

Introduction to Organic Chemistry

A-Level Chemistry ■ Topic 13

A-Level Chemistry



What we will cover

- 1 Types of formula
- 2 Bond fission
- 3 Nucleophiles & electrophiles
- 4 Mechanisms
- 5 Hybridisation & shapes
- 6 Isomerism



the feedstock of organics

1

Formulas and reactions

Types of formula

empirical

CH_2 – simplest ratio

molecular

C_2H_4 – actual numbers

structural

$\text{CH}_2=\text{CH}_2$ – how they join

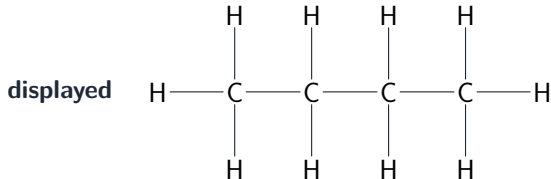
displayed

every bond drawn

Types of formula, in detail

molecular C_4H_{10}

structural $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$



skeletal



The same molecule (butane) shown four ways: each formula reveals different structural detail.

The formula types, and the reaction types

empirical formula 实验式	the simplest whole-number ratio of atoms
molecular formula	the actual number of each atom in one molecule
displayed formula 展开式	every atom and every bond drawn out
hydrolysis 水解	a molecule is split apart by water
condensation 缩合	two molecules join and a small molecule such as water is lost
organic redox	[O] stands for one oxygen atom from an oxidising agent, and [H] for one hydrogen from a reducing agent

[O] and [H] are a shorthand that keeps organic equations balanced without writing out the whole oxidising agent. Use them – the mark scheme does.

Five ways to write the same compound

General formula	The pattern for a whole family: alkanes are C_nH_{2n+2} .
Molecular formula	The actual number of each atom: C_4H_{10} .
Structural formula	The groups in order: $CH_3CH_2CH_2CH_3$.
Displayed formula	Every atom and every bond drawn out – what a mechanism question needs.
Skeletal formula	Lines for bonds, carbons at the corners, hydrogens on carbon not shown.

A **homologous series** 同系列 is a family sharing one functional group and one general formula, successive members differing by CH_2 .

Naming

Nomenclature 命名法 a **stem** for the number of carbons + an **ending** for the functional group.

meth-
1 C

eth-
2 C

prop-
3 C

but-
4 C

pent-
5 C

hex-
6 C

prop

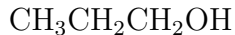
3 carbons

an

single C—C
bonds

-1-ol

OH on
carbon 1



Track the bonding electrons

Your turn

A Cl–Cl bond breaks under ultraviolet light. Each chlorine receives one bonding electron. Name the fission and draw the products.

Now a C–Br bond breaks with both bonding electrons going to Br. State the charges produced and name the fission.

Follow the two bonding electrons; use dots for unpaired electrons and signs for charges.

Bond fission

- **homolytic fission** 均裂 – one electron each $\rightarrow$ two **free radicals** 自由基
- **heterolytic fission** 异裂 – both electrons to one atom $\rightarrow$ two ions

homolytic fission



one electron each
 $\Rightarrow$ two **radicals**

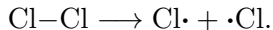
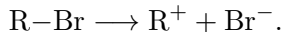
heterolytic fission



both electrons to one
 $\Rightarrow$ two **ions**

One electron or an electron pair?

Fission	Electron allocation	Products
Homolytic	one to each atom	two radicals
Heterolytic	both to one atom	a cation and an anion



A full curly arrow moves two electrons. A half-headed arrow moves one electron.
R represents the organic group.

Classify by electron-pair behaviour

Your turn

Compare OH^- , NH_3 and H^+ . Which can donate a lone pair to an electron-poor carbon? Which accepts a pair from an alkene?

Explain why charge alone is an incomplete test.

Nucleophiles and electrophiles

nucleophile



a lone pair attacks
the electron-poor
($\delta+$) carbon

electrophile



it is drawn to the
electron-rich C=C
double bond

- a **nucleophile** 亲核试剂 (lone pair) attacks an electron-**poor** centre
- an **electrophile** 亲电试剂 is drawn to an electron-**rich** centre (C=C)

Reaction types: **addition** 加成,
substitution 取代,
elimination 消去,
hydrolysis 水解.

A neutral species can be a nucleophile

Species	Relevant feature	Behaviour
OH^-	oxygen lone pair	electron-pair donor
NH_3	nitrogen lone pair	electron-pair donor
H^+	accepts a pair	electron-pair acceptor

Use precise definitions

A **nucleophile** 亲核试剂 donates an electron pair to an electron-poor centre. An **electrophile** 亲电试剂 accepts an electron pair from an electron-rich region.

The $\text{C}=\text{C}$ π bond is an electron-rich region. Ammonia shows why a nucleophile need not be negative.

Mechanisms

free-radical substitution

自由基取代 – alkanes

electrophilic addition 亲电加成

– alkenes

nucleophilic substitution

亲核取代 – halogenoalkanes

nucleophilic addition 亲核加成

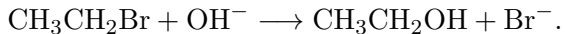
– carbonyls

Free-radical steps: **initiation** 引发 → **propagation** 增长 → **termination** 终止. A full **curly arrow** 弯箭头 shows a **pair** of electrons moving.

Classify what changes in each equation

Your turn

Name each reaction type. Identify the bond or group change that supports your choice.



Use the structural change as evidence

Example	Reaction type	Evidence
Ethene + HBr	addition	C=C opens; two join as one
Bromoethane + OH ⁻	substitution	Br is replaced by OH
Ethanol to ethene	elimination	water lost; C=C forms

Nucleophilic substitution combines the electron-pair behaviour with the group replacement. A reagent name alone is not the reaction type.

Water consumed or water formed?

Hydrolysis versus condensation

Ester + water $\longrightarrow$ carboxylic acid + alcohol:

hydrolysis, because water is used to break the molecule apart.

Carboxylic acid + alcohol $\longrightarrow$ ester + water:

condensation, because joining the molecules forms a small molecule.

Check the role of water. Its presence somewhere in a reaction mixture does not by itself establish hydrolysis.

Original exam: follow the stated mechanism

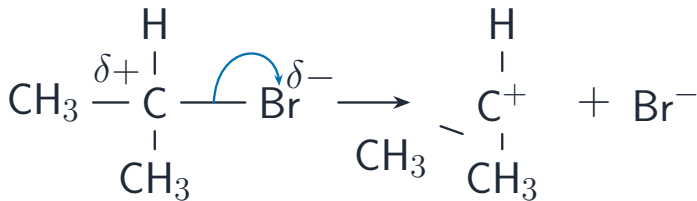
9701/24 N25 Q3(b)(ii)

The paper states that 2-bromopropane reacts with $(\text{CH}_3)_2\text{CHO}^-$ by an S_N1 mechanism. Sketch the two stages, including dipoles, charges, a lone pair and curly arrows.

- 1 Break C–Br heterolytically and show the intermediate.
- 2 Show the oxygen lone pair forming the new C–O bond.

Use the mechanism stated in this question; do not infer it solely from the word secondary.

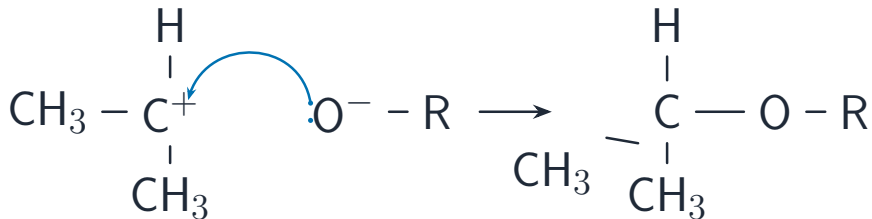
SN1 stage one: the bond pair leaves



Bond pair moves to Br; the carbon intermediate has a positive charge.

Both C–Br electrons go to Br: bromide and a carbocation form. Start the full curly arrow on the bond.

SN1 stage two: donate an oxygen lone pair



An oxygen lone pair forms the C–O bond. Here $\text{R} = \text{CH}(\text{CH}_3)_2$.

Start the full curly arrow at the oxygen lone pair and end it at C^+ . The new bond uses that pair.

Compare the worksheet substitution mechanisms

Worksheet case	Description	Intermediate
2-bromo-2-methylpropane	S_N1 , two stages	tertiary carbocation
1-bromobutane	S_N2 , one stage	no carbocation

Explain, rather than name only

Three alkyl groups help stabilise the tertiary carbocation by their electron-releasing effect. A primary carbocation is much less stable. In the worksheet's primary case, attack and leaving-group departure occur together.

For S_N2 , show lone-pair-to-carbon and bond-to-Br arrows in the same stage.

Use equations to identify radical chain stages

Stage	Methane + chlorine under UV light
Initiation	$\text{Cl}_2 \longrightarrow 2\text{Cl}\cdot$
Propagation	$\text{Cl}\cdot + \text{CH}_4 \longrightarrow \text{HCl} + \cdot\text{CH}_3$
Propagation	$\cdot\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$
Termination	$\cdot\text{CH}_3 + \text{Cl}\cdot \longrightarrow \text{CH}_3\text{Cl}$

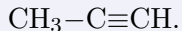
Initiation makes radicals; each propagation step consumes and regenerates one; termination consumes two without regenerating a radical.

2

Shape and isomerism

Original exam: classify each carbon in propyne

9701/14 N25 Q6



Identify the hybridisation at each of the three carbons. Which two types are present?

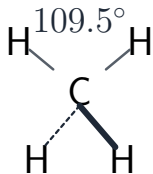
For each carbon, count regions of bonding electron density; a multiple bond counts as one region for shape.

A triple bond does not make every carbon sp

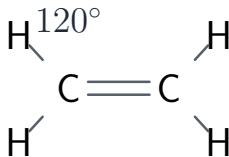
Carbon in propyne	Regions	Hybridisation	Local shape
CH ₃ end	four	sp ³	tetrahedral, 109.5°
Both C≡C atoms	two each	sp	linear, 180°

Original answer B: sp and sp³ only. Classify each carbon locally; there is no sp² carbon here.

Hybridisation and shapes, in detail



sp³: 4 single bonds
tetrahedral



sp²: 1 double + 2 single
planar (flat)



sp: 1 triple bond
linear

The shape at a carbon follows from its hybridisation: sp³ is tetrahedral (109.5°), sp² is planar (120°), sp is linear (180°)

Count the entire molecule, not only C=C

Your turn

Count all σ and π bonds in methane, ethene and ethyne. Include the C–H bonds.

Use one σ for each bonded atom pair; add one π for a double bond and two π for a triple bond.

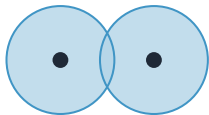


Check the bond counts against the structures

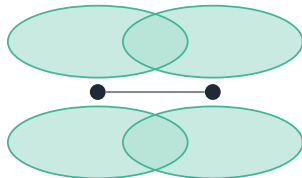
Molecule	σ	π	Count of σ bonds
Methane	4	0	four C–H
Ethene	5	1	four C–H + one C–C
Ethyne	3	2	two C–H + one C–C

A triple bond contains one σ and two π bonds. The two overlapping regions of one π bond are not two separate π bonds.

Connect the count to orbital overlap



σ bond:
head-on overlap



π bond: sideways overlap
of p orbitals

σ : head-on overlap along the internuclear axis. π : sideways overlap of parallel p orbitals, with density on both sides of the axis.

Original exam: test both methanal statements

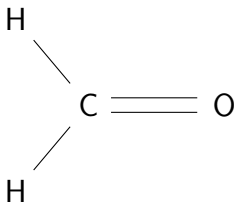
9701/12 N25 Q25

Methanal is $\text{H}_2\text{C}=\text{O}$. Are both statements correct?

1. The molecule is planar.
2. It contains three σ bonds.

Determine the carbon's local geometry, then count every bonded atom pair.

Methanal: planar and three sigma bonds



Carbon has three bonding regions: sp^2 , trigonal planar, approximately 120° . All four atoms lie in one plane.

Two C–H σ bonds plus one C–O σ bond give three. C=O also has one π bond.

Both statements are correct: original answer A.

Transfer the sp model to nitrogen

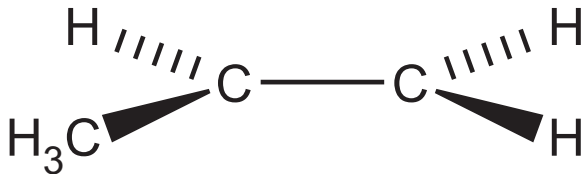
9701/12 N25 Q5: the question specifies sp hybridisation

Each N atom in N_2 has two sp orbitals: one holds a lone pair, and one forms the N–N σ bond by head-on sp–sp overlap.

Two remaining p orbitals on each N overlap sideways to form two π bonds.

Original answer B: sp–sp σ overlap and a lone pair in an sp orbital. This is a transfer of the bonding model, not an organic nitrogen compound.

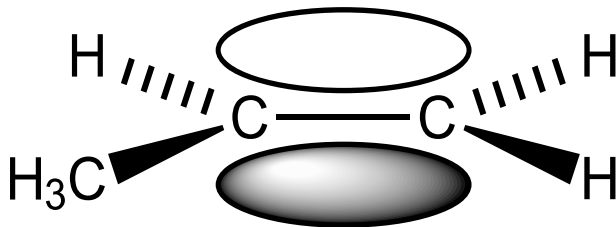
Original exam: draw the pi overlap in propene



9701/24 N25 Q3(a)(iv): your turn

Add the π bond formed by orbital overlap to the original propene framework. Show the electron-density regions relative to the atoms' plane.

A pi bond has density on both sides of the plane



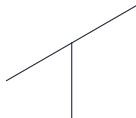
Original scheme: sideways p-orbital overlap gives density above and below the plane. These two regions belong to one π bond.

Structural isomerism

chain



butane

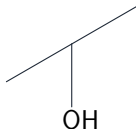


2-methylpropane

positional

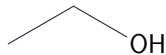


propan-1-ol

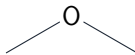


propan-2-ol

functional



ethanol (alcohol)

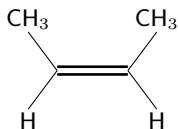


methoxymethane (ether)

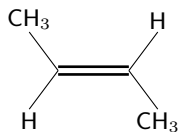
Same molecular formula, atoms joined differently:

- **chain** 链异构
- **positional** 位置异构
- **functional group** 官能团异构

Stereoisomerism

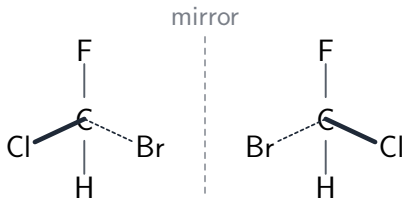


cis
both CH₃
same side

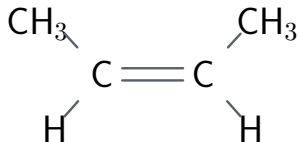


trans
CH₃
opposite sides

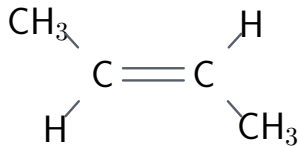
cis vs trans at C=C



Cis and trans isomers at a C=C bond



cis: both CH₃ on
the same side



trans: CH₃ on
opposite sides

Cis-trans isomerism at a C=C bond: the methyl groups are fixed on the same side (cis) or opposite sides (trans) because the bond cannot rotate

Isomerism, and where stereoisomerism comes from

structural isomerism	the atoms are joined in a different order
chain, position, functional group 官能团	the three kinds – a different skeleton, a different position, or a different group entirely
stereoisomerism 立体异构	the atoms are joined in the same order but point in different directions in space
<i>cis-trans</i>	restricted rotation about a C=C double bond, or around a ring (cyclic 环状)
optical isomerism	a chiral centre 手性中心: a carbon with four different groups
the test	a chiral molecule is non-superimposable on its mirror image, and rotates plane-polarised light

Look for the C=C or the four-different-groups carbon. At a C=C bond, check for two different groups on each carbon as well as restricted rotation.

The kinds of isomerism

Chain isomerism

Structural: the carbon skeleton is branched differently.

Positional isomerism

Positional isomerism 位置异构: the same functional group sits on a different carbon.

Functional group isomerism

Functional group isomerism 官能团异构: the same atoms form a *different* functional group – an alcohol and an ether.

Geometrical isomerism

Stereo: **geometrical isomerism** 几何异构 (cis/trans) at a C=C double bond, because the double bond cannot rotate.

Optical isomerism

Stereo: a carbon with four different groups gives two non-superimposable mirror images.

saturated 饱和: only single C–C bonds. **unsaturated** 不饱和: a C=C or C≡C is present.

Test each double-bond carbon separately

Your turn

But-1-ene is $\text{CH}_2=\text{CHCH}_2\text{CH}_3$. But-2-ene is $\text{CH}_3\text{CH}=\text{CHCH}_3$. Which has cis-trans isomers? Give both conditions and explain the difference.

Restricted rotation is necessary, but test the attached groups too.

Restricted rotation alone is insufficient

Molecule	Groups on C=C carbons	Result
But-1-ene	one carbon has H and H	no cis-trans pair
But-2-ene	each has H and CH ₃	cis and trans possible

Both have restricted rotation. Two different groups on each C=C carbon distinguish but-2-ene. Triple-bond unsaturation alone does not meet this test.

Shapes of organic molecules



Organic molecules have definite three-dimensional shapes.

Exam tips

- Know the difference between **general, molecular, structural, displayed and skeletal** formulas – questions ask for a specific one.
- Name systematically: longest chain, lowest locants, substituents alphabetical; a wrong locant loses the mark.
- Classify each reaction by **type and reagent** (addition, substitution, elimination, oxidation).
- **E/Z isomerism** needs restricted rotation about a $C = C$ **and** two different groups on each carbon.

3

Recap

Worked example – structural isomers

Draw and name the structural isomers of C_4H_{10} , and state the type of isomerism.

- Straight chain: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ – **butane**.
- Branched: $(\text{CH}_3)_3\text{CH}$ – **2-methylpropane**.
- There are **only two**: a 3-carbon chain cannot take a CH_3 anywhere else.
- Same molecular formula, different skeleton $\Rightarrow$ **chain isomerism**.

Isomers share a **molecular** formula. **Chain** = different skeleton; **position** = group moved; **functional group** = a different group entirely.

Topic 13 – key takeaways

1

Functional group

the reactive part sets the properties

2

Bond fission

homolytic (radicals) vs heterolytic (ions)

3

Shapes

$sp^3/sp^2/sp$ give
tetrahedral/planar/linear

4

Isomerism

structural; cis/trans; optical (chiral)

Check yourself

- 1 Homolytic fission makes two of what?
- 2 A nucleophile attacks an electron-rich or electron-poor centre?
- 3 What is the shape at an sp^2 carbon?
- 4 A chiral carbon has how many different groups?



Answers 1. free radicals 2. electron-poor 3. planar (120°) 4. four