

Halogen compounds A2

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Last checked 1 October 2026

Read first: [Halogen compounds](#), [Hydrocarbons](#)

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What you need to know

At AS you met halogen atoms joined to an alkyl chain. At A Level the new idea is a halogen joined **directly to a benzene ring** (a halogenoarene, or aryl halide), and the topic asks for just two things:

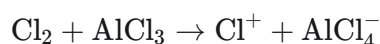
1. **How to put Cl or Br onto a ring.** Mix the arene with the halogen and an aluminium halide catalyst (AlCl_3 for chlorine, AlBr_3 for bromine). Benzene itself gives chlorobenzene. Methylbenzene gives two main products, one with the chlorine on the carbon next to the methyl group and one with it on the carbon opposite.
2. **Why a ring halogen is so much harder to replace than a chain halogen.** Chloroethane swaps its Cl for OH when warmed with water or hydroxide ions; chlorobenzene does not react at all under the same conditions. You must be able to say what you would see and explain it in terms of the C–Cl bond.

Exam questions on this topic almost always compare the ring halogen with other compounds you already know: halogenoalkanes (AS topic 15) and, in a third of the questions, acyl chlorides (topic 33). Those comparisons are included here. The mechanism of electrophilic substitution belongs to the topic "Hydrocarbons" and is only recapped.

Understand it

Making a halogenoarene

Chlorine or bromine on its own does not react with benzene: the ring's six π electrons are spread over six carbons, so the ring cannot pull the halogen molecule apart. A **halogen carrier** catalyst solves this. Aluminium chloride has an empty orbital and accepts a chloride ion from Cl_2 , leaving a positive chlorine ion that the ring can attack:

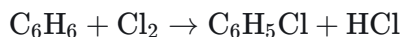


The reaction then follows the two-step **electrophilic substitution** mechanism from "Hydrocarbons":

1. A pair of electrons from the delocalised π system forms a bond to Cl^+ . The ring carbon that gains the Cl becomes sp^3 (it now holds H and Cl), and the intermediate is a horseshoe of five sp^2 carbons sharing a + charge.

2. The electrons of that carbon's C–H bond move back into the ring, rebuilding the full delocalised system, and H^+ leaves.

The H^+ meets the AlCl_4^- and gives the catalyst back: $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{HCl} + \text{AlCl}_3$. So the overall equation contains no catalyst:



For bromine use AlBr_3 (iron(III) bromide, FeBr_3 , also works), so that no chlorine ends up in the product: $\text{Br}_2 + \text{AlBr}_3 \rightarrow \text{Br}^+ + \text{AlBr}_4^-$. The conditions are room temperature, in the dark, and with no water present (water destroys the catalyst).

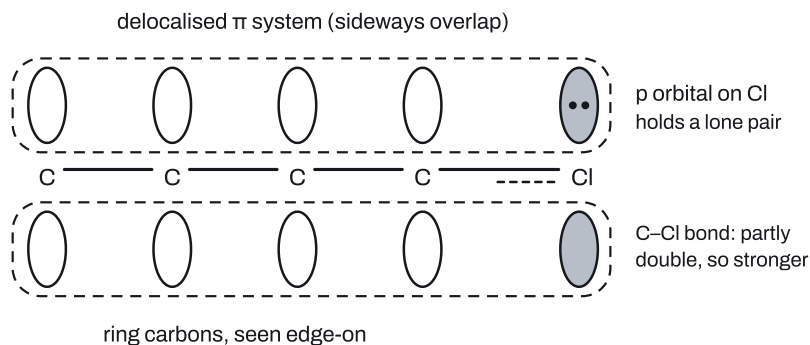
An arene with a side chain. An alkyl group on the ring donates electrons and sends the incoming halogen to positions 2 and 4 (next to it, or opposite it). So chlorinating methylbenzene gives mostly 2-chloromethylbenzene and 4-chloromethylbenzene, and very little of the 3-isomer. The halogen goes onto the **ring** only because of the catalyst. In ultraviolet light and with no catalyst, the halogen replaces hydrogens on the **side chain** instead, by free-radical substitution.

Two kinds of C–Cl bond

Chloroethane, $\text{CH}_3\text{CH}_2\text{Cl}$, and chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, both contain a carbon–chlorine bond, but they behave very differently:

	Chloroethane	Chlorobenzene
Warm NaOH(aq)	nucleophilic substitution: ethanol + Cl^-	no reaction
Warm water or AgNO_3 (aq/ethanol)	slow hydrolysis; white precipitate of AgCl forms	no reaction; no precipitate
Carbon joined to Cl	sp^3	sp^2 , part of the ring

The reason is what happens to the chlorine's lone pairs. In chloroethane the Cl is joined to an sp^3 carbon, which has no spare p orbital, so the C–Cl bond is an ordinary single bond (340 kJ mol^{-1} in the Data Booklet). In chlorobenzene the ring carbon is sp^2 , and every ring carbon has a p orbital sticking up and down from the plane of the ring. One of chlorine's lone pairs is in a p orbital that lies **parallel** to these, so it overlaps sideways with them.



That overlap has two effects:

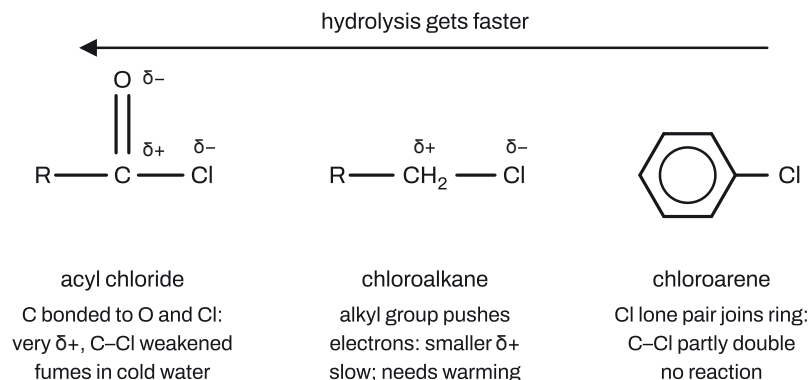
- the lone pair is **delocalised into the ring**: it becomes part of the π system;
- the C–Cl bond gains **partial double-bond character**, so it is shorter and **stronger**, and much harder to break.

A nucleophile such as OH^- or H_2O cannot break a bond that strong under normal conditions, so chlorobenzene does not undergo nucleophilic substitution. (The ring's cloud of π electrons also repels an approaching nucleophile, and the ring blocks attack from behind the carbon, but the mark schemes reward the two points above.) The same is true for bromobenzene and iodobenzene: all halogenoarenes resist hydrolysis.

The halogen must be on the ring itself. In (chloromethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, the Cl is on the CH_2 carbon, which is sp^3 . Its lone pairs cannot overlap with the ring, so this compound reacts like a primary halogenoalkane and gives a precipitate with silver nitrate. Look at which carbon carries the halogen, not whether the molecule contains a ring.

Three chlorides compared

Acyl chlorides, RCOCl , complete the picture. Their carbon is joined to **two** electronegative atoms, O and Cl, so it is strongly $\delta+$ and very attractive to nucleophiles; the C–Cl bond is also weakened. They react rapidly with cold water, giving steamy fumes of HCl.



So the ease of hydrolysis is

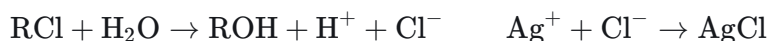


- Acyl chloride, fastest:** the carbon is bonded to O and Cl, so it is the most electron-deficient; the C–Cl bond is the weakest of the three.
- Chloroalkane, in between:** the carbon is bonded to only one electronegative atom, and the alkyl group's **positive inductive effect** pushes electron density towards it, so it is less $\delta+$ than in the acyl chloride.
- Chloroarene, slowest (no reaction):** the lone pair on Cl is delocalised into the ring, giving the C–Cl bond partial double-bond character, so it is the strongest.

A molecule with two different C–Cl bonds reacts only at the weaker one under mild conditions. For example, a Cl on the ring survives while a Cl on a side-chain CH_2 , or in a COCl group, is replaced.

The silver nitrate test

Silver nitrate does not react with a C–X bond; it reacts with **halide ions**. The halide ion is released only if the compound is hydrolysed first:



AgCl is a white precipitate, AgBr cream and AgI yellow. A chloroalkane gives a white precipitate slowly on warming; a chloroarene gives **no precipitate**; an acyl chloride gives one almost at once. This makes aqueous silver nitrate (warm, with ethanol to help the compound mix with the water) the standard reagent to show the difference between an alkyl and an aryl halide. Sodium hydroxide on its own shows nothing visible.

Key facts and formulas

"Given" means it is printed on the Periodic Table or in the Data Booklet in the exam. "Learn it" means you must remember it; reagents, conditions, colours and explanations are never printed.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, O 16.0, Cl 35.5, Br 79.9, Ag 107.9	Given
Bond energies: C–Cl 340 kJ mol ⁻¹ , C–Br 280 kJ mol ⁻¹	Given
Making a halogenoarene: X ₂ with AlX ₃ (or FeBr ₃), room temperature, dark, dry	Learn it
X ₂ + AlX ₃ → X ⁺ + AlX ₄ ⁻ and H ⁺ + AlX ₄ ⁻ → HX + AlX ₃	Learn it
C ₆ H ₆ + X ₂ → C ₆ H ₅ X + HX (electrophilic substitution)	Learn it
An alkyl group on the ring sends the halogen to positions 2 and 4	Learn it
Chloroalkane + NaOH(aq), heat → alcohol (nucleophilic substitution); chloroarene: no reaction	Learn it
Reason: Cl lone pair (p orbital) delocalised into the ring → C–Cl partial double bond → stronger	Learn it
Ease of hydrolysis: acyl chloride > chloroalkane > chloroarene	Learn it
Ag ⁺ + X ⁻ → AgX: AgCl white, AgBr cream, AgI yellow	Learn it

How to do it

In the Paper 4 questions we have tagged for this topic (12 questions, 2021–2025; 8 different questions, 4 of them repeated in another variant), the types came up this often. Every one of the 12 mixes more than one type, so the counts add up to 27. The halogen part is usually one part of a longer question about arenes or acyl chlorides.

Question type	Questions
Explain why a halogenoarene is less reactive	12
Silver nitrate: observations and equations	6

Question type	Questions
Order acyl, alkyl and aryl chlorides by ease of hydrolysis	4
Make a halogenoarene: catalyst, equations, isomers	3
Reactions of the halogenoalkane that does react	2

1. Explain why a halogenoarene is less reactive (12 questions)

Asked in every question on this topic, usually for 2 marks ("any two [1], all three [2]").

1. **Say which is less reactive** in a full comparison: "chlorobenzene is less reactive than chloroethane" (or "does not react").
2. **The lone pair point:** a lone pair in a p orbital on the halogen overlaps with (is delocalised into) the π system of the ring.
3. **The bond point:** so the C–X bond has partial double-bond character and is **stronger**, and harder to break.

Variations you will meet:

- **Bromine instead of chlorine** (bromobenzene): the same explanation, with Br and C–Br.
- **A side-chain halogen**, such as $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$: it is joined to an sp^3 carbon, so no overlap with the ring; it reacts like a halogenoalkane.
- **Against an acyl chloride** instead of a halogenoalkane: add the acyl chloride point from type 3.

2. Silver nitrate: observations and equations (6 questions)

1. **Reagent:** aqueous silver nitrate (with ethanol), warm. NaOH(aq) or $\text{NH}_3\text{(aq)}$ alone give nothing visible, so they do not show the difference.
2. **Observations for each compound:** the halogenoalkane gives a precipitate of the right colour (white AgCl , cream AgBr , yellow AgI), slowly; the halogenoarene gives **no precipitate** (no change).
3. **Two equations** for the compound that reacts:
 - hydrolysis, for example $\text{C}_3\text{H}_7\text{Br} + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_7\text{OH} + \text{H}^+ + \text{Br}^-$;
 - precipitation, $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$.

Write **no** equation for the halogenoarene: it does not react.

4. **Explain** with the two points from type 1.

3. Order acyl, alkyl and aryl chlorides by ease of hydrolysis (4 questions)

1. **The order:** acyl chloride (fastest) > chloroalkane > chloroarene (slowest; no reaction). Read which end of the answer line is "fastest" or "easiest" before writing.
2. **Give a reason for each compound**, linked to the order:

- acyl chloride: C bonded to two electronegative atoms (O and Cl), most electron-deficient, C–Cl bond weakened;
- chloroalkane: only one electronegative atom, and the alkyl group's positive inductive effect makes the carbon less $\delta+$;
- chloroarene: lone pair on Cl delocalised into the ring, C–Cl partial double bond, strongest.

3. **Link each reason to the bond:** "harder to break" or "weaker" beats a bare statement.

Variation: only two compounds (for example an acyl chloride and a chloroarene, "with water"). Give the comparison, then the point for each.

4. Make a halogenoarene: catalyst, equations, isomers (3 questions)

1. **Catalyst:** AlCl_3 for chlorine, AlBr_3 (or FeBr_3) for bromine.
2. **Electrophile equation**, with charges: $\text{Br}_2 + \text{AlBr}_3 \rightarrow \text{Br}^+ + \text{AlBr}_4^-$.
3. **Overall equation**, no catalyst: arene + $\text{X}_2 \rightarrow$ halogenoarene + HX .
4. **Name the mechanism:** electrophilic substitution. The electrophile is X^+ , and an X atom replaces an H atom on the ring.

Variations you will meet:

- **Isomers from a substituted ring.** An alkyl group gives the 2- and 4-isomers as the main products. The **3-isomer** forms in the smallest amount, because the alkyl group is 2,4-directing (it donates electrons). Draw it with one ring carbon between the two groups.
- **The mechanism**, with curly arrows (see "Hydrocarbons"): arrow from inside the ring to X^+ ; the horseshoe intermediate with + inside and H and X on the sp^3 carbon; arrow from the C–H bond into the ring, and H^+ .
- **"Where is this pair of electrons?"** In step 1 the pair starts in the delocalised π system and ends in the new C–X bond. In step 2 it starts in the C–H bond and ends back in the delocalised π system.
- **Hybridisation in the intermediate** of $\text{C}_6\text{H}_6 + \text{X}^+$: no sp carbons, five sp^2 (the horseshoe) and one sp^3 (the carbon holding H and X).

5. Reactions of the halogenoalkane that does react (2 questions)

The AS halogenoalkane reactions appear alongside the comparison. The arene ring and any ring halogen stay unchanged.

- **NaOH(aq) , heat:** nucleophilic substitution, giving the alcohol (chloroethane $\rightarrow$ ethanol).
- **KCN (or NaCN) in ethanol, heat:** nucleophilic substitution, giving a nitrile with one extra carbon.
- **NH_3 in ethanol, heated under pressure:** an amine.

Name the mechanism in full ("nucleophilic substitution", not just "substitution") and name the product.

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.
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Example 1

Butylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, reacts with chlorine in the presence of aluminium chloride, in the dark.

- (a) Write an equation to show how aluminium chloride produces the electrophile. **[1]**
- (b) Name the two main organic products, and explain why very little 1-butyl-3-chlorobenzene forms. **[3]**
- (c) Write an overall equation for the formation of one of the main products. **[1]**
- (d) 6.70 g of butylbenzene gave 6.32 g of a mixture of the monochlorinated products. Calculate the percentage yield. **[2]**

(a) $\text{Cl}_2 + \text{AlCl}_3 \rightarrow \text{Cl}^+ + \text{AlCl}_4^-$ **B1**, charges needed.

(b) 1-butyl-2-chlorobenzene **B1** and 1-butyl-4-chlorobenzene **B1**. The butyl group donates electrons to the ring, so it directs the chlorine to positions 2 and 4; position 3 is not favoured. **B1**

(c) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$ **B1**

(d) $M_r(\text{C}_{10}\text{H}_{14}) = 10(12.0) + 14(1.0) = 134.0$, so $6.70 \div 134.0 = 0.0500$ mol. The products, $\text{C}_{10}\text{H}_{13}\text{Cl}$, have $M_r = 120.0 + 13.0 + 35.5 = 168.5$, so the maximum mass is $0.0500 \times 168.5 = 8.425$ g. **M1**

Percentage yield = $6.32 \div 8.425 \times 100 = 75.0\%$. **A1**

Example 2

Compound J, 1-chloro-4-(chloromethyl)benzene, $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$, has one chlorine on the ring and one on the side chain.

- (a) J is heated with NaOH(aq) . Name the type of reaction and draw or name the organic product. **[2]**
- (b) Explain why only one of the chlorine atoms reacts. **[3]**

(c) 1.61 g of J was heated with excess NaOH(aq). The mixture was acidified with dilute nitric acid and excess aqueous silver nitrate was added. 1.43 g of white precipitate formed. Show that this mass confirms your answer to (b). **[3]**

(a) Nucleophilic substitution. **B1** The product is (4-chlorophenyl)methanol, $\text{ClC}_6\text{H}_4\text{CH}_2\text{OH}$: the side-chain Cl is replaced by OH and the ring Cl stays. **B1**

(b) The side-chain Cl is bonded to an sp^3 carbon, so its C–Cl bond is an ordinary single bond, like a primary chloroalkane's. **B1** The ring Cl has a lone pair in a p orbital that overlaps with the delocalised π system of the ring. **B1** This gives the ring C–Cl bond partial double-bond character, so it is stronger and is not broken by OH^- . **B1**

(c) $M_r(\text{C}_7\text{H}_6\text{Cl}_2) = 84.0 + 6.0 + 71.0 = 161.0$, so $1.61 \div 161.0 = 0.0100$ mol of J. **M1**

$M_r(\text{AgCl}) = 107.9 + 35.5 = 143.4$. If one Cl per molecule is released, the precipitate is $0.0100 \times 143.4 = 1.434$ g, which is 1.43 g. **M1** If both were released it would be $2 \times 1.434 = 2.87$ g. The measured 1.43 g shows one chloride ion per molecule. **A1**

(The nitric acid removes the excess OH^- , which would otherwise give a brown precipitate of silver oxide.)

Example 3

(a) A small amount of each of propanoyl chloride, 2-chloropropane and 1,4-dichlorobenzene is shaken with cold water. Which one reacts fastest? Rank all three by how quickly they react, justify your ranking, and say what you would observe for the fastest. **[5]**

(b) 2-Chloropropanoyl chloride, $\text{CH}_3\text{CHClCOCl}$, is added to cold water. Write an equation for the reaction and explain which chlorine atom is replaced. **[2]**

(a) Propanoyl chloride reacts fastest, then 2-chloropropane (very slowly), and 1,4-dichlorobenzene not at all.

B1 With propanoyl chloride the sample reacts at once, giving steamy fumes of HCl and a warm, acidic solution. **B1**

- Propanoyl chloride: the carbon of the C–Cl bond is also bonded to an oxygen atom, so it is joined to two electronegative atoms and is the most electron-deficient; the C–Cl bond is weakened.
- 2-Chloropropane: the carbon is joined to only one electronegative atom, and the two methyl groups' positive inductive effect makes it less δ^+ .
- 1,4-Dichlorobenzene: a lone pair on each Cl is delocalised into the ring, so each C–Cl bond is partly double and stronger; it is not hydrolysed.

Any two points **B1**, all three **B2**, and **B1** for linking each to how easily the C–Cl bond breaks.

(b) $\text{CH}_3\text{CHClCOCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHClCOOH} + \text{HCl}$ **B1**

The Cl of the COCl group is replaced, because that carbon is bonded to both O and Cl and is far more δ^+ ; the Cl on the CH carbon behaves like a chloroalkane's and reacts only slowly, when heated. **B1** The product is 2-chloropropanoic acid.

Common mistakes

- **Only one of the two points.** Examiners reported in 2022 and again in 2023 that most candidates gave only one reason why chlorobenzene is not hydrolysed. You need both: the lone pair on Cl overlaps with the ring, **and** so the C–Cl bond is stronger (partial double bond).
- **Saying the C–Cl bond in chlorobenzene is less polar or non-polar.** It is still polar. The rate is decided by bond **strength**, as with halogenoalkanes at AS.
- **Choosing NaOH(aq) or NH₃(aq) to show the difference.** The 2022 report noted this was the common wrong answer. Neither gives a visible change; silver nitrate gives a precipitate with one compound and none with the other.
- **Writing an equation for the halogenoarene.** If it does not react, it has no equation.
- **Treating every ring compound as unreactive.** A halogen on a side-chain CH₂ is joined to an *sp*³ carbon and reacts like a halogenoalkane.
- **Getting the order the wrong way round.** Answer lines run "hardest to easiest" in some papers and "fastest to slowest" in others. Read the labels first; acyl chlorides always go at the fast (easy) end.
- **Order without explanation.** The 2021 report says many correct orders came with explanations that lacked detail. Give a reason for each compound, not just for one.
- **Wrong catalyst or conditions for making a halogenoarene.** UV light puts the halogen on a side chain, not on the ring; the ring needs AlCl₃ or AlBr₃. Match the catalyst's halogen to the reagent's.
- **Charges missing** from X⁺ and AlX₄[−] in the electrophile equation.

How to get the marks

- **"Describe the difference in reactivity"** needs the comparison (which is less reactive) plus what happens, for example "chloroethane is hydrolysed to ethanol; chlorobenzene does not react".
- **"Explain"** needs both halves of the reason in the same answer: lone pair delocalised into the ring, **so** the C–X bond is stronger. Mark schemes typically give one mark for any two of the three points (comparison, overlap, stronger bond) and two marks for all three.
- **"State the expected observations"**: give one for **each** compound, including "no precipitate" or "no change" for the one that does not react, and give the precipitate's colour.
- **Equations for the silver nitrate test**: one for the hydrolysis that releases X[−] and one for Ag⁺ + X[−] → AgX. Ionic or full equations both score.
- **Ordering questions**: the order earns a mark on its own, then "any two, any three" reasons earn the rest. Name the feature of each compound (two electronegative atoms; positive inductive effect; delocalised lone pair).
- **"Name the mechanism"**: in full, "nucleophilic substitution" or "electrophilic substitution".
- **"Suggest"** means an unfamiliar compound: find the carbon holding each halogen and ask whether it is a ring carbon, an *sp*³ carbon or a C=O carbon.
- **Calculations**: use the *A_r* values from the Periodic Table and give answers to 3 significant figures.

Quick check

1. (1-Methylethyl)benzene, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, is brominated on the ring. Give the reagent and catalyst, name the two main products, and write the overall equation for making one of them.
2. Predict what you would see when each compound is warmed with aqueous silver nitrate in ethanol: (a) 2-bromo-2-methylpropane; (b) 1,3-dibromobenzene; (c) (2-chloroethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl}$.
3. A student writes: "Chlorobenzene does not react with $\text{NaOH}(\text{aq})$ because its $\text{C}-\text{Cl}$ bond is non-polar." Correct the explanation.
4. 2.625 g of 3-chlorobenzoyl chloride, $\text{ClC}_6\text{H}_4\text{COCl}$, is added to excess cold water, and excess aqueous silver nitrate is then added. Calculate the mass of precipitate that forms.

Answers

1. Br_2 with AlBr_3 (or FeBr_3), room temperature, dark. The alkyl group is 2,4-directing, so the products are 1-bromo-2-(1-methylethyl)benzene and 1-bromo-4-(1-methylethyl)benzene. $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2 + \text{Br}_2 \rightarrow \text{BrC}_6\text{H}_4\text{CH}(\text{CH}_3)_2 + \text{HBr}$, that is $\text{C}_9\text{H}_{12} + \text{Br}_2 \rightarrow \text{C}_9\text{H}_{11}\text{Br} + \text{HBr}$.
2. (a) A cream precipitate (AgBr), forming quickly: it is a tertiary halogenoalkane. (b) No precipitate: both Br atoms are on the ring, so their lone pairs are delocalised into it and the C–Br bonds are too strong to break. (c) A white precipitate (AgCl), forming slowly: the Cl is on an sp^3 carbon of the side chain, so it reacts like a primary chloroalkane.
3. The C–Cl bond is still polar. The real reason is that a lone pair in a p orbital on Cl overlaps with the delocalised π system of the ring, which gives the C–Cl bond partial double-bond character; the bond is stronger than in a chloroalkane and is not broken by OH^- .
4. $M_r(\text{C}_7\text{H}_4\text{Cl}_2\text{O}) = 84.0 + 4.0 + 71.0 + 16.0 = 175.0$, so $2.625 \div 175.0 = 0.0150$ mol. Only the COCl chlorine is hydrolysed ($\text{ClC}_6\text{H}_4\text{COCl} + \text{H}_2\text{O} \rightarrow \text{ClC}_6\text{H}_4\text{COOH} + \text{HCl}$); the ring chlorine stays. So 0.0150 mol AgCl forms: $0.0150 \times 143.4 = 2.151$, which is 2.15 g.

Past questions to try

- **9701/42/M/J/23 Q8**: part (a), chloroethane against chlorobenzene with hydroxide ions, then the reactions of a chloro-ester.
- **9701/43/O/N/22 Q8**: part (c), choosing a reagent that shows the difference, the equations and the explanation.
- **9701/42/M/J/21 Q8**: part (a), ordering acyl, alkyl and aryl chlorides by rate of hydrolysis, with a reason for each.