Halogen compounds

A-Level Chemistry

Making halogenoarenes

A **halogenoarene** 卤代芳烃 (also called an aryl halide) is formed when an **arene** 芳烃 reacts with Cl_2 or Br_2, using $AlCl_3$ or $AlBr_3$ as a **catalyst** 催化剂. This is the electrophilic substitution from the arenes topic —the halogen replaces a hydrogen on the ring.

- benzene gives chlorobenzene.
- methylbenzene gives 2-chloromethylbenzene and 4-chloromethylbenzene (the methyl group directs the chlorine to positions 2 and 4).

Many pesticides and herbicides are halogenoarenes —chlorine atoms bonded to a benzene ring

Image: John Messina, Public domain (commons.wikimedia.org)

Why a halogenoarene is less reactive than a halogenoalkane

Compare chloroethane (a **halogenoalkane** 卤代烷) with chlorobenzene (a halogenoarene).

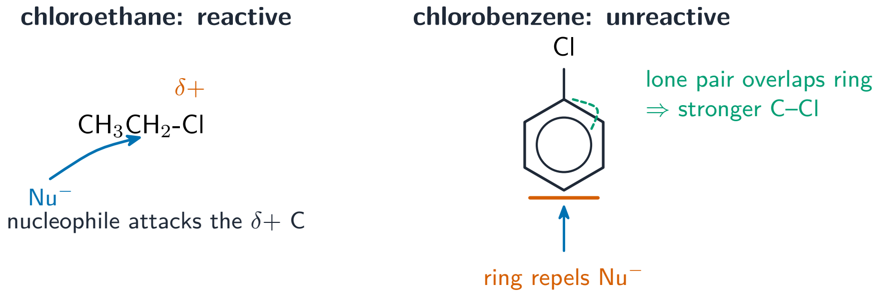
A halogenoalkane reacts easily by **nucleophilic substitution** 亲核取代: its C–Cl bond is polar, so a nucleophile can attack the slightly positive carbon and push the halogen out.

A halogenoarene is **very unreactive** towards nucleophilic substitution. There are two reasons:

- a **lone pair** 孤对电子 on the chlorine overlaps sideways with the **delocalised** 离域 ring of electrons. This gives the C–Cl bond partial double-bond character, making it shorter and stronger, so it is much harder to break.

- the electron-rich ring repels an approaching **nucleophile** 亲核试剂.

So chlorobenzene does **not** react with nucleophiles such as OH^- under normal conditions, while chloroethane does.


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