Halogen compounds (A Level)

Making halogenoarenes and explaining why they are much less reactive towards nucleophilic substitution than halogenoalkanes.

31.1 Halogen compounds

Preparation of halogenoarenes

Substitution of an arene with Cl_2 or Br_2 in the presence of a **halogen carrier catalyst** ($AlCl_3$, $AlBr_3$ or $FeBr_3$):

$$C_6H_6 + Cl_2 \xrightarrow{AlCl_3} C_6H_5Cl + HCl$$

Methylbenzene gives a mixture of **2-chloromethylbenzene** and **4-chloromethylbenzene**, because the methyl group directs to the 2- and 4- positions.

Halogenoarenes are far less reactive than halogenoalkanes

Chlorobenzene does **not** undergo the nucleophilic substitution that chloroethane does with NaOH(aq), KCN or $AgNO_3(aq)$ under ordinary conditions. A halogenoarene shows **no precipitate** with silver nitrate, even on heating.

The reasons:

- The **lone pair on the chlorine** overlaps with the delocalised π system of the ring, so the **C–Cl bond has partial double-bond character**: it is **shorter and stronger** than the C–Cl bond in a halogenoalkane, and harder to break.
- For the core examination explanation, emphasise that lone-pair overlap strengthens C–Cl. The usual alkyl SN1/SN2 pathways also do not transfer straightforwardly to an aryl carbon; a phenyl cation is not the stabilised benzyl cation formed on a side chain.

> **TRY IT**
>
> Compare what happens when chloroethane and chlorobenzene are warmed with aqueous NaOH, then acidified with HNO_3 and $AgNO_3(aq)$ is added.

Chloroethane is hydrolysed to ethanol and Cl^-, which gives a **white precipitate of AgCl**. Chlorobenzene does not react (the C–Cl bond is strengthened by the overlap of the chlorine lone pair with the ring), so there is **no precipitate**.

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The attachment point determines the class

A halogenoarene has the halogen bonded **directly to an aromatic carbon**. A compound containing both a benzene ring and a halogen is not automatically a halogenoarene: $C_6H_5CH_2Cl$ has chlorine on a side-chain carbon and behaves differently from C_6H_5Cl. Draw the bond to the ring explicitly when comparing reactivity.

Worked comparison: chlorobenzene has six carbons, chlorine attached to a ring carbon and no aliphatic C–Cl bond. Phenylmethyl chloride has seven carbons and a CH_2Cl group. The latter can release chloride through substitution under ordinary conditions much more readily. Similar names do not imply the same bond type.

> **TRY IT**
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> Is $C_6H_5CH_2Br$ a brominated arene at the reacting carbon or a side-chain halogeno compound? Explain its expected hydrolysis behaviour relative to bromobenzene.

Answer: Bromine is on the side-chain CH_2 carbon, not directly on the ring. It is substantially more susceptible to ordinary nucleophilic substitution than bromobenzene. Classify by connectivity, not simply by the presence of benzene somewhere in the molecule.

Making the required attachment

Halogenation of benzene with a suitable carrier replaces a ring H with halogen through electrophilic substitution. The carrier polarises the halogen and facilitates electrophile formation. Attack interrupts aromaticity temporarily; proton loss restores it. The by-product is HX, and the carbon skeleton remains the six-membered ring.

For methylbenzene, changing conditions changes the site. Carrier conditions favour ring substitution at positions directed by methyl; UV conditions allow radical side-chain substitution. A synthesis question that gives only “chlorine” is incomplete because it does not specify which bond is being formed.

Worked example: to form 4-chloromethylbenzene as a ring-substituted product, use chlorine with an appropriate halogen carrier under conditions favouring ring substitution; a mixture including the 2-isomer is expected. To form $C_6H_5CH_2Cl$, use radical side-chain conditions. The latter is properly distinguished as (chloromethyl)benzene or phenylmethyl chloride. A bracket or explicit structure avoids ambiguity.

> **TRY IT**
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> Why would simply writing UV above the arrow from benzene to chlorobenzene not give the standard syllabus preparation?

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Answer: The standard ring-substitution route requires electrophilic activation by a halogen carrier. UV is characteristic of radical substitution in an alkane side chain and does not describe that preparation correctly.

Why the usual SN1/SN2 routes fail

For ordinary halogenoalkanes, SN1 requires C–X ionisation to a carbocation and SN2 requires suitable backside approach with simultaneous bond breaking. Direct aryl substitution is different. The aryl C–Cl bond has partial double-bond character through lone-pair overlap with the ring and is shorter/stronger. Forming an aryl carbocation is highly unfavourable, and the ring geometry/electronic environment prevents the ordinary alkyl SN2 pathway.

Use these arguments together rather than saying chlorine is "held by the benzene circle". The C–Cl bond is not simply a weakly bound chloride ion that can diffuse away. The existence of an electron-withdrawing chlorine atom does not override the bonding and mechanistic barriers.

The statement of unreactivity is conditional: chlorobenzene resists the **ordinary aqueous nucleophile conditions** used for the comparison. More forcing conditions or activated aromatic structures can undergo other substitution mechanisms. Those exceptions do not make the standard experimental comparison wrong, but "no aryl halide can ever react" would be too broad.

> **TRY IT**
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> Why does the greater strength of the aryl C–Cl bond matter even though hydroxide is attracted to partially positive carbon?

Answer: Attraction is only part of a reaction pathway. Bond breaking and the geometry/energy of intermediates or transition states determine the activation barrier. A polar bond does not guarantee rapid nucleophilic substitution.

Design and interpret the silver-nitrate comparison

Compare matched amounts and keep temperature and solvent conditions the same. Water or hydroxide first needs to liberate halide from the organic compound. Silver ions then detect the **free halide ions** by precipitation. Silver nitrate is not a direct colour test for every covalently bound chlorine atom.

Worked interpretation: chloroethane releases chloride on suitable hydrolysis; acidification followed by silver nitrate gives white AgCl. Chlorobenzene gives no comparable chloride release under the usual conditions, so no precipitate appears. A separate sodium chloride solution would precipitate AgCl immediately because its chloride ions were already free in water.

Use nitric acid rather than hydrochloric acid when acidifying for the final halide test, because HCl would add chloride and invalidate the comparison. If alkaline hydrolysis was used, acidification also removes

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interfering hydroxide before adding silver nitrate. Keep reagent-only controls in mind when explaining an unexpected precipitate.

> **TRY IT**
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> A sample containing covalently bound chlorine gives no precipitate with silver nitrate. Has chlorine been disproved?

Answer: No. The test requires free chloride ions under the test conditions. A resistant aryl C–Cl bond may not hydrolyse to supply them. The negative result concerns chloride availability, not the total elemental composition.

Chapter check: draw the halogen attachment point, distinguish ring from side-chain preparation, and explain resistance using bond character and mechanism. Review **AS halogenoalkanes** before comparing the two classes.

References and further reading

Scope follows section 31 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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