

Halogen compounds

AS

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

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What you need to know

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

1. **Recall how halogenoalkanes are made** (reagents and conditions):
 - (a) **free-radical substitution** of an alkane by Cl_2 or Br_2 in ultraviolet light, using ethane as the example;
 - (b) **electrophilic addition** to an alkene of a halogen, X_2 , or a hydrogen halide, $\text{HX}(\text{g})$, at room temperature;
 - (c) **substitution of an alcohol** by $\text{HX}(\text{g})$; by KCl with concentrated H_2SO_4 or concentrated H_3PO_4 ; by PCl_3 and heat; by PCl_5 ; or by SOCl_2 .
2. **Classify** a halogenoalkane as primary, secondary or tertiary.
3. **Describe four nucleophilic substitution reactions**:
 - (a) with $\text{NaOH}(\text{aq})$ and heat, giving an **alcohol**;
 - (b) with KCN in ethanol and heat, giving a **nitrile**;
 - (c) with NH_3 in ethanol, heated under pressure, giving an **amine**;
 - (d) with aqueous silver nitrate in ethanol, used to **identify the halogen** (bromoethane is the example).
4. **Describe elimination** with NaOH in ethanol and heat, giving an **alkene** (bromoethane is the example).
5. **Describe the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms**, including the inductive effect of alkyl groups.
6. **Recall which mechanism each class uses**: primary mostly $\text{S}_{\text{N}}2$, tertiary mostly $\text{S}_{\text{N}}1$, secondary a mixture of the two depending on the structure.
7. **Describe and explain why halogenoalkanes react at different rates**, using the strengths of the C-X bonds, as shown by their reactions with aqueous silver nitrate.

Understand it

What a halogenoalkane is

A **halogenoalkane** is an alkane with one or more hydrogen atoms replaced by halogen atoms (F, Cl, Br or I). Name it like an alkane, with the halogen as a prefix and the lowest possible number: $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$ is 2-bromobutane, and $(\text{CH}_3)_2\text{CClCH}_2\text{CH}_3$ is 2-chloro-2-methylbutane. We write RX for a general one, where R

is the alkyl group and X the halogen.

Classify it by the carbon that carries the halogen. Count how many **other carbon atoms** are bonded to that carbon:

Class	Carbon bonded to X is joined to	Example
Primary	one other carbon (or none, as in CH_3Br)	1-iodopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$
Secondary	two other carbons	3-chloropentane, $\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{CH}_3$
Tertiary	three other carbons	2-bromo-2-methylpentane, $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_2\text{CH}_3$

Count carbons on the C–X carbon, not along the chain: $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ has a branch, but its C–Cl carbon is joined to only one carbon, so it is primary.

Making halogenoalkanes

You met the first two routes in Hydrocarbons; here they are side by side with the third.

- **From an alkane: free-radical substitution.** Chlorine or bromine and **ultraviolet light**. The halogen molecule splits evenly (homolytic fission) into two radicals, and a chain reaction swaps H atoms for halogen atoms: $\text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl}$. It gives a mixture, because further substitution makes dichloro and trichloro products too.
- **From an alkene: electrophilic addition** at room temperature. $\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br}$, or with a halogen $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br}$. With an unsymmetrical alkene the halogen of HX goes mainly to the carbon that gives the more stable carbocation.
- **From an alcohol: substitution of the –OH group.** The OH is replaced by a halogen atom. For a chloroalkane (bromo versions such as PBr_3 work the same way):

Reagent and conditions	Equation (R = alkyl group)
HCl(g)	$\text{ROH} + \text{HCl} \rightarrow \text{RCl} + \text{H}_2\text{O}$
KCl with concentrated H_2SO_4 or H_3PO_4 (makes HCl in the flask)	$\text{ROH} + \text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{RCl} + \text{KHSO}_4 + \text{H}_2\text{O}$
PCl_3 , heat	$3\text{ROH} + \text{PCl}_3 \rightarrow 3\text{RCl} + \text{H}_3\text{PO}_3$
PCl_5 , room temperature	$\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$
SOCl_2	$\text{ROH} + \text{SOCl}_2 \rightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$

PCl_5 reacts vigorously and gives off misty fumes of HCl. With SOCl_2 both by-products are gases, so the chloroalkane is easy to separate.

The polar C–X bond and nucleophiles

Chlorine, bromine and iodine are all more electronegative than carbon, so the C–X bond is polar: $C^{\delta+} - X^{\delta-}$. The slightly positive carbon attracts **nucleophiles**. A nucleophile is a species that **donates a lone pair of electrons** to form a new covalent bond. It can be negative (OH^- , CN^- , CH_3O^-) or neutral (NH_3 , H_2O), but it always has a lone pair.

In **nucleophilic substitution** the nucleophile bonds to the carbon and the halogen leaves as a halide ion, X^- , taking both electrons of the C–X bond with it (heterolytic fission). The halide ion is the **leaving group**.

The four substitution reactions

The solvent matters. Water favours substitution; ethanol with NaOH favours elimination (next section). Every reaction here needs heat, since the C–X bond must break.

Reagent and conditions	Nucleophile	Product	Example with 1-bromo-2-methylpropane, $RBr = (CH_3)_2CHCH_2Br$
NaOH(aq), heat under reflux	OH^-	alcohol	$RBr + NaOH \rightarrow (CH_3)_2CHCH_2OH + NaBr$
KCN in ethanol, heat under reflux	CN^- (bonds through C)	nitrile	$RBr + KCN \rightarrow (CH_3)_2CHCH_2CN + KBr$
excess NH_3 in ethanol, heat in a sealed tube (under pressure)	NH_3	amine	$RBr + 2NH_3 \rightarrow (CH_3)_2CHCH_2NH_2 + NH_4Br$
$AgNO_3$ (aq) in ethanol, warm	H_2O	alcohol + silver halide precipitate	$RBr + H_2O \rightarrow (CH_3)_2CHCH_2OH + HBr$, then $Ag^+ + Br^- \rightarrow AgBr$

- **The nitrile has one more carbon** than the halogenoalkane: 1-bromo-2-methylpropane (C_4) gives 3-methylbutanenitrile, $(CH_3)_2CHCH_2CN$ (C_5). This is how chemists lengthen a carbon chain. Count the CN carbon in the name. Use **KCN in ethanol**: never HCN, and never acid (HCN with a carbonyl compound is a different reaction).
- **Ammonia**: the first product, $(CH_3)_2CHCH_2NH_3^+Br^-$, loses H^+ to a second NH_3 , which is why the equation uses $2NH_3$ and makes NH_4Br . Ammonia is a gas, so the mixture is heated in a sealed tube, under pressure.
- **Silver nitrate test**. Ethanol is there so that the halogenoalkane and the aqueous silver nitrate mix. Water slowly substitutes the halogen, and the halide ion that is released meets Ag^+ and gives a precipitate. Its colour tells you the halogen:

Halogen	Precipitate	Colour	How fast it appears
Cl	AgCl	white	slowest

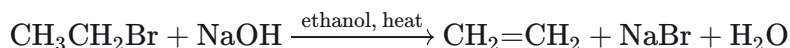
Halogen	Precipitate	Colour	How fast it appears
Br	AgBr	cream	medium
I	AgI	yellow	fastest

(From Group 17: AgCl dissolves in dilute $\text{NH}_3(\text{aq})$, AgBr only in concentrated, AgI not at all. This confirms a colour that is hard to judge.)

- **Two halogens on one carbon.** Each is substituted by OH, and a carbon with two OH groups loses water at once, leaving $\text{C}=\text{O}$. So $\text{CH}_3\text{CH}_2\text{CHBr}_2$ with $\text{NaOH}(\text{aq})$ gives propanal. The first step is still substitution.

Elimination: NaOH in ethanol

Heat the halogenoalkane with NaOH (or KOH) **dissolved in ethanol** and a different reaction wins. The hydroxide ion acts as a **base**: it removes an H^+ from a carbon **next to** the C–X carbon, and the halide ion leaves. A $\text{C}=\text{C}$ bond forms between those two carbons:



A small molecule, HX, has been removed, so this is **elimination**. Always write H_2O and NaX (not HX) as the other products when NaOH is the reagent.

More than one alkene. Look at every carbon next to the C–X carbon that carries at least one H. Each one can lose the H, so each can give a different alkene. Then check each alkene for **cis/trans isomers**: both carbons of the $\text{C}=\text{C}$ must carry two different groups. For 2-chloro-3-methylbutane, $\text{CH}_3\text{CHClCH}(\text{CH}_3)_2$:

- losing H from C1 gives 3-methylbut-1-ene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$ (no cis/trans: C1 has two H);
- losing H from C3 gives 2-methylbut-2-ene, $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$ (no cis/trans: C3 has two CH_3 groups).

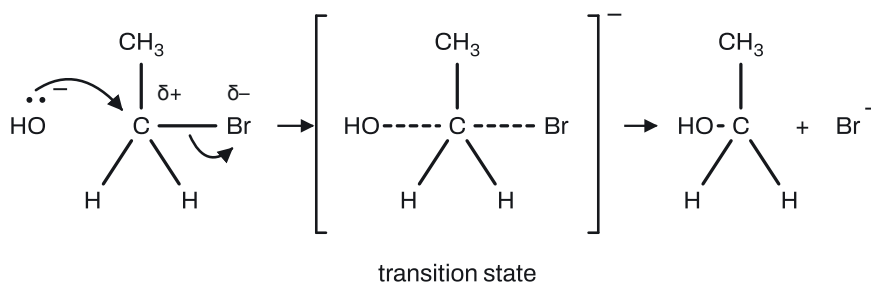
That is 2 alkenes in all. A halogenoalkane whose neighbouring carbons carry **no H** cannot eliminate: $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ only substitutes. A **dihalide** with excess ethanolic NaOH loses two HX and gives a diene: 1,6-dibromohexane gives hexa-1,5-diene, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$.

Any strong base does the same job: the methoxide ion, CH_3O^- , behaves as a Brønsted–Lowry base when it removes H^+ .

In practice both reactions happen at once. **Water as solvent** gives mainly the alcohol; **ethanol as solvent** and higher temperature give mainly the alkene. Tertiary halogenoalkanes eliminate most easily.

The $\text{S}_{\text{N}}2$ mechanism

$\text{S}_{\text{N}}2$ means **substitution**, **nucleophilic**, **2** species in the rate-determining step. It happens in **one step**:

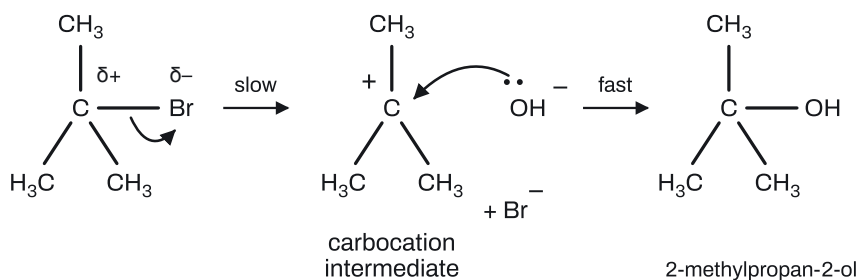
S_N2: hydroxide ion and bromoethane

1. The lone pair on the nucleophile is attracted to the $\delta+$ carbon and attacks it from the side **opposite** the halogen. At the same time the C–X bond breaks and both electrons go to X.
2. For an instant the carbon is half-bonded to both groups: the **transition state**. It is not an intermediate; it cannot be isolated and exists only at the top of the energy barrier. It carries the nucleophile's negative charge, spread out.
3. The halide ion leaves.

Two species (halogenoalkane and nucleophile) take part in this single step. For the arrows: one from the **lone pair** of the nucleophile to the **carbon**, and one from the **middle of the C–X bond** to the **X atom**. With cyanide, the arrow starts from the lone pair on the **carbon** of $\text{:C}\equiv\text{N}^-$, because the carbon is what bonds.

The S_N1 mechanism

S_N1: **1** species in the rate-determining step. It happens in **two steps**:

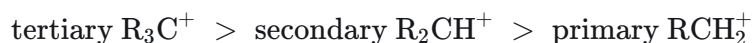
S_N1: 2-bromo-2-methylpropane and hydroxide ion

1. **Slow**: the C–X bond breaks on its own (heterolytic fission). X leaves as X^- and a **carbocation** is left, a carbon with only three bonds and a positive charge. This is an **intermediate**: it has a real, if short, existence.
2. **Fast**: the nucleophile's lone pair attacks the positive carbon.

Only the halogenoalkane is involved in the slow step, hence the "1". The carbocation is flat (three groups around the carbon), so the nucleophile can attack from either side.

Why tertiary goes S_N1 and primary goes S_N2

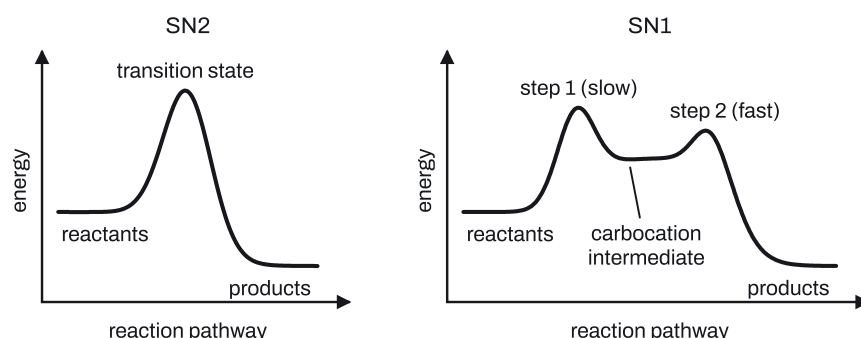
Alkyl groups push electrons. An alkyl group releases electron density towards the carbon it is attached to: the **positive inductive effect**. Around a positive carbon, this spreads out (disperses) the charge and makes the carbocation more stable. More alkyl groups means more stability:



- **Tertiary:** three alkyl groups make a stable carbocation, so step 1 of S_N1 is possible. The three groups also crowd the carbon, which blocks attack from behind. So tertiary reacts **by** S_N1.
- **Primary:** a primary carbocation (one alkyl group) is too unstable to form, and the carbon is easy to reach. So primary reacts **by** S_N2.
- **Secondary:** in between, so a **mixture of both**, depending on the structure.

The mechanism depends on the halogenoalkane, not on which nucleophile you use: (CH₃)₃CCl reacts by S_N1 with OH[−], CN[−] and NH₃ alike.

Reaction pathway diagrams



Each step has its own hump (its own transition state and activation energy). So S_N2 has **one** hump and S_N1 has **two**, with the carbocation in the dip between them. In S_N1 the **first hump is higher**, because breaking C–X is the slow step.

Reactivity and the strength of the C–X bond

Every one of these reactions breaks the C–X bond, so **the weaker the bond, the faster the reaction**. The C–X bond gets longer and weaker down Group 17, because the halogen atom is bigger and its bonding electrons are further from the carbon nucleus:

Bond	Bond energy / kJ mol ^{−1} (Data Booklet)	Rate of substitution
C–F	467	very slow (fluoroalkanes are almost unreactive)
C–Cl	340	slow
C–Br	280	faster
C–I	240	fastest

So **iodoalkanes react fastest and chloroalkanes slowest**: with silver nitrate in ethanol, the yellow AgI appears first and the white AgCl last.

Polarity points the other way. C–Cl is **more** polar than C–I (Cl is more electronegative), so if polarity controlled the rate, chloroalkanes would react fastest. They don't. **Bond strength**, not polarity, decides. This is the classic trap in multiple-choice options.

The class matters as well: under the same conditions a tertiary halogenoalkane is hydrolysed faster than a primary one with the same halogen, because it can form a stable carbocation.

Key facts and formulas

"Given" means it is in the 9701 Data Booklet. "Learn it" means you must remember it. Reagents, conditions, colours and mechanisms are never printed.

Formula or fact	Status
Bond energies: C–F 467, C–Cl 340, C–Br 280, C–I 240 kJ mol ⁻¹	Given
Relative atomic masses (C 12.0, H 1.0, N 14.0, O 16.0, Cl 35.5, Br 79.9, I 126.9)	Given
$\text{RX} + \text{OH}^- \rightarrow \text{ROH} + \text{X}^-$ (NaOH(aq), heat)	Learn it
$\text{RX} + \text{CN}^- \rightarrow \text{RCN} + \text{X}^-$ (KCN in ethanol, heat): one extra carbon	Learn it
$\text{RX} + 2\text{NH}_3 \rightarrow \text{RNH}_2 + \text{NH}_4\text{X}$ (ethanol, heat, pressure)	Learn it
$\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightarrow \text{AgX}(\text{s})$: AgCl white, AgBr cream, AgI yellow	Learn it
Elimination: $\text{RCH}_2\text{CH}_2\text{X} + \text{NaOH} \rightarrow \text{RCH}=\text{CH}_2 + \text{NaX} + \text{H}_2\text{O}$ (NaOH in ethanol, heat)	Learn it
Primary $\rightarrow \text{S}_{\text{N}}2$ (one step, transition state); tertiary $\rightarrow \text{S}_{\text{N}}1$ (two steps, carbocation intermediate); secondary $\rightarrow$ both	Learn it
Carbocation stability: tertiary > secondary > primary (positive inductive effect of alkyl groups)	Learn it
Rate: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$, because C–X bond energy decreases from F to I	Learn it
Making RX from ROH: $\text{HX}(\text{g})$; KCl + conc. H_2SO_4 or H_3PO_4 ; PCl_3 + heat; PCl_5 ; SOCl_2	Learn it
Percentage yield = $\frac{\text{actual amount}}{\text{theoretical amount}} \times 100$	Learn it

How to do it

We have tagged 95 questions on this topic from 2021–2025 (83 different, since some papers share questions). 32 of the 83 mix more than one type, so the counts add up to more than 83.

Question type	Questions
Reagents, conditions and products: substitution or elimination	40
S _N 1 or S _N 2: choose it and describe its features	26
Compare and explain rates	22
Elimination products: count the alkenes or work back	13
Making halogenoalkanes	13
Silver nitrate test	9
Draw an S _N 1 or S _N 2 mechanism	6
Classify and name	4

1. Reagents, conditions and products: substitution or elimination (40 questions)

1. **Read the reagent and the solvent together.** NaOH(aq) → alcohol (substitution). NaOH in ethanol → alkene (elimination). KCN in ethanol → nitrile. NH₃ in ethanol under pressure → amine.
2. **Write the product.** For substitution, put the new group exactly where the halogen was. For elimination, put the C=C between the C–X carbon and a neighbouring carbon that has an H.
3. **Name the reaction type** in full: "nucleophilic substitution", "elimination".
4. **Give reagent, solvent and condition** when asked, all three: "KCN in ethanol, heat under reflux".

Variations you will meet:

- **Same halogenoalkane, two solvents.** Water gives the alcohol; ethanol gives the alkene. The inorganic products are NaX and (for elimination) H₂O, not HX.
- **A step in a longer route.** An alcohol → halogenoalkane (step 1) → nitrile or amine (step 2). Count carbons: only the cyanide step adds one. What happens to the nitrile afterwards belongs to later topics.
- **Work back from a product.** If NaOH(aq) turns X into hexan-3-ol, X is a 3-haloheptane, and with KCN in ethanol it would give CH₃CH₂CH(CN)CH₂CH₂CH₃.
- **Pick the lowest (or highest) M_r product.** Work out each product in turn: elimination loses HX, substitution by OH swaps X for OH, cyanide adds a carbon.
- **Two halogens on one carbon** → aldehyde or ketone after hydrolysis (first step: substitution).
- **An alkoxide, RO[–], or hydroxide pulling off H⁺** is acting as a Brønsted–Lowry base, and the reaction is elimination.

2. S_N1 or S_N2: choose it and describe its features (26 questions)

1. **Classify** the halogenoalkane (count the carbons on the C–X carbon).
2. **Primary** → S_N2, **tertiary** → S_N1, secondary → either or both.
3. **Match the feature** to the mechanism:

Feature	S _N 2	S _N 1
Steps	one	two
First event	nucleophile attacks the δ^+ carbon	C–X breaks heterolytically
Species formed	transition state (not isolable)	carbocation intermediate
Species in the slow step	two	one
Pathway diagram	one hump	two humps, first one higher

Variations you will meet:

- **"What is true of every nucleophile?"** It donates a lone pair. It need not be charged or a single atom.
- **Roles in hydrolysis.** OH[−] is the attacking nucleophile; the halide ion leaves, and it is also a nucleophile (it has lone pairs).
- **Most stable carbocation.** The one with the most alkyl groups on the positive carbon: tertiary.
- **Which reaction is S_N1?** It must be a **substitution** of a **tertiary** halogenoalkane. A tertiary halogenoalkane with KOH in ethanol is elimination, not S_N1.
- **NH₃ or OH[−], which nucleophile reacts faster?** OH[−]: its negative charge makes it more strongly attracted to the δ^+ carbon.

3. Compare and explain rates (22 questions)

1. **Different halogens, same skeleton:** the rate goes I > Br > Cl > F.
2. **Explain with bond strength:** "the C–Br bond is weaker than (has a lower bond energy than) the C–Cl bond, so it breaks more easily". Compare the two bonds by name.
3. **Different classes, same halogen:** tertiary is faster (it forms a stable carbocation).
4. **"Time taken" questions:** a faster reaction means a **shorter** time for the precipitate.

Variations you will meet:

- **Multiple-choice explanations.** Reject polarity ("C–Cl is more polar"), ionisation energy and "chlorine is more reactive". The only right reason is **bond energy**.
- **One molecule, several halogens.** In ICH₂CH₂CH₂Cl, the C–I bond breaks first, so with warm silver nitrate the first precipitate is yellow AgI and the first organic product is HOCH₂CH₂CH₂Cl.
- **Fluoroalkanes** hardly react at all: C–F (467 kJ mol^{−1}) is the strongest.
- **Rate plus a yield calculation:** see Example 3 for the yield method.

4. Elimination products: count the alkenes or work back (13 questions)

1. **Mark the C–X carbon** and its neighbouring carbons. Keep only neighbours with at least one H.
2. **Draw one alkene per different neighbour** (two neighbours that are the same by symmetry give the same alkene).
3. **Check each alkene for cis/trans:** both C=C carbons must carry two different groups. If so, count 2.
4. **A diene with two cis/trans C=C bonds gives 4 combinations, unless the molecule is symmetrical.** If the two C=C bonds are equivalent (the molecule reads the same from either end), cis,trans and trans,cis are the same molecule, so there are only **3**: cis,cis; trans,trans; cis,trans. Hexa-2,4-diene, $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_3$, has 3 stereoisomers, not 4.
5. **Add up**, and also count any **chiral centre** left in the alkene as 2 optical isomers if the question says "stereoisomerism should be considered".

Variations you will meet:

- **Two halogenoalkanes mixed:** list the alkenes from each, then count the **different** ones (the same alkene from both counts once).
- **Dihalides with excess base:** remove both HX. For each halogen, list its possible C=C positions, combine them, and count stereoisomers of each diene (step 4 for a symmetrical one). 2,5-dibromohexane, $\text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{CHBrCH}_3$, gives hexa-1,5-diene (1), hexa-1,4-diene (2: its internal C=C is cis or trans) and hexa-2,4-diene (3, not 4): **6** in all.
- **"Which one cannot form an alkene?"** The one whose C–X carbon has no neighbouring C–H, such as 1-bromo-2,2-dimethylpropane.
- **Work back:** from the alkenes formed, place the halogen on a carbon that joins both alkene positions.

5. Making halogenoalkanes (13 questions)

1. **From an alcohol:** give one reagent from the list (PCl_5 , SOCl_2 , PCl_3 + heat, KCl + conc. H_2SO_4 , HCl(g)). The reaction type is **substitution**.
2. **From an alkane:** Cl_2 or Br_2 with **UV light**; free-radical substitution. Initiation $\text{Cl}_2 \rightarrow 2\text{Cl}\bullet$ (homolytic fission); propagation $\text{C}_2\text{H}_6 + \text{Cl}\bullet \rightarrow \text{C}_2\text{H}_5\bullet + \text{HCl}$ and $\text{C}_2\text{H}_5\bullet + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}\bullet$; termination, two radicals joining.
3. **From an alkene:** HX(g) or X_2 at room temperature; electrophilic addition, with the halogen of HX mainly on the carbon that gives the more stable (more substituted) carbocation.

Variations you will meet: by-products such as a dichloroalkane from further substitution; "misty fumes" (HCl) with PCl_5 ; naming the dichloro product from a diol and excess PCl_5 .

6. Silver nitrate test (9 questions)

1. **Method:** add a few drops of the halogenoalkane to aqueous silver nitrate **in ethanol** and warm.
2. **Observation:** white (Cl), cream (Br) or yellow (I) **precipitate**. Say "precipitate", not "solution".
3. **Ionic equation:** $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr(s)}$.

4. **Organic product:** the alcohol; the halogen has been replaced by OH (water is the nucleophile).

Variations: confirming the halide with ammonia (AgCl dissolves in dilute NH_3); two bottles of isomers with different halogens, told apart by colour and speed.

7. Draw an $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism (6 questions)

Mark schemes give three marks, like this for $\text{S}_{\text{N}}1$:

1. **M1:** $\delta+$ on C and $\delta-$ on X, **and** a curly arrow from the **middle of the C–X bond** to X.
2. **M2:** the carbocation intermediate, with its + charge on the correct carbon, and X^- .
3. **M3:** a curly arrow from a **lone pair** on the nucleophile (drawn as two dots on O of OH^- , N of NH_3 or O of RO^-) to the C^+ .

For $\text{S}_{\text{N}}2$: the arrow from the nucleophile's lone pair goes to the $\delta+$ carbon (for CN^- , from the lone pair on **C**), the C–X arrow goes to X, and the transition state is drawn in square brackets with dashed partial bonds and a negative charge.

8. Classify and name (4 questions)

1. Find the **longest chain** containing the C–X carbon and number from the end that gives the lowest numbers.
2. Put the prefixes in **alphabetical order**: 3-bromo-3-methylhexane (b before m).
3. Classify by the number of carbons joined to the C–X carbon; define tertiary as "the carbon bonded to the halogen is bonded to **three other carbon atoms**".

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

1-bromo-3-methylbutane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$, is used to make three different products.

- (a) Classify 1-bromo-3-methylbutane as primary, secondary or tertiary. Explain your answer. **[1]**
- (b) Complete the table for each conversion. **[6]**

Product	Reagent and conditions	Type of reaction
3-methylbutan-1-ol		
4-methylpentanenitrile		
3-methylbut-1-ene		

(c) Write an equation for the formation of 3-methylbut-1-ene. **[1]**

(a) Primary: the carbon bonded to Br is bonded to only **one** other carbon atom. **B1**

(b)

Product	Reagent and conditions	Type of reaction
3-methylbutan-1-ol	NaOH(aq), heat under reflux	nucleophilic substitution
4-methylpentanenitrile	KCN in ethanol, heat under reflux	nucleophilic substitution
3-methylbut-1-ene	NaOH in ethanol, heat	elimination

One mark for each reagent with its conditions and one for each type: **B1** × 6. The solvent is the whole difference between rows 1 and 3. The nitrile, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CN}$, has six carbons, one more than the bromide, which is why its longest chain is a pentane.

(c) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br} + \text{NaOH} \rightarrow (\text{CH}_3)_2\text{CHCH}=\text{CH}_2 + \text{NaBr} + \text{H}_2\text{O}$ **B1**

Example 2

2-bromo-2,3-dimethylbutane, $(\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2$, is warmed with NaOH(aq). It forms 2,3-dimethylbutan-2-ol by an $\text{S}_{\text{N}}1$ mechanism.

(a) Explain why this halogenoalkane reacts by $\text{S}_{\text{N}}1$ rather than $\text{S}_{\text{N}}2$. **[2]**

(b) Describe the mechanism, stating what each curly arrow shows. **[3]**

(c) Its isomer 1-bromo-2,3-dimethylbutane reacts with NaOH(aq) by $\text{S}_{\text{N}}2$. Give **two** ways in which its mechanism differs from the one in (b). **[2]**

(d) When 2-bromo-2,3-dimethylbutane is heated with NaOH in ethanol, it forms two alkenes. Give their structures and explain why neither has cis/trans isomers. **[3]**

(a) It is **tertiary**: the C–Br carbon carries three alkyl groups. **B1** Their positive inductive effect pushes electron density towards the positive carbon and stabilises the tertiary carbocation, so it can form. **B1** (The three groups also crowd the carbon, hindering attack from behind.)

(b)

- Step 1 (slow): the C–Br bond is polar, $\text{C}^{\delta+} - \text{Br}^{\delta-}$; a curly arrow from the middle of the C–Br bond to Br shows the bond breaking heterolytically, both electrons going to Br. **M1**
- This leaves the carbocation $(\text{CH}_3)_2\text{C}^+\text{CH}(\text{CH}_3)_2$ and Br^- . **M2**

- Step 2 (fast): a curly arrow from a lone pair on the O of OH^- to the positive carbon forms the C–O bond, giving $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)_2$. **M3**

(c) Any two: $\text{S}_{\text{N}}2$ has **one step**, not two; it goes through a **transition state**, not a carbocation intermediate; the nucleophile attacks **as** the C–Br bond breaks, not after; **two** species take part in the slow step, not one. **B1 B1**

(d) The C–Br carbon has two different kinds of neighbour carrying H. Losing H from a CH_3 gives $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ (2,3-dimethylbut-1-ene); losing the H from the CH gives $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ (2,3-dimethylbut-2-ene). **B1 B1** Neither has cis/trans isomers because in each alkene at least one C=C carbon carries two identical groups (two H atoms in the first; two CH_3 groups on both carbons in the second). **B1**

Example 3

8.25 g of 3-bromohexane, $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_2\text{CH}_3$, is heated under reflux with an excess of KOH in ethanol. Structural isomerism and stereoisomerism should be considered.

- (a) How many different alkenes can form? Explain your answer. **[3]**
- (b) The alkenes are collected: 2.73 g in total. Calculate the percentage yield. **[3]**
- (c) Suggest why the yield is below 100%, apart from losses when collecting the product. **[1]**

(a) Both neighbours of the C–Br carbon (C2 and C4) carry H. **M1**

- Losing H from C2 gives hex-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$.
- Losing H from C4 gives hex-3-ene, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$. **A1**

Each C=C carbon carries an H and an alkyl group, so both alkenes have cis and trans forms: $2 + 2 = 4$ alkenes. **A1**

(b) M_r of $\text{C}_6\text{H}_{13}\text{Br} = 6(12.0) + 13(1.0) + 79.9 = 164.9$; amount = $8.25 \div 164.9 = 0.0500$ mol. **M1**

Every alkene is C_6H_{12} , $M_r = 84.0$, and 1 mol of bromide gives 1 mol of alkene, so the maximum amount is 0.0500 mol. Actual amount = $2.73 \div 84.0 = 0.0325$ mol. **M1**

$$\text{percentage yield} = \frac{0.0325}{0.0500} \times 100 = 65.0\%$$

A1

(c) Some 3-bromohexane undergoes **substitution** instead (the hydroxide acts as a nucleophile), giving hexan-3-ol rather than an alkene. **B1**

Example 4

Cyclohexylamine, $\text{C}_6\text{H}_{11}\text{NH}_2$, is made from cyclohexanol, $\text{C}_6\text{H}_{11}\text{OH}$, in two steps.



- (a) Give a reagent for step 1 and write an equation for the reaction with it. [2]
- (b) Give the reagent and conditions for step 2, and write its equation. [3]
- (c) 5.00 g of cyclohexanol is used. Step 1 has a 72.0% yield. Calculate the mass of chlorocyclohexane made. [2]
- (d) A sample of the chlorocyclohexane is warmed with aqueous silver nitrate in ethanol. State what you would see, and explain whether bromocyclohexane would give its precipitate faster or more slowly. [3]

(a) PCl_5 (or SOCl_2 , PCl_3 with heat, or KCl with concentrated H_2SO_4). **B1**



(b) An excess of ammonia in ethanol, heated in a sealed tube (under pressure). **B1 B1**



(c) M_r of $\text{C}_6\text{H}_{12}\text{O} = 100.0$, so $5.00 \div 100.0 = 0.0500$ mol of cyclohexanol. At 72.0%, $0.0500 \times 0.720 = 0.0360$ mol of $\text{C}_6\text{H}_{11}\text{Cl}$. **M1**

M_r of $\text{C}_6\text{H}_{11}\text{Cl} = 72.0 + 11.0 + 35.5 = 118.5$, so mass = $0.0360 \times 118.5 = 4.27$ g. **A1**

(d) A **white precipitate** (of AgCl) forms slowly. **B1** Bromocyclohexane would give its (cream) precipitate **faster**, **B1** because the $\text{C}-\text{Br}$ bond (280 kJ mol^{-1}) is weaker than the $\text{C}-\text{Cl}$ bond (340 kJ mol^{-1}), so it breaks more easily. **B1**

Common mistakes

- **Leaving out the solvent.** "NaOH" alone scores nothing when the question hinges on substitution against elimination. Write "NaOH(aq)" or "NaOH in ethanol", plus "heat".
- **Using HCN, or acid, to make a nitrile from a halogenoalkane.** Examiner reports note it again and again, along with leaving out the ethanol. It is **KCN in ethanol**, heated under reflux; HCN is for carbonyl compounds.
- **Explaining rates with polarity or electronegativity.** Rate depends on **bond energy**: $\text{C}-\text{I}$ is weakest, so iodoalkanes react fastest. Reports often note answers that talk about electronegativity or mix up bond energy with ionisation energy.
- **Vague curly arrows.** An arrow must start from a lone pair or the middle of a bond and point clearly at an atom. Common faults: an arrow starting on the carbon instead of the $\text{C}-\text{X}$ bond; no lone pair drawn on the nucleophile (including the lone pair on the C of CN^-); a charge missing from the carbocation.
- **Drawing $\text{S}_\text{N}2$ when $\text{S}_\text{N}1$ was asked** (or the reverse). Check the class first; a tertiary halogenoalkane needs the two-step route with a carbocation.
- **Calling the carbocation a transition state**, or the $\text{S}_\text{N}2$ transition state an intermediate.
- **Saying the halogenoalkane is stable** when asked about $\text{S}_\text{N}1$. It is the **carbocation** that is stabilised, by the **inductive effect** of the alkyl groups; say both words.

- **Giving HBr as the product of elimination with NaOH.** The products are the alkene, NaBr and H₂O.
- **Miscounting alkenes.** Forgetting cis/trans forms, or counting the same alkene twice when it comes from two halogenoalkanes or two equivalent carbons.
- **Counting 4 stereoisomers for a symmetrical diene.** In hexa-2,4-diene, cis,trans and trans,cis are the same molecule (turn it end to end), so there are 3, not 4. Ask whether the two C=C bonds are equivalent before doubling twice.
- **Silver nitrate observations.** "White solution" is wrong: it is a **precipitate**. Mixing up the colours cream and yellow for Br and I is also common.

How to get the marks

- **"Reagent and conditions"** needs the reagent, the solvent and the heating: "KOH in ethanol, heat". "Under pressure" is needed for ammonia. Write clearly: "ethanolic" (in ethanol) and "ethanoic" (an acid) are different things.
- **"Type of reaction"** means the full name: "nucleophilic substitution", "elimination", "free-radical substitution", "electrophilic addition". "Substitution" alone may lose the mark when the mechanism is the point.
- **"Identify the mechanism"**: S_N1 or S_N2, with a reason based on the class (primary or tertiary).
- **Mechanisms** are marked on dipoles, arrows, lone pairs, charges and the intermediate or transition state. "Include charges, dipoles, lone pairs of electrons and curly arrows, as appropriate" is a checklist: tick each one.
- **"Explain" a rate difference** needs two things: the comparison ("slower") and the reason naming both bonds ("C–Cl is stronger than C–Br").
- **"Observation"** means what you see: "cream precipitate", not "AgBr forms".
- **Equations** must balance, with the right inorganic products (NaBr, H₂O, NH₄Br). Structural formulas must be unambiguous: write CH₃CH₂CN, not C₃H₅N.
- **Counting questions** that say "structural isomerism and stereoisomerism should be considered" want cis/trans and optical isomers included.
- **Calculations:** show M_r , moles and the ratio; give the answer to 3 significant figures unless told otherwise.

Quick check

1. Give the reagent and conditions to turn 1-chloropentane into (a) pentan-1-ol, (b) hexanenitrile, (c) pent-1-ene, (d) pentan-1-amine, C₅H₁₁NH₂.
2. Classify each halogenoalkane and state the mechanism by which it is mainly hydrolysed by NaOH(aq): (a) 1-iodopentane, (b) 3-iodo-3-methylpentane, (c) 2-chloropentane.
3. 4-iodoheptane, CH₃CH₂CH₂CHICH₂CH₂CH₃, is warmed with aqueous silver nitrate in ethanol. (a) What is seen? (b) Write the ionic equation. (c) Name the organic product. (d) How many alkenes (including stereoisomers) form when 4-iodoheptane is heated with NaOH in ethanol?

4. Put 1-fluorohexane, 1-chlorohexane and 1-iodohexane in order of rate of hydrolysis, fastest first, and explain. Why is "C–F is the most polar bond" not a reason for 1-fluorohexane to react fastest?
5. Chlorocyclopentane, $\text{C}_5\text{H}_9\text{Cl}$, can be made from cyclopentane, cyclopentene or cyclopentanol. Give the reagent and conditions for each route, and write the equation for the route from cyclopentanol with SOCl_2 .

Answers

1. (a) NaOH(aq), heat under reflux. (b) KCN in ethanol, heat under reflux (the CN adds the sixth carbon). (c) NaOH in ethanol, heat. (d) An excess of NH_3 in ethanol, heated under pressure.
2. (a) Primary: the C–I carbon is bonded to one other carbon; $\text{S}_{\text{N}}2$. (b) Tertiary: the C–I carbon is bonded to three other carbons; $\text{S}_{\text{N}}1$. (c) Secondary: bonded to two other carbons; a mixture of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.
3. (a) A yellow precipitate, forming quickly. (b) $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$. (c) Heptan-4-ol. (d) Both neighbours (C3 and C5) are equivalent by symmetry, so only hept-3-ene forms; each C=C carbon carries H and an alkyl group, so cis and trans: **2** alkenes.
4. 1-iodohexane > 1-chlorohexane > 1-fluorohexane. The C–X bond breaks in the reaction, and bond energies are C–I 240, C–Cl 340, C–F 467 kJ mol⁻¹: the weaker the bond, the faster it breaks. Polarity would predict the opposite order; the very strong C–F bond means 1-fluorohexane hardly reacts, however polar it is.
5. From cyclopentane: Cl_2 in UV light (free-radical substitution). From cyclopentene: HCl(g) at room temperature (electrophilic addition). From cyclopentanol: SOCl_2 (or PCl_5 , PCl_3 with heat, or KCl with concentrated H_2SO_4). Equation: $\text{C}_5\text{H}_9\text{OH} + \text{SOCl}_2 \rightarrow \text{C}_5\text{H}_9\text{Cl} + \text{SO}_2 + \text{HCl}$.

Past questions to try

- **9701/22/M/J/22 Q5**: reagents, conditions and reaction types for three reactions of one halogenoalkane, then a rate explanation.
- **9701/24/O/N/25 Q3**: drawing an $\text{S}_{\text{N}}1$ mechanism with an alkoxide nucleophile, and a rate comparison.
- **9701/11/M/J/25 Q30**: counting the dienes from a dihalide, stereoisomers included (watch for a symmetrical diene).
- **9701/12/M/J/25 Q33**: why the silver nitrate precipitates appear at different rates.