$. C5 is now a C=O carbon, so it is no longer a chiral centre; C4 still carries H, CH_3 , $CH=CHCH_3$ and $COCH=CHCH_3$, so it is still chiral. **M1** Both C=C bonds still show cis/trans isomerism, so there are 3 stereo features: $2^3 = 8$ stereoisomers. **A1**

Common mistakes

- **Miscounting carbons or hydrogens in skeletal formulas.** Candidates lose the formula mark by forgetting the carbon at a line end or the H atoms on ring carbons. Go carbon by carbon and use the " $2n + 2$ minus 2 per ring or double bond" check.
- **Giving the molecular formula when the empirical formula is asked,** or the other way round. Read which one the question wants, and cancel down only for the empirical formula.
- **Drawing a "skeletal" formula with C or H atoms on carbon,** or a structural formula that is ambiguous. Use exactly the form asked.
- **Vague stereoisomerism definitions.** "Different arrangement in space" alone is not enough: say same molecular **and structural** formula. Writing "molecular formula" instead of "structural formula" is a common slip.
- **Half an explanation of cis/trans.** Examiners see "restricted rotation" without "two different groups on each carbon of the C=C" (or the other way round). Give both.
- **Loose words about chiral centres.** Write "a carbon atom **bonded to** four different atoms or groups", not "surrounded by", and not "four different molecules".
- **Missing a chiral centre next to a C=C** or in a ring, or counting a CH_2 as chiral. Test every CH and every carbon with no H.
- **Adding instead of multiplying** stereoisomers: three features give 8, not 6.
- **Repeating an isomer.** A structure turned round or drawn upside down is the same compound; so is a stereoisomer drawn twice. Check each new drawing.

- **Naming the wrong kind of isomerism:** giving "optical" or "cis/trans" when the question asks for a type of **structural** isomerism.
- **Mixing up homolytic and heterolytic fission.** Homolytic gives radicals (use dots), heterolytic gives ions.
- **Saying bonds are sp^2 hybridised.** Hybridisation is for atoms; bonds are σ (head-on overlap) or π (sideways overlap of p orbitals). Orbital diagrams need labels.
- **Forgetting C–H and O–H bonds** when counting σ bonds.

How to get the marks

- **Definitions** are usually 2 marks for 2 separate points (for example "same general formula" **and** "similar chemical properties"). Learn the key words; each missing idea loses a mark.
- **"Explain" a stereoisomerism question** needs the cause (π bond, no rotation; or chiral centre) **and** the condition (two different groups on each C=C carbon; four different groups on the chiral carbon).
- **"Draw" follows the form in the question:** skeletal, displayed (every bond, including O–H), or structural. For 3D optical isomers show a clear tetrahedral arrangement with wedge and dash, and make the two drawings real mirror images.
- **"Identify" or "mark"** a chiral centre: an asterisk on the right carbon is enough.
- **"Name"** means the full systematic name with numbers, spelled correctly: 5-hydroxy-4-methylpentan-2-one, not 4-methyl-5-hydroxy....
- **"State" or "name the type"** needs the syllabus word itself (electrophilic addition, homolytic, condensation). A description instead of the word usually earns nothing.
- **Equations with [O] or [H]** must balance, counting [O] and [H] as atoms, and use structural formulas for organic species.
- **Multiple choice:** draw the molecule and write the H atoms in before counting anything. Most wrong answers come from a skipped H or a hidden chiral centre.

Quick check

1. Give the structural formula, molecular formula and empirical formula of **ethyl hexanoate**, and name the alcohol and the acid it is made from.
2. For 2-methylpropenal, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$, state the number of σ and π bonds, the hybridisation of each carbon, and whether the molecule is planar.
3. How many chiral centres are there in 2,3-dichloropentane, $\text{CH}_3\text{CHClCHClCH}_2\text{CH}_3$, and how many stereoisomers does it have?
4. Classify each reaction by type (and mechanism where there is one), then write the equation for (d) using [O]. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^-$ (b) $\text{Cl}_2 \rightarrow 2\text{Cl}\bullet$ in ultraviolet light (c) $\text{propan-2-ol} \rightarrow \text{propene} + \text{water}$ (d) $\text{butan-2-ol} \rightarrow \text{butanone}$
5. How many aldehydes and ketones have the molecular formula $\text{C}_5\text{H}_{10}\text{O}$? How many are there if stereoisomers are also counted?

Answers

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$. Molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$; dividing by 2 gives the empirical formula $\text{C}_4\text{H}_8\text{O}$. It is made from ethanol and hexanoic acid.
2. $\text{C}_4\text{H}_6\text{O}$ has 11 atoms and no ring, so 10 σ bonds; $\text{C}=\text{C}$ and $\text{C}=\text{O}$ give 2 π bonds: 10 σ bonds and 2 π bonds. The $\text{CH}_2=$, the central C and the CHO carbon are sp^2 ; the CH_3 carbon is sp^3 . It is not fully planar: the carbon skeleton and O lie in one plane, but the H atoms of the tetrahedral CH_3 group cannot all lie in that plane.
3. C2 carries H, Cl, CH_3 and CHClC_2H_5 ; C3 carries H, Cl, C_2H_5 and CHClCH_3 . Two chiral centres, so $2^2 = 4$ stereoisomers.
4. (a) Substitution (hydrolysis) by nucleophilic substitution; OH^- is the nucleophile. (b) Homolytic fission, the initiation step of free-radical substitution. (c) Elimination (water is removed and a $\text{C}=\text{C}$ forms). (d) Oxidation: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_2\text{CH}_3 + \text{H}_2\text{O}$.
5. Aldehydes: pentanal, 2-methylbutanal, 3-methylbutanal, 2,2-dimethylpropanal. Ketones: pentan-2-one, pentan-3-one, 3-methylbutan-2-one. That is 7 structural isomers. Only 2-methylbutanal has a chiral centre (C2: H, CHO, CH_3 , C_2H_5), so with stereoisomers there are 8.

Past questions to try

- [9701/22/O/N/25 Q3](#): homologous series, chain isomers of hexane and their boiling points.
- [9701/24/M/J/25 Q5](#): positional isomers of an alkene, and explaining and drawing its cis/trans isomer.
- [9701/13/O/N/25 Q25](#): deciding the kind of isomerism between four skeletal formulas.
- [9701/12/M/J/24 Q36](#): counting the stereoisomers of an unsaturated alcohol.