

Hydrocarbons

AS

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Read first: [An introduction to AS Level organic chemistry](#)

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What you need to know

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

1. Alkanes (14.1)

- (a) Recall two ways to **make alkanes**: adding hydrogen to an alkene (**hydrogenation**: $\text{H}_2(\text{g})$ with a Pt or Ni catalyst and heat), and **cracking** a longer alkane (heat with an Al_2O_3 catalyst).
- (b) Describe **complete and incomplete combustion** of alkanes.
- (c) Describe the **free-radical substitution** of alkanes by Cl_2 or Br_2 in ultraviolet light, using ethane as the example, and its mechanism: **initiation, propagation and termination**.
- (d) Suggest how **cracking** turns heavy crude-oil fractions into more useful smaller alkanes and alkenes.
- (e) Explain why alkanes are **unreactive**, including towards polar reagents: strong C–H bonds with almost no polarity.
- (f) Recognise the harm done by **carbon monoxide, oxides of nitrogen and unburnt hydrocarbons** from car engines, and how a **catalytic converter** removes them.

2. Alkenes (14.2)

- (a) Recall three ways to **make alkenes**: **elimination** of HX from a halogenoalkane (ethanolic NaOH, heat), **dehydration** of an alcohol (a heated catalyst such as Al_2O_3 , or a concentrated acid such as H_2SO_4), and **cracking**.
- (b) Describe the **electrophilic addition** to alkenes of hydrogen (H_2 , Pt/Ni, heat), steam ($\text{H}_2\text{O}(\text{g})$, H_3PO_4 catalyst), a hydrogen halide ($\text{HX}(\text{g})$ at room temperature) and a halogen (X_2).
- (c) Describe oxidation by **cold dilute acidified** KMnO_4 (makes a diol) and by **hot concentrated acidified** KMnO_4 (splits the $\text{C}=\text{C}$), and use the products to find where the $\text{C}=\text{C}$ was in a larger molecule.
- (d) Describe **addition polymerisation** of ethene and propene.
- (e) Use **aqueous bromine** to show that a $\text{C}=\text{C}$ bond is present.
- (f) Describe the **mechanism of electrophilic addition**, using bromine with ethene and hydrogen bromide with propene.
- (g) Explain how the **inductive effect** of alkyl groups makes tertiary carbocations more stable than secondary, and secondary more stable than primary, and use this to explain **Markovnikov addition** (which product is the major one).

Understand it

Alkanes: saturated and unreactive

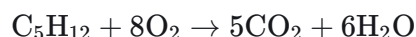
Alkanes, C_nH_{2n+2} , contain only C–C and C–H single bonds (σ bonds). They are **saturated**. Two facts make them unreactive:

- **The bonds are strong.** C–H is about 410 kJ mol^{-1} and C–C about 350 kJ mol^{-1} , so a lot of energy is needed to break them.
- **The bonds are almost non-polar.** Carbon and hydrogen have similar electronegativities, so there is no $\delta+$ or $\delta-$ site. A nucleophile (which looks for $\delta+$) or an electrophile (which looks for electron-rich regions) has nothing to attack.

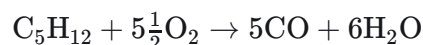
So alkanes don't react with acids, alkalis, or oxidising agents such as $KMnO_4$. They only react when something supplies a lot of energy: burning, or ultraviolet light splitting a halogen into reactive radicals.

Combustion

With plenty of oxygen, alkanes burn **completely** to carbon dioxide and water. Balance C first, then H, then O (a half is fine for O_2):



With too little oxygen (as in a car engine), combustion is **incomplete**: some carbon ends up as **carbon monoxide** or as **soot** (carbon):

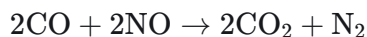


Pollutants from the car engine

Pollutant	Where it comes from	Why it is harmful
carbon monoxide, CO	incomplete combustion of the fuel	toxic: it binds to haemoglobin in the blood, so less oxygen is carried
oxides of nitrogen, NO and NO ₂ ("NO _x ")	nitrogen and oxygen from the air react at the very high temperature in the engine: $N_2 + O_2 \rightarrow 2NO$, then $2NO + O_2 \rightarrow 2NO_2$	acid rain (NO ₂ forms nitric acid with water and oxygen) and photochemical smog
unburnt hydrocarbons	fuel that passes through without burning	react with NO _x in sunlight to make photochemical smog , which contains the irritant PAN

The nitrogen in NO_x comes from the air, not from the fuel: alkanes contain no nitrogen.

A **catalytic converter** in the exhaust has a honeycomb coated with platinum, palladium and rhodium. It gives a large surface area on which the pollutants react to make harmless gases:



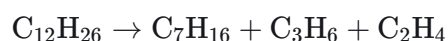
The CO is oxidised and the NO is reduced in the same reaction.

Cracking

Crude oil is separated by fractional distillation, but it contains more heavy, long-chain fractions than are needed, and too little petrol. **Cracking** breaks long alkanes into shorter ones. It is done by heating the vapour with an **aluminium oxide** (Al_2O_3) **catalyst** (or at a very high temperature without a catalyst). The products are:

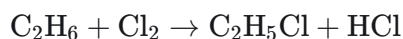
- **smaller alkanes**, useful as fuels such as petrol, which are in high demand;
- **alkenes**, which are used to make polymers and other chemicals.

At least one product must be an alkene: an alkane $\text{C}_n\text{H}_{2n+2}$ has only enough hydrogen to make **one** smaller alkane, so the rest must be C_nH_{2n} . Atoms are conserved, so the product formulas add up to the starting formula:



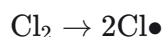
Free-radical substitution

In ultraviolet light (or sunlight), alkanes react with chlorine or bromine. A hydrogen atom is **substituted** by a halogen atom and a hydrogen halide is also made:

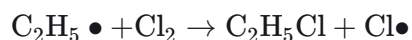
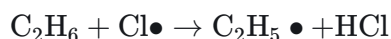


A **free radical** is a species with an **unpaired electron**, written with a dot: $\text{Cl}\bullet$. The reaction is a chain reaction with three stages.

1. Initiation. UV light supplies the energy to break the Cl–Cl bond (the weakest bond present). Each atom takes one electron from the shared pair: this is **homolytic fission**, and it makes two radicals.

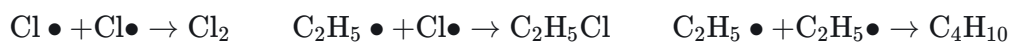


2. Propagation. Each step uses one radical and makes another, so the chain keeps going:



The $\text{Cl}\bullet$ made in the second step starts the first step again, so one photon can make thousands of product molecules. Notice that the chlorine radical takes a **hydrogen atom** (making HCl): an $\text{H}\bullet$ radical is never formed.

3. Termination. Two radicals meet and join, which removes radicals and stops a chain:



The last step explains why **butane** turns up in the product of chlorinating ethane.

Why you get a mixture. A $\text{Cl}\bullet$ can take an H atom from a product molecule just as easily as from ethane: $\text{C}_2\text{H}_5\text{Cl} + \text{Cl}\bullet \rightarrow \text{C}_2\text{H}_4\text{Cl}\bullet + \text{HCl}$. This leads on to $\text{C}_2\text{H}_4\text{Cl}_2$ (two isomers), and so on up to C_2Cl_6 . An **excess of the alkane** makes monosubstitution more likely; an **excess of halogen** gives more multi-substituted products. In a larger alkane, every different kind of H atom can be replaced, so you get several positional isomers. Bromine reacts the same way, just more slowly.

Alkenes and the π bond

Alkenes, C_nH_{2n} , have a $\text{C}=\text{C}$ bond made of a σ bond and a **π bond**. The π bond is formed by sideways overlap of p orbitals, so its electrons sit **above and below** the line between the two carbons. This makes the $\text{C}=\text{C}$ a region of **high electron density** that is exposed and easy to reach, and the π bond is **weaker** than the σ bond. **Electrophiles** (electron-pair acceptors such as $\text{H}^{\delta+}$ in HBr , or a polarised Br_2 molecule) are attracted to it, and the π bond breaks while the σ bond stays. That is why alkenes do **addition** reactions: two molecules join to make one product. Once the π bond is gone (as in an alkane or poly(ethene)), there is nothing for an electrophile to attack.

Making alkenes

- **Elimination** from a halogenoalkane: heat with **NaOH in ethanol**. H and X come off neighbouring carbons: $\text{CH}_3\text{CHBrCH}_3 + \text{NaOH} \rightarrow \text{CH}_2=\text{CHCH}_3 + \text{NaBr} + \text{H}_2\text{O}$. (NaOH in **water** gives an alcohol instead, by substitution.)
- **Dehydration** of an alcohol: pass the vapour over **heated** Al_2O_3 , or heat with **concentrated** H_2SO_4 (or H_3PO_4), which acts as a dehydrating agent: $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$.
- **Cracking** of a long-chain alkane, as above.

When the halogen or OH is in the middle of a chain, H can come off either side, so more than one alkene can form (2-bromobutane gives but-1-ene and both cis- and trans-but-2-ene).

Addition reactions of alkenes

Reagent	Conditions	Propene gives
hydrogen, $\text{H}_2(\text{g})$	Ni or Pt catalyst, heat	propane, $\text{CH}_3\text{CH}_2\text{CH}_3$
steam, $\text{H}_2\text{O}(\text{g})$	H_3PO_4 catalyst, heat, high pressure	propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (major)
hydrogen halide, $\text{HX}(\text{g})$	room temperature	2-halopropane, e.g. $\text{CH}_3\text{CHBrCH}_3$ (major)
halogen, X_2	room temperature, in the dark	1,2-dihalopropane, e.g. $\text{CH}_3\text{CHBrCH}_2\text{Br}$

In every case the two new atoms or groups go onto the **two carbons that were joined by the double bond**, and each $\text{C}=\text{C}$ adds one molecule. A molecule with two $\text{C}=\text{C}$ bonds reacts with two molecules of H_2 , Br_2 or HBr , and so on. Hydrogenation is how vegetable oils are hardened into margarine.

Testing for $\text{C}=\text{C}$. Shake the compound with **aqueous bromine**. An alkene turns it from **orange** to **colourless** (it is decolourised) because bromine adds across the $\text{C}=\text{C}$. An alkane (or any saturated compound) leaves it orange. Always give both colours, and say "colourless", not "clear".

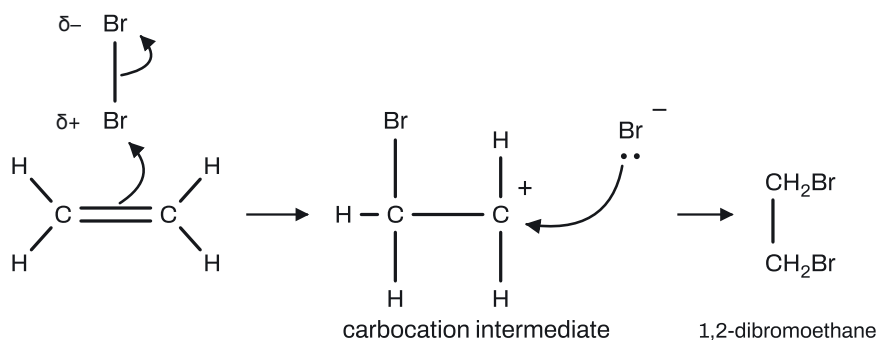
The mechanism of electrophilic addition

A **curly arrow** shows a pair of electrons moving. It starts at a **bond or a lone pair** and points to the **atom** that receives the pair.

Bromine and ethene. Br_2 is not polar, but as it approaches the electron-rich $\text{C}=\text{C}$, the π electrons repel the electrons in the $\text{Br}-\text{Br}$ bond. This **induces a dipole**: the nearer Br becomes δ^+ and the further one δ^- .

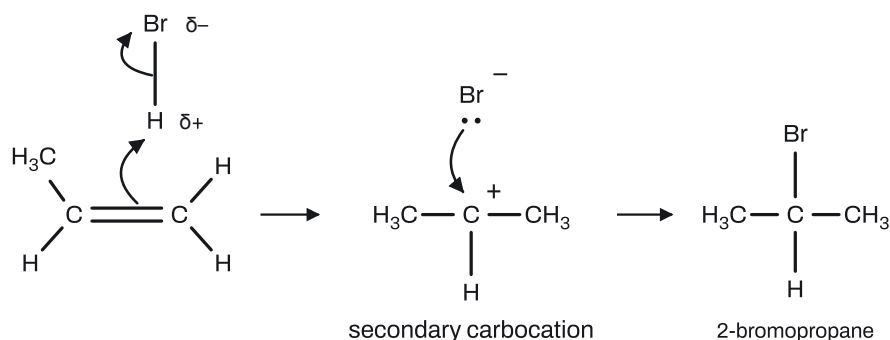
1. The π electrons move to the $\text{Br}^{\delta+}$, forming a $\text{C}-\text{Br}$ bond (arrow from the $\text{C}=\text{C}$ to the Br).
2. At the same time the $\text{Br}-\text{Br}$ bond breaks **heterolytically**: both electrons go to the far Br, which leaves as Br^- (arrow from the $\text{Br}-\text{Br}$ bond to the Br).
3. The other carbon has lost its share of the π pair, so it carries a **positive charge**: a **carbocation** intermediate.
4. A **lone pair** on Br^- forms a bond to the C^+ (arrow from the lone pair to the C).

electrophilic addition of bromine to ethene



Hydrogen bromide and propene. $\text{H}-\text{Br}$ is already polar ($\text{H}^{\delta+}-\text{Br}^{\delta-}$), and H is the electrophile. The steps are the same: arrow from the $\text{C}=\text{C}$ to the H, arrow from the $\text{H}-\text{Br}$ bond to the Br, carbocation, then Br^- attacks.

electrophilic addition of hydrogen bromide to propene



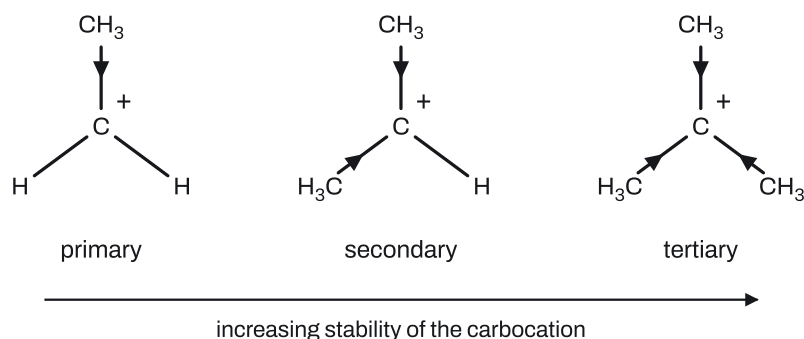
Steam adds in the same way, with H^+ from the acid catalyst as the electrophile: the carbocation then bonds to the O of a water molecule, which loses H^+ to give the alcohol (so the acid is given back).

Carbocation stability and Markovnikov addition

When $\text{H}-\text{X}$ adds to an **unsymmetrical** alkene such as propene, the H could go on either carbon of the $\text{C}=\text{C}$, giving two different carbocations:

- H on the CH₂ end: CH₃⁺CHCH₃, a **secondary** carbocation (the C⁺ carries two alkyl groups) → 2-bromopropane;
- H on the middle carbon: CH₃CH₂CH₂⁺, a **primary** carbocation (one alkyl group) → 1-bromopropane.

Alkyl groups **push electron density towards** the carbon they are bonded to: this is their **positive inductive effect**. Around a C⁺, this spreads out (reduces) the positive charge and makes the ion more stable. More alkyl groups on the C⁺ mean more stabilisation:



primary < secondary < tertiary (stability of the carbocation)

The more stable carbocation forms more easily and faster, so the product that comes from it is the **major product**. This is **Markovnikov addition**. A quick way to predict it: the H goes onto the C=C carbon that already has **more H atoms**, and X (or OH) goes onto the carbon with **more alkyl groups**. The explanation, though, is always about the **carbocation**: "via the more stable secondary (or tertiary) carbocation, because of the greater positive inductive effect of more alkyl groups".

If both carbons of the C=C carry the same number of alkyl groups (as in pent-2-ene), both carbocations are of the same type, so both products form in similar amounts. A symmetrical alkene such as but-2-ene gives only one product.

Oxidation with acidified potassium manganate(VII)

Cold, dilute, acidified KMnO₄ adds an OH group to each carbon of the C=C, giving a **diol**. The purple solution turns colourless:

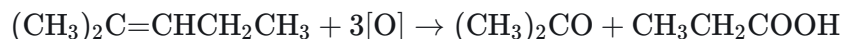


Hot, concentrated, acidified KMnO₄ breaks the C=C **completely** (both the σ and π bonds). Each carbon of the old double bond becomes a C=O, and what happens next depends on what else that carbon carried:

Carbon of the C=C	Becomes	Oxygen atoms used
=CR ₂ (two alkyl groups)	a ketone , R ₂ C=O (no further oxidation)	1[O]
=CHR (one alkyl group, one H)	an aldehyde, which is oxidised further to a carboxylic acid , RCOOH	2[O]

Carbon of the C=C	Becomes	Oxygen atoms used
$=\text{CH}_2$ (two H atoms)	methanoic acid, which is oxidised further to $\text{CO}_2 + \text{H}_2\text{O}$	$3[\text{O}]$

For example, 2-methylpent-2-ene, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$, gives propanone and propanoic acid:



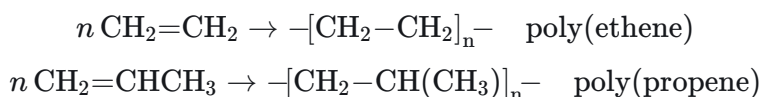
Working backwards. Take the products, turn each new C=O back into a C=C end, and join the ends:

- a **ketone** $\text{R}_2\text{C}=\text{O}$ came from $\text{R}_2\text{C}=\text{}$;
- an **acid** RCOOH came from $\text{RCH}=\text{}$;
- CO_2 came from a $=\text{CH}_2$ end;
- a product with **two** C=O groups (a diacid, a diketone or a keto-acid) came from a carbon chain with a C=C at each end: either a **ring** that has opened, or the middle piece of a **diene**;
- a **single** product with the **same number of carbons** as the alkene means the C=C was in a ring (the ring opens into one chain), or the alkene was symmetrical and gave two identical halves.

Counting carbons helps: the carbons in all the products (including CO_2) add up to the carbons in the alkene.

Addition polymerisation

Under suitable conditions, thousands of alkene molecules (**monomers**) add to one another. The π bond of each C=C opens and the carbons join into one long saturated chain, with nothing else produced:



The **repeat unit** is the two carbons that came from the C=C, with their groups, and a bond sticking out at each end (continuation bonds). The side group (CH_3 in poly(propene)) hangs off the chain; it is **not** part of the main chain. To find the monomer from a polymer, take one two-carbon repeat unit and put the C=C back between those two carbons.

Key facts and formulas

"Given" means it is printed in the 9701 Data Booklet or on the paper's Periodic Table. "Learn it" means you must remember it. The Data Booklet does not print reagents, conditions, colours or equations.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, O 16.0, Cl 35.5, Br 79.9	Given
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions	Given
Bond energies, e.g. C-H 410, C-C 350, C=C 610, Cl-Cl 242, Br-Br 193 kJ mol^{-1}	Given

Formula	Status
Alkanes C_nH_{2n+2} ; alkenes (one C=C, no ring) C_nH_{2n}	Learn it
Complete combustion: $C_xH_y + (x + \frac{y}{4}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$	Learn it
Free-radical substitution: $X_2 + \text{UV light}$; initiation $X_2 \rightarrow 2X\bullet$ (homolytic)	Learn it
Hydrogenation: $H_2(g)$, Ni or Pt, heat · steam: $H_2O(g)$, H_3PO_4 · $HX(g)$, room temperature · X_2 , room temperature, dark	Learn it
Cracking: heat, Al_2O_3 catalyst · elimination: NaOH in ethanol, heat · dehydration: heated Al_2O_3 or concentrated H_2SO_4	Learn it
Cold dilute acidified $KMnO_4$: diol · hot concentrated acidified $KMnO_4$: $=CR_2 \rightarrow$ ketone, $=CHR \rightarrow RCOOH$, $=CH_2 \rightarrow CO_2 + H_2O$	Learn it
Carbocation stability: tertiary > secondary > primary (positive inductive effect of alkyl groups)	Learn it
One C=C adds one H_2 (24.0 dm ³ per mole of C=C), one X_2 or one HX	Learn it
Bromine water: orange $\rightarrow$ colourless with C=C	Learn it
Catalytic converter: $2CO + 2NO \rightarrow 2CO_2 + N_2$	Learn it

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (118 questions, 2021–2025), the types came up this often. 29 of the 118 questions mix more than one type, so the counts add up to more than 118.

Question type	Questions
Deduce products or the starting alkene from oxidation by acidified $KMnO_4$	32
Write or identify free-radical substitution steps, conditions and products	27
Predict and explain the major product of an unsymmetrical addition	23
Predict the product of an addition reaction	19
Draw an electrophilic addition mechanism	13
Give reagents and conditions	13
Name or classify the reaction type or mechanism	11
Cracking: name it, predict or check products	9

Question type	Questions
Draw an addition polymer repeat unit or its monomer	8
Combustion equations and pollutants from engines	6
Use bromine to test for C=C	5
Explain the unreactivity of alkanes or why alkenes react with electrophiles	3

1. Deduce products or the starting alkene from oxidation by acidified KMnO₄ (32 questions)

Forwards (alkene → products):

- Check the conditions.** Cold and dilute: add OH to both carbons of each C=C (a diol). Hot and concentrated: split each C=C.
- Draw the alkene with all its groups**, and mark each C=C.
- Cut every C=C** and put =O on both new ends.
- Finish each end** with the table: R₂C=O stays a ketone; RCH=O becomes RCOOH; H₂C=O becomes CO₂ + H₂O.
- Write the equation** if asked: count 1, 2 or 3 [O] for each carbon of the C=C (ketone, acid, CO₂), add H₂O for each CO₂, and check the atoms balance.

Backwards (products → alkene):

- Turn each ketone C=O into R₂C=, each COOH into RCH=, each CO₂ into =CH₂.
- Join the ends in pairs with C=C. A molecule with two C=O groups joins to something at **both** ends (a ring opening, or the middle of a diene).
- Check the carbon count** and the molecular formula against the question.

Variations you will meet:

- Rings.** A C=C in a ring opens into **one** chain with a C=O group at each end, so the product has the same number of carbons as the ring. Cyclohexene gives hexanedioic acid, HOOC(CH₂)₄COOH; a ring C=C carbon that carries a methyl group gives a ketone end instead of an acid end.
- Natural products** (limonene, pinenes, carotenes): treat each C=C separately. Count how many ends are =CR₂ (ketones), =CHR (acids) or =CH₂ (CO₂), or work out each product's molecular formula.
- Tests on the products.** Ketones and aldehydes give an orange precipitate with 2,4-DNPH; carboxylic acids react with Na, NaOH and Na₂CO₃ (fizzing); diols react with Na (1 mol H₂ per 2 OH) but not with Na₂CO₃; CO₂ turns limewater (Ca(OH)₂) milky.
- Only one acid, or only one product:** the alkene must be symmetrical about the C=C (like dec-5-ene giving only pentanoic acid), or the C=C must be in a ring.
- State the conditions** for making the diol: KMnO₄ that is **cold**, **dilute** and **acidified**; all three words are needed. Its role is an **oxidising agent**.

2. Write or identify free-radical substitution steps, conditions and products (27 questions)

1. **Name** it: free-radical substitution. **Condition**: ultraviolet light (or sunlight). Its job is to split the halogen molecule into atoms by **homolytic fission**, not to heat the mixture and not to break C–H bonds.
2. **Initiation**: $X_2 \rightarrow 2X\bullet$.
3. **Propagation 1**: alkane + $X\bullet \rightarrow$ alkyl radical + HX.
4. **Propagation 2**: alkyl radical + $X_2 \rightarrow$ halogenoalkane + $X\bullet$.
5. **Termination**: any two radicals joining. Choose the one that gives the product asked for.

Put the dot on the atom with the unpaired electron, and balance each step.

Variations you will meet:

- **Classify given steps.** Radical + molecule $\rightarrow$ radical + molecule is propagation (even when the molecule is a product such as CH_3Cl); two radicals $\rightarrow$ one molecule is termination; one molecule $\rightarrow$ two radicals is initiation.
- **Pick a valid propagation step.** It must have exactly one radical on each side, and it never makes $H\bullet$.
- **Termination products.** Two alkyl radicals join into a bigger alkane (two $CH_3\bullet$ give ethane). Hydrogen gas is never a product.
- **Count products.** List every different kind of H atom (by symmetry) for monosubstitution; include optical isomers if the question says so. With excess halogen, list products by number of halogen atoms, then by where they are.
- **Other starting molecules** (a halogenoalkane such as CH_2Cl_2 , a cycloalkane, or an alkene's CH_3 group): the steps are the same.
- **Electrons in a radical.** A $Br\bullet$ radical is a neutral atom: 35 electrons.

3. Predict and explain the major product of an unsymmetrical addition (23 questions)

1. **Draw the alkene** and find the two carbons of the $C=C$.
2. **Draw both possible carbocations** (H on one carbon, + on the other) and classify each as primary, secondary or tertiary by counting the alkyl groups on the C^+ .
3. **The major product comes from the more stable carbocation.** X or OH goes onto the carbon that was C^+ .
4. **Explain in two points:** (a) it forms via the more stable (secondary or tertiary) carbocation; (b) because more alkyl groups give a greater positive inductive effect, which stabilises the positive charge.

Variations you will meet:

- **Name the product**, such as 2-bromo-2-methylpentane from 2-methylpent-2-ene: number the chain after adding.
- **Dienes and alkynes with excess HX:** apply the rule at each $C=C$ (and at each stage for $C\equiv C$: propyne with excess HBr puts both Br atoms on the middle carbon).

- **Order alkenes by rate**, or pick the most stable intermediate: more alkyl groups on the C^+ that can form means a faster reaction.
- **Steam or IBr**: the same rule applies. In IBr, I is the δ^+ end, so I goes where the H would go.

4. Predict the product of an addition reaction (19 questions)

1. Find every $C=C$.
2. Add the reagent across **each** $C=C$ (if it is in excess): H and H; Br and Br; H and Br (Markovnikov); H and OH.
3. Leave the rest of the molecule, including rings, unchanged.

Variations you will meet:

- **Amounts of hydrogen.** Moles of H_2 = moles of alkene $\times$ number of $C=C$. Volume at room conditions = moles $\times 24.0 \text{ dm}^3$. A $C\equiv C$ takes two H_2 . Ring bonds don't react.
- **Counting $C=C$ from data.** Work out the moles of H_2 (or Br_2) per mole of compound; or compare molecular formulas with the saturated compound (each $C=C$ or ring removes two H).
- **M_r changes.** Adding HBr raises M_r by 80.9; Br_2 by 159.8; H_2 by 2.0. Use this to find the alkene or to check the number of $C=C$.
- **Number of products or isomers** (structural, sometimes stereo): after adding, look for new chiral centres. Adding Br_2 or HBr to a ring $C=C$ often makes two chiral centres or cis/trans ring isomers.
- **Which compound can be made by addition:** two new atoms must be on neighbouring carbons (1,2-dibromopentane can come from pent-1-ene; 1,3-dibromopentane cannot come from any alkene by one addition).

5. Draw an electrophilic addition mechanism (13 questions)

Usually 4 marks, one for each of these:

1. **Curly arrow from the $C=C$** (the middle of the double bond) to the δ^+ atom of the reagent (H of HBr, the near Br of Br_2).
2. **Dipole and curly arrow on the reagent:** show δ^+ and δ^- , and an arrow from the H-Br (or Br-Br) bond to the δ^- atom.
3. **The correct carbocation**, with the + on the right carbon (the more stable one for HX), and the halide ion shown as Br^- with a lone pair.
4. **Curly arrow from the lone pair** on Br^- to the C^+ .

Draw the product if asked. **Variations:** HOCl adds with Cl as the δ^+ end and OH as the ion; steam in two steps (H^+ is the electrophile); pick the correct mechanism in multiple choice (check where each arrow starts and ends).

6. Give reagents and conditions (13 questions)

Always give the **reagent and every condition** (state, catalyst, heat, solvent, concentration):

Change	Reagent and conditions
alkene → alkane	$\text{H}_2(\text{g})$, Ni or Pt catalyst, heat
long alkane → shorter alkane + alkene	heat with Al_2O_3 catalyst
alkene → alcohol	steam, H_3PO_4 catalyst, heat and pressure
alkene → halogenoalkane	$\text{HX}(\text{g})$, room temperature
alkene → dihalogenoalkane	X_2 , room temperature, in the dark
alkane → halogenoalkane	X_2 , UV light
alkene → diol	KMnO_4 , cold, dilute, acidified
alkene → split into $\text{C}=\text{O}$ compounds	KMnO_4 , hot, concentrated, acidified
halogenoalkane → alkene	NaOH in ethanol, heat
alcohol → alkene	heated Al_2O_3 , or concentrated H_2SO_4 (or H_3PO_4) and heat

Variations: two-step routes (propan-1-ol → propene by dehydration, then propene → propan-2-ol with steam); the **role** of concentrated H_2SO_4 in dehydration (dehydrating agent; it is not an oxidising agent here).

7. Name or classify the reaction type or mechanism (11 questions)

- Two molecules become one: **addition**. With an alkene and an electrophile: **electrophilic addition**. Steam with ethene is addition (not hydrolysis).
- A $\text{C}=\text{C}$ forms and a small molecule (HX or H_2O) leaves: **elimination** (for an alcohol, **dehydration**).
- H swapped for X in UV light: **free-radical substitution**.
- Define addition reaction:** two or more molecules react to form a single product.
- Redox:** alkene + KMnO_4 is oxidation of the alkene. Adding a halogen is also redox: the two carbons gain electronegative halogen atoms (they are oxidised) and the halogen is reduced to oxidation state -1 . Adding H_2O or HX , dehydration and hydrolysis are not redox.

8. Cracking: name it, predict or check products (9 questions)

- Name it:** cracking; give the catalyst (Al_2O_3) and heat if asked. The raw material is crude oil (a heavy fraction such as naphtha or gas oil).
- Missing product:** subtract the known products' C and H from the starting alkane.
- Check a suggested product:** every product must be smaller than the starting molecule; all the C and H must add up; there can be at most one alkane among the products (because $\text{C}_n\text{H}_{2n+2}$ has only enough H for one), and the rest are alkenes.
- Why it is useful:** it makes smaller alkanes (fuels, in greater demand) and alkenes (for polymers) from heavy fractions that are in less demand.

9. Draw an addition polymer repeat unit or its monomer (8 questions)

1. Draw the two C=C carbons side by side with a **single** bond between them.
2. Put each carbon's other two groups above and below.
3. Add a **continuation bond** out of each end, through the brackets if you use them.
4. **Monomer from polymer:** find a two-carbon repeat along the main chain and put a C=C between the pair.

Side chains and functional groups (such as CH₃, COOCH₃) stay as branches; only the two C=C carbons go into the chain.

10. Combustion equations and pollutants from engines (6 questions)

1. **Equation:** write the formula; C atoms give that number of CO₂ (or CO); H atoms ÷ 2 give H₂O; count O on the right and halve it for O₂ (halves are allowed).
2. **Moles of CO₂ and H₂O from a skeletal formula:** first write the molecular formula carefully.
3. **Pollutants:** CO (incomplete combustion; toxic), NO_x (N₂ and O₂ from air at high engine temperature; acid rain and smog), unburnt hydrocarbons (with NO_x and sunlight → photochemical smog, PAN).
Removal: catalytic converter, $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$.

11. Use bromine to test for C=C (5 questions)

- Observation: **orange** (or yellow-orange) bromine water becomes **colourless**. No change (stays orange) with an alkane, a halogenoalkane, a carboxylic acid or an ester that has no C=C.
- Product with Br₂: a Br on each carbon of the former C=C, for example
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH} \rightarrow \text{CH}_2\text{BrCBr}(\text{CH}_3)\text{COOH}$.
- Bromine **in the dark** is used so that the alkene reacts by addition only, without free-radical substitution.

12. Explain the unreactivity of alkanes or why alkenes react with electrophiles (3 questions)

- **Alkanes:** C–H bonds are **strong** (high bond energy) and **non-polar** (no δ⁺ or δ[–] sites to attract polar reagents). Give both points: each earns a mark.
- **Alkenes:** the π bond is a region of **high electron density** above and below the C–C σ bond; it is **weaker** than a σ bond and exposed, so it attracts electrophiles. A saturated polymer such as poly(ethene) has no π bond, so it does not react with electrophiles.

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

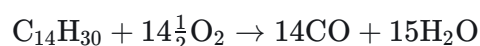
One molecule of tetradecane, $C_{14}H_{30}$, is cracked to give one molecule each of octane, ethene and compound G.

- (a) Give the molecular formula of G. **[1]**
- (b) Name the catalyst used, and explain why cracking heavy fractions is useful. **[3]**
- (c) Construct an equation for the incomplete combustion of tetradecane in which carbon monoxide and water are the only products. **[1]**
- (d) Explain how oxides of nitrogen form in a car engine, and give an equation for the reaction that removes carbon monoxide and nitrogen monoxide in a catalytic converter. **[2]**
- (e) Describe a test that distinguishes octane from ethene. **[2]**

(a) Carbon: $14 - 8 - 2 = 4$. Hydrogen: $30 - 18 - 4 = 8$. G is C_4H_8 (a butene). **B1**

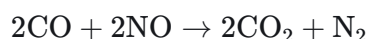
(b) Aluminium oxide, Al_2O_3 (with heat). **B1** Cracking makes smaller alkanes such as octane, which are used as fuels (petrol) and are in greater demand than the heavy fractions **B1**, and alkenes, which are used to make polymers. **B1**

(c) 14 C give 14 CO; 30 H give 15 H_2O ; oxygen atoms on the right = $14 + 15 = 29$, so $14\frac{1}{2} O_2$:



B1

(d) Nitrogen and oxygen from the air react at the high temperature inside the engine: $N_2 + O_2 \rightarrow 2NO$. **B1**



B1

(e) Add aqueous bromine to each. Ethene turns it from orange to colourless; with octane it stays orange. **M1** for the reagent, **A1** for both observations with both colours.

Example 2

2,2-Dimethylpropane, $\text{C}(\text{CH}_3)_4$, reacts with bromine in ultraviolet light.

(a) Name the mechanism, and state the type of bond fission that happens in the initiation step. **[2]**

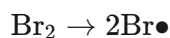
(b) Write equations for the initiation step, the two propagation steps, and a termination step that gives a hydrocarbon with formula $\text{C}_{10}\text{H}_{22}$. **[4]**

(c) Explain why only one monobromo compound, $\text{C}_5\text{H}_{11}\text{Br}$, is formed. **[1]**

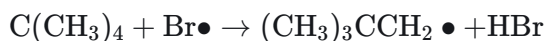
(d) The product also contains $\text{C}_5\text{H}_{10}\text{Br}_2$. Draw the structural formulas of the two isomers of $\text{C}_5\text{H}_{10}\text{Br}_2$ that can form, and suggest how to make less of them. **[3]**

(a) Free-radical substitution. **B1** Homolytic fission. **B1**

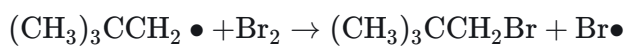
(b)



B1



B1



B1



B1 (2,2,5,5-tetramethylhexane, $\text{C}_{10}\text{H}_{22}$.)

(c) All 12 H atoms are equivalent: they are on four identical CH_3 groups joined to the same carbon, so whichever H is replaced, the product is the same, 1-bromo-2,2-dimethylpropane. **B1**

(d) The second Br goes either on the same CH_3 group or on a different one:

- $(\text{CH}_3)_3\text{CCHBr}_2$ **B1**
- $\text{BrCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{Br}$ **B1**

Use an excess of 2,2-dimethylpropane, so that a $\text{Br}\bullet$ is more likely to meet an alkane molecule than a bromo product. **B1**

Example 3

2,3-Dimethylbut-1-ene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$, reacts with hydrogen chloride gas at room temperature. The major product is 2-chloro-2,3-dimethylbutane.

(a) Describe the mechanism of this reaction. Include the dipole, the intermediate and what each curly arrow shows. **[4]**

(b) Explain why 2-chloro-2,3-dimethylbutane is the major product rather than 1-chloro-2,3-dimethylbutane. [2]

(c) Give the name of the major organic product when 2,3-dimethylbut-1-ene reacts with steam in the presence of H_3PO_4 . [1]

(d) Construct an equation for the reaction of 2,3-dimethylbut-1-ene with hot, concentrated, acidified KMnO_4 . Use [O] for an atom of oxygen from the oxidising agent. [2]

(a) $\text{H}-\text{Cl}$ is polar, $\text{H}^{\delta+}-\text{Cl}^{\delta-}$. **M1** for the dipole with a curly arrow from the $\text{H}-\text{Cl}$ bond to the Cl .

A curly arrow goes from the $\text{C}=\text{C}$ to the H , which bonds to the CH_2 carbon. **M1**

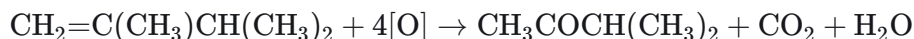
This gives the tertiary carbocation $\text{CH}_3\overset{+}{\text{C}}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ and a chloride ion, Cl^- . **M1**

A curly arrow goes from a lone pair on Cl^- to the C^+ , forming $(\text{CH}_3)_2\text{CClCH}(\text{CH}_3)_2$. **M1** (The drawing looks like the propene one in "Understand it", with Cl for Br .)

(b) The major product forms via the **tertiary** carbocation, which is more stable than the **primary** carbocation $^+\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ that would give the 1-chloro isomer. **M1** The C^+ of the tertiary ion has three alkyl groups, whose positive inductive effect pushes electron density towards it and stabilises the positive charge more than the one alkyl group of the primary ion. **A1**

(c) OH goes to the same carbon as Cl did: 2,3-dimethylbutan-2-ol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)_2$. **B1**

(d) The $=\text{CH}_2$ end becomes $\text{CO}_2 + \text{H}_2\text{O}$ (3 [O]); the $=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ end becomes the ketone 3-methylbutan-2-one (1 [O]). **M1**



A1 (Check: $\text{C } 6 = 5 + 1$; $\text{H } 12 = 10 + 2$; $\text{O } 4 = 1 + 2 + 1$.)

Example 4

Three hydrocarbons, P, Q and R, have the molecular formula C_8H_{14} . Each contains one six-membered ring of carbon atoms and one $\text{C}=\text{C}$ bond. Each is heated with an excess of hot, concentrated, acidified KMnO_4 .

- P gives a single organic product, $\text{C}_8\text{H}_{14}\text{O}_2$, which gives an orange precipitate with 2,4-DNPH but does not react with sodium carbonate.
- Q gives two organic products: cyclohexanone, $\text{C}_6\text{H}_{10}\text{O}$, and ethanoic acid.
- R gives carbon dioxide and one organic product, $\text{C}_7\text{H}_{12}\text{O}_2$, which fizzes with sodium carbonate.

(a) Identify P and its product. Explain your answer. [3]

(b) Identify Q, and construct an equation for its reaction. Use [O] for an atom of oxygen from the oxidising agent. [2]

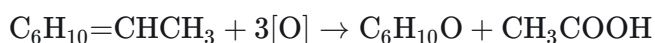
(c) Identify R, and construct an equation for its reaction. [2]

(d) Give the structural formula of the major product when R reacts with HBr, and explain why it has optical isomers. **[2]**

(e) Calculate the volume of hydrogen, at room conditions, that reacts with 2.20 g of P in the presence of a nickel catalyst. **[2]**

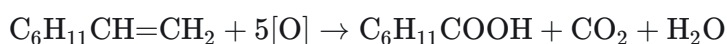
(a) A single product with all 8 carbons means the C=C was in the ring, which opens into one chain. The product has two C=O groups (it reacts with 2,4-DNPH) but no COOH (no reaction with Na_2CO_3), so both carbons of the C=C had **no** H: both were $=\text{CR}_2$ and became ketones. **M1** Each of those ring carbons must carry a CH_3 to make 8 carbons: P is **1,2-dimethylcyclohexene**. **A1** The product is octane-2,7-dione, $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{COCH}_3$. **A1**

(b) The ketone end $(\text{CH}_2)_5\text{C}=\text{O}$ came from a ring carbon $(\text{CH}_2)_5\text{C}=\text{}$; ethanoic acid came from $=\text{CHCH}_3$. Joining them: Q is ethylenecyclohexane, the ring with an exocyclic $=\text{CHCH}_3$. **B1**



B1 (1 [O] for the ketone end and 2 [O] for the acid end.)

(c) CO_2 comes from a $=\text{CH}_2$ end; the acid $\text{C}_6\text{H}_{11}\text{COOH}$ (cyclohexanecarboxylic acid) came from $\text{C}_6\text{H}_{11}\text{CH}=\text{}$. R is cyclohexylethene, $\text{C}_6\text{H}_{11}\text{CH}=\text{CH}_2$. **B1**



B1 (Check: C 8 = 7 + 1; H 14 = 12 + 2; O 5 = 2 + 2 + 1.)

(d) H adds to the CH_2 end, giving the secondary carbocation, so Br goes on the carbon next to the ring: $\text{C}_6\text{H}_{11}\text{CHBrCH}_3$, (1-bromoethyl)cyclohexane. **B1** That carbon carries four different groups (H, Br, CH_3 and the cyclohexyl ring), so it is a chiral centre. **B1**

(e) $M_r(\text{C}_8\text{H}_{14}) = 8(12.0) + 14(1.0) = 110.0$, so $2.20 \div 110.0 = 0.0200$ mol. **M1** P has one C=C, so 0.0200 mol H_2 reacts: $0.0200 \times 24.0 = 0.480 \text{ dm}^3$ (480 cm^3). **A1**

Common mistakes

- **Sloppy curly arrows.** Examiners stress this every year: an arrow must start at the **middle of a bond** or at a **lone pair**, and point clearly at the **atom** that receives the electrons. Common faults are arrows starting from an atom, going the wrong way, or ending between atoms.
- **Missing parts of the mechanism.** The dipole on H–Br, the lone pair on Br^- , the + charge on the right carbon, or a carbocation whose carbon chain doesn't match the alkene. Draw the intermediate with every carbon of the starting alkene.
- **Explaining Markovnikov without the carbocation.** "The secondary halogenoalkane is more stable" or just quoting "Markovnikov's rule" earns nothing. Say the major product forms **via the more stable carbocation**, and that this is because of the **greater positive inductive effect of more alkyl groups**, using the actual ions in the question.
- **Mixing up primary, secondary and tertiary carbocations.** Count the alkyl groups on the C^+ itself.

- **Incomplete conditions for KMnO_4 .** For the diol it must be **cold, dilute and acidified**; candidates often leave one word out. For splitting the $\text{C}=\text{C}$ it is **hot, concentrated and acidified**.
- **Wrong products from hot KMnO_4 .** Stopping at an aldehyde (it is oxidised on to an acid), turning a ketone end into an acid, or forgetting that a $=\text{CH}_2$ end becomes CO_2 . Count carbons to check.
- **Homolytic versus heterolytic.** Radicals come from homolytic fission. Writing ions (Cl^+ , Cl^-) in initiation, or making $\text{H}\bullet$ in propagation, loses the mark.
- **Missing the radical dot**, or writing a termination step as a propagation step. Termination has two radicals on the left and none on the right.
- **Confusing the two NaOH reactions.** NaOH in **ethanol** with heat gives the alkene (elimination) plus NaBr and water; NaOH in **water** gives the alcohol.
- **Calling concentrated H_2SO_4 an oxidising agent** in dehydration. It is a dehydrating agent (and catalyst).
- **Bromine water colours.** Give the starting colour (orange) and the final one (colourless). "Clear" is not a colour, and bromine water is never "white".
- **Unreactivity with one reason.** Two marks need two points: strong C-H bonds **and** non-polar bonds.

How to get the marks

- **"Describe the mechanism" or "complete the mechanism"** means curly arrows, dipoles, charges, lone pairs and the intermediate. Each of these usually carries a mark; words alone won't do.
- **"Explain"** Markovnikov questions have two marks: more stable carbocation (**M1**) and the inductive effect of more alkyl groups (**M2**). Name the carbocations in the question (secondary, tertiary).
- **Reagents and conditions** are marked together: " H_2 and Ni " alone may lose the mark if heat is expected; " KMnO_4 " alone always does. Give state symbols or words where they matter (HBr(g) , steam, ethanolic).
- **Free-radical steps** earn one mark each. Balance every step, put the dot on the radical, and use the formulas from the question (propane, cyclopentane) rather than a general R .
- **"Construct an equation" with [O]** must balance, counting each [O] as one O atom; include H_2O and CO_2 when they are products.
- **"Suggest the structure"** of an alkene from its oxidation products: draw it clearly (structural or skeletal) and check the molecular formula matches.
- **"State"** needs the key word only: cracking, homolytic, termination, electrophilic addition, elimination.
- **Combustion equations** may use fractions of O_2 ($9\frac{1}{2}\text{O}_2$) unless whole numbers are asked for.
- **Multiple choice on KMnO_4 or addition products:** redraw the molecule with every $\text{C}=\text{C}$, work out the product yourself, then compare formulas with the options.

Quick check

1. Give the reagents and conditions for each change: (a) hexan-1-ol $\rightarrow$ hex-1-ene; (b) hex-1-ene $\rightarrow$ hexane; (c) hex-1-ene $\rightarrow$ hexane-1,2-diol; (d) hex-1-ene $\rightarrow$ 2-bromohexane. (e) Draw the repeat unit of the polymer formed from hex-1-ene.

2. Undecane, $C_{11}H_{24}$, is cracked to give pentane and one other product. Give the formula of the other product, explain why it must be an alkene, and write an equation for its complete combustion.
3. 2,2-Dimethylbutane, $CH_3C(CH_3)_2CH_2CH_3$, reacts with bromine in UV light. (a) How many structural isomers of $C_6H_{13}Br$ can form? (b) Write the propagation step that makes the radical leading to the isomer with a chiral centre.
4. Pent-2-ene reacts with HBr. Explain why 2-bromopentane and 3-bromopentane form in similar amounts.
5. Hexa-1,5-diene is $CH_2=CHCH_2CH_2CH=CH_2$. (a) Construct an equation for its reaction with hot, concentrated, acidified $KMnO_4$. (b) What volume of hydrogen at room conditions reacts with 0.150 mol of it?

Answers

- (a) Heated Al_2O_3 (pass the vapour over it), or heat with concentrated H_2SO_4 . (b) $\text{H}_2(\text{g})$ with a Ni or Pt catalyst and heat. (c) Cold, dilute, acidified KMnO_4 . (d) $\text{HBr}(\text{g})$ at room temperature (Br goes to C2 via the secondary carbocation). (e) Two chain carbons with a continuation bond at each end: $-\text{CH}_2-\text{CH}(\text{C}_4\text{H}_9)-$; the butyl group is a side branch.
- Carbon $11 - 5 = 6$, hydrogen $24 - 12 = 12$: C_6H_{12} . Pentane already uses the "+2" hydrogens of the $\text{C}_n\text{H}_{2n+2}$ formula, so the other product has the formula C_nH_{2n} and (being non-cyclic) is an alkene, a hexene. $\text{C}_6\text{H}_{12} + 9\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$.
- (a) There are three kinds of H: on the three CH_3 groups joined to C2, on the CH_2 (C3), and on the end CH_3 (C4). So **3** structural isomers: 1-bromo-2,2-dimethylbutane, 3-bromo-2,2-dimethylbutane and 1-bromo-3,3-dimethylbutane. (b) The chiral one is 3-bromo-2,2-dimethylbutane, $(\text{CH}_3)_3\text{CCHBrCH}_3$ (its C3 carries H, Br, CH_3 and $\text{C}(\text{CH}_3)_3$). Its radical, with the unpaired electron on C3, forms in $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3 + \text{Br}\bullet \rightarrow (\text{CH}_3)_3\text{C}\dot{\text{C}}\text{HCH}_3 + \text{HBr}$.
- Pent-2-ene is $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$. H on C3 gives $\text{CH}_3\text{CH}^+\text{CH}_2\text{CH}_2\text{CH}_3$; H on C2 gives $\text{CH}_3\text{CH}_2\text{CH}^+\text{CH}_2\text{CH}_3$. Both are **secondary** carbocations (two alkyl groups on the C^+), so they are similarly stable, form at similar rates, and neither product is strongly favoured.
- (a) Each $=\text{CH}_2$ end gives $\text{CO}_2 + \text{H}_2\text{O}$ (3 [O] each); the two $=\text{CH}-$ ends become the two COOH groups of butanedioic acid (2 [O] each): $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2 + 10[\text{O}] \rightarrow \text{HOOCCH}_2\text{CH}_2\text{COOH} + 2\text{CO}_2 + 2\text{H}_2\text{O}$. (b) Two $\text{C}=\text{C}$, so $2 \times 0.150 = 0.300 \text{ mol H}_2$; $0.300 \times 24.0 = 7.20 \text{ dm}^3$.

Past questions to try

- 9701/22/O/N/25 Q4**: the free-radical substitution of propane, step by step.
- 9701/22/M/J/25 Q3**: the HBr and propene mechanism, Markovnikov addition, and a diene worked out from its oxidation products.
- 9701/23/M/J/25 Q3**: the cracking catalyst, photochemical smog and a hydrogenation catalyst.
- 9701/13/M/J/25 Q35**: cyclohexene with cold dilute and with hot concentrated acidified KMnO_4 .