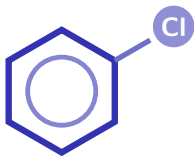


Halogen Compounds

A-Level Chemistry ■ Topic 31

A-Level Chemistry



What we will cover

- 1 Making halogenoarenes
- 2 Why they are unreactive



*many pesticides are
halogenoarenes*



Making halogenoarenes



A **halogenoarene** forms when an arene reacts with Cl_2 or Br_2 with an AlCl_3 **catalyst** .

This is **electrophilic substitution** – the halogen replaces an H on the ring (benzene $\rightarrow$ chlorobenzene).

Why they are unreactive

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

- the Cl **lone pair** 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

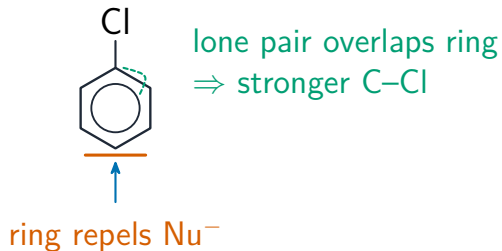
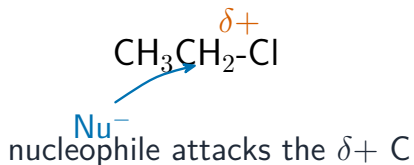
the general rule

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 **chlorobenzene: unreactive**



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).



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

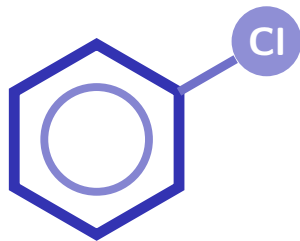
4

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