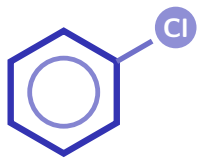
Halogen Compounds

A-Level Chemistry ▪ Topic 31

A-Level Chemistry



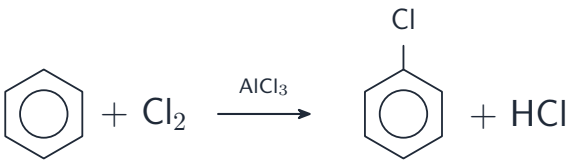
What we will cover

1. Making halogenoarenes
2. Why they are unreactive

many pesticides are halogenoarenes

1 Halogenoarenes

Making halogenoarenes



A **halogenoarene** 卤代芳烃 forms when an arene reacts with Cl_2 or Br_2 with an $AlCl_3$ **catalyst** 催化剂.

This is **electrophilic substitution** 亲电取代 – the halogen replaces an H on the ring (benzene → chlorobenzene).

Why they are unreactive

A halogenoarene resists **nucleophilic substitution** 亲核取代 (unlike a halogenoalkane):

- the Cl **lone pair** 孤对电子 overlaps the ring, strengthening the C–Cl bond
- the electron-rich ring repels a nucleophile

Making halogenoarenes, and where the substituent goes

the reagents	Cl_2 or Br_2 with a halogen carrier – $AlCl_3$ or $FeBr_3$
the mechanism	electrophilic substitution: the carrier polarises the halogen to make the electrophile
with benzene	gives chlorobenzene, one product
with methylbenzene	gives 1-chloro-2- and 1-chloro-4-methylbenzene
why those two	the methyl group directs the incoming chlorine to the 2- and 4-positions
the general rule	electron-donating groups direct to 2- and 4-; electron-withdrawing groups direct to 3-

Directing effects are about where the ring's electron density is highest. Naming the directing group and the positions it favours is the whole answer.

Why they are unreactive, in detail

chloroethane: reactive

$\delta+$

$CH_3\overset{\delta+}{C}H_2$-Cl

Nu^-

nucleophile attacks the $\delta+$ C

chlorobenzene: unreactive

lone pair overlaps ring
$\Rightarrow$ stronger C–Cl

ring repels Nu^-

Chloroethane reacts (a nucleophile attacks the $\delta+$ carbon), but chlorobenzene does not: the Cl lone pair strengthens the C–Cl bond and the ring repels nucleophiles

Exam tips

- A **halogenoarene** is **less reactive** than a halogenoalkane: the lone pair delocalises into the ring, giving the C-X bond partial double-bond character.
- Distinguish a halogen **on the ring** (needs a catalyst, unreactive to substitution) from one on a **side chain** (reacts like a halogenoalkane).

2 Recap

Worked example – why won't chlorobenzene react?

Explain why chlorobenzene does not hydrolyse with aqueous NaOH but chloroethane does.

- In chlorobenzene a Cl lone pair overlaps with the ring's delocalised π system.
- That gives the C–Cl bond partial double-bond character: shorter and stronger.
- The ring's π electrons also repel the approaching OH^- nucleophile.
- In chloroethane C–Cl is a plain polar single bond $\Rightarrow$ hydrolyses on reflux.

Delocalisation into the ring strengthens C–Cl. The same reason phenol's C–O will not substitute either.

Topic 31 – key takeaways

1 Making

electrophilic substitution with $AlCl_3$

2 Halogenoalkane

reacts by nucleophilic substitution

3 Halogenoarene

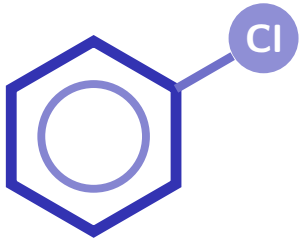
the lone pair strengthens the C–Cl bond

4 Ring

electron-rich ring repels nucleophiles

Check yourself

1. What catalyst makes a halogenoarene?
2. Which mechanism makes a halogenoarene?
3. Why is the C–Cl bond stronger in chlorobenzene?
4. Does chlorobenzene react with OH^- normally?



Answers **1.** $AlCl_3$ **2.** electrophilic substitution **3.** the Cl lone pair overlaps the ring **4.** no