

9. HALOARENES

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Learning outcomes

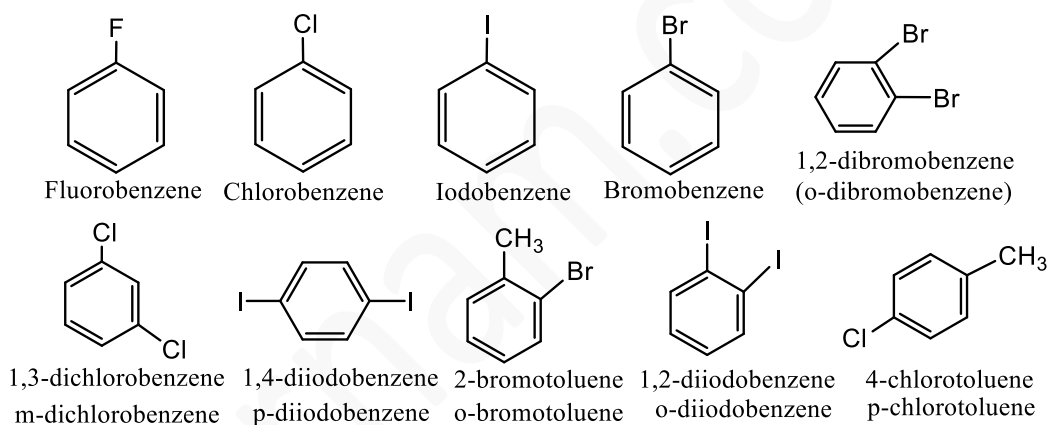
After the lesson, learners should be able to:

- ✓ Describe the nomenclature and isomerism of haloarenes.
- ✓ Show the preparation of chlorobenzene from benzene and benzene diazonium chloride.
- ✓ State the physical properties of haloarenes.
- ✓ Explain the low reactivity of haloarenes as compared to haloalkanes in terms of nucleophilic substitution reactions.
- ✓ Explain the chemical properties of haloarenes:
 - reduction of chlorobenzene,
 - electrophilic substitution reactions,
 - action with Na (Fittig and Wurtz-Fittig reaction)
 - and action with chloral.
- ✓ State important uses of haloarenes

Introduction, Nomenclature and Isomerism

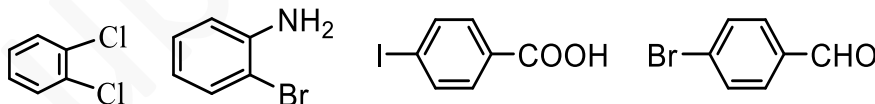
Haloarenes or aryl halides are aromatic compounds in which a halogen atom is directly bonded to an aromatic ring.

General formula: Ar-X, where Ar = aryl group, and X = halogen (F, Cl, Br or I).



Try it yourself

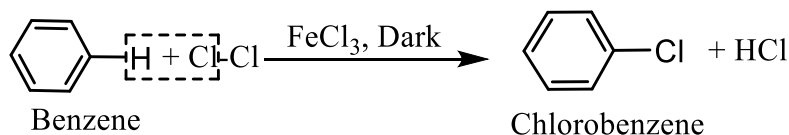
Name these compounds according to IUPAC rules.



Preparation

1. From benzene (by halogenation)

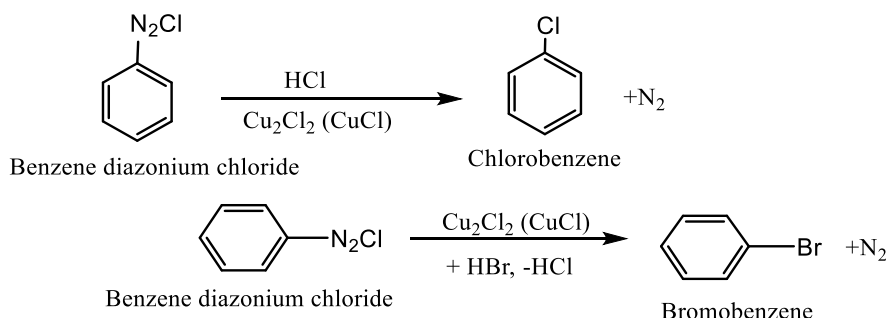
(Electrophilic aromatic substitution of benzene)



2. From benzene diazonium chloride

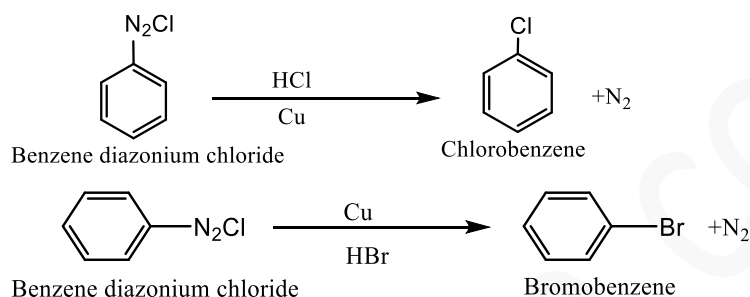
Sandmeyer reaction

In the Sandmeyer reaction, the diazonium group ($-N_2^+$) of benzene diazonium chloride is replaced by $-Cl$ or $-Br$, using cuprous chloride or cuprous bromide dissolved in the corresponding halogen acid at room temperature or when warmed.



Gattermann reaction

Benzene diazonium chloride gives halobenzene when warmed with copper powder and hydrochloric acid or hydrobromic acid. This is called the Gattermann reaction.



Exam Tip:

[The **Raschig** process is a chemical reaction used to produce chlorobenzene from benzene, hydrochloric acid, and oxygen in the presence of a catalyst like copper or iron chloride. This is one of the methods for commercial production of chlorobenzene. -Not in the Grade 12 NEB syllabus but appeared in 2080 NEB examination]

Physical Properties

Property	Haloarenes
Physical state	Usually oily liquids or crystalline solids
Solubility	Insoluble in water; soluble in organic solvents
Chlorobenzene	Colourless liquid with characteristic odour

Chemical Properties

Big Idea

Haloarenes are similar to haloalkanes, but their halogen atom is directly attached to an aromatic ring. This makes their reactions different – especially nucleophilic substitution.

Key question: Why is chlorobenzene much less reactive than chloroethane?

1. Nucleophilic substitution reaction

Unlike haloalkanes, haloarenes undergo nucleophilic substitution reactions with extreme difficulty. Such low reactivity can be explained as:

a. Carbon-to-halogen bonds in haloarenes are strong: **Resonance effect**

Chlorobenzene is a resonance hybrid of the following structures.

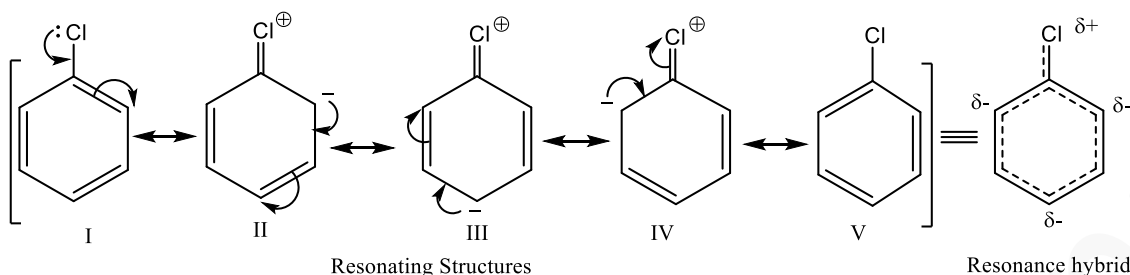
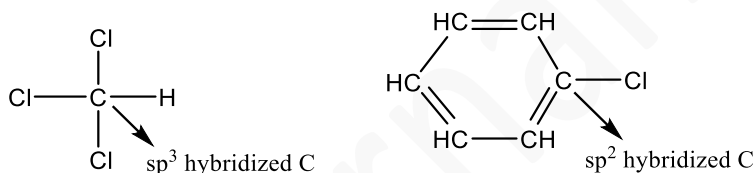


Fig: resonating structure and hybrid of Chlorobenzene

The lone pair of electrons on chlorine can participate in resonance with the benzene ring. As a result, the C-Cl bond acquires some partial double-bond character. Therefore, the bond is shorter and stronger than a normal C-Cl single bond and is difficult to break.

b. Carbon-halogen bond in haloarenes is less polar: **Hybridisation effect**

In haloarenes, the halogen atom is bonded to sp^2 -hybridised carbon, whereas in haloalkanes the halogen atom is bonded to sp^3 carbon. An sp^2 carbon (with 33.33% s-character) holds its electrons more strongly (*is more electronegative*) than sp^3 carbon (25% s-character). Hence, the carbon-halogen bond in haloarenes is less polar than that of haloalkanes.



$sp^2 \rightarrow 33.3\%$ s-character $\rightarrow$ stronger hold on electrons

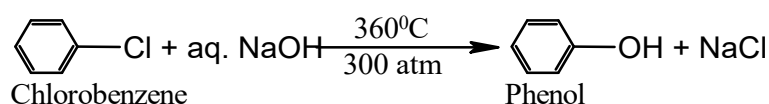
$sp^3 \rightarrow 25\%$ s-character $\rightarrow$ weaker hold on electrons

Quick Check

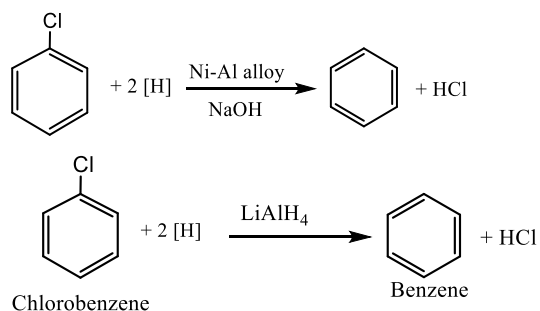
Which of the following helps explain why chlorobenzene resists nucleophilic substitution?

- A. The C-Cl bond has partial double-bond character.
- B. Chlorobenzene is ionic.
- C. Chlorine has no lone pair.
- D. Benzene contains no π electrons.

For example, chlorobenzene reacts with aqueous NaOH only at 360°C and 300 atm, producing phenol. (Dow process)



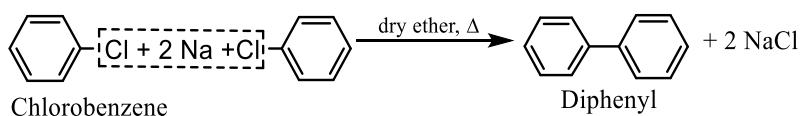
2. Reduction of Chlorobenzene(with Ni-Al alloy- NaOH, Δ or LiAlH_4)(preparation of benzene)



3. Reaction with Na

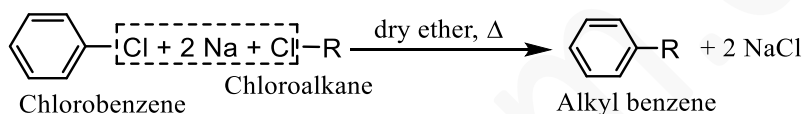
Fittig reaction

Aryl halides, when heated with sodium in dry ether solvent, give biphenyl compounds, as in the Wurtz reaction; this is called the Fittig reaction.

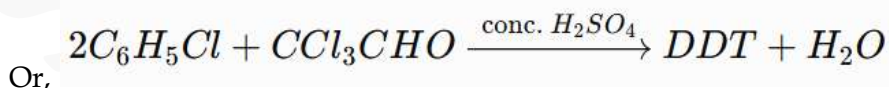
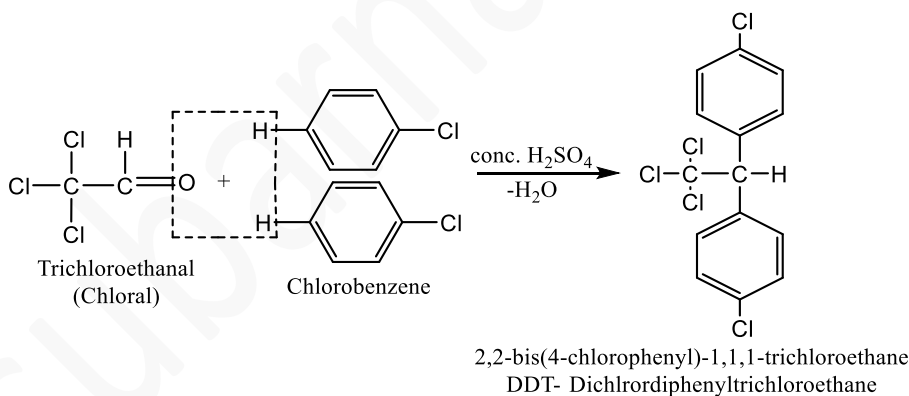


Wurtz-Fittig reaction

Aryl halides, when heated with alkyl halides in the presence of sodium metal and dry ether as a solvent, give alkylbenzene; this is called the Wurtz-Fittig reaction.



4. Reaction with chloral

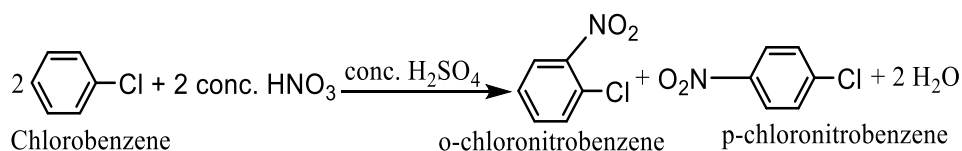


✓ DDT is an insecticide.

5. Electrophilic substitution reaction

The halogen atom is deactivating but ortho/para-directing. Therefore, electrophilic substitution occurs mainly at the ortho and para positions, although more slowly than in benzene.

a. nitration



Similarly, sulphonation and halogenation also occur at either the ortho or para positions. [practice writing these reactions]

Reaction	Reagent	Main products
Nitration	conc. HNO ₃ /H ₂ SO ₄	o- and p-nitrochlorobenzene
Sulphonation	conc. H ₂ SO ₄	o- and p-chlorobenzenesulphonic acid
Halogenation	Cl ₂ /FeCl ₃	o- and p-dichlorobenzene

★ **Remember**

Halogens are ▼ deactivating but ortho/para-directing groups.

Uses of chlorobenzene

1. As a starting material to prepare chlorotoluene, aniline, phenol, etc.
2. To manufacture DDT.

★ **Haloarenes – 5 things to remember**

1. **Ar-X = haloarene**
2. Chlorobenzene can be prepared from **benzene** and from **benzene diazonium chloride**.
3. Haloarenes are **less reactive than haloalkanes** towards nucleophilic substitution.
4. Halogens are **deactivating but ortho/para-directing**.
5. Chlorobenzene + chloral → **DDT**.

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