

9. HALOARENES

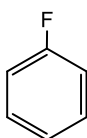
Learning outcomes

After the lesson, learners should be able to:

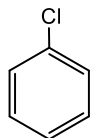
- ✓ Describe briefly the nomenclature and isomerism of haloarenes.
- ✓ Show the preparation of chlorobenzene from benzene and benzene diazonium chloride.
- ✓ State physical properties of haloarenes.
- ✓ Describe the low reactivity of haloarenes as compared to haloalkanes in terms of nucleophilic substitution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

Introduction, Nomenclature and Isomerism

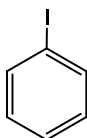
Halogen derivatives of arenes where the halo group is directly bonded to an aromatic ring are called haloarenes or aryl halides. It may be represented by Ar-X , where Ar is an aryl group, and X is a halogen (F, Cl, Br or I).



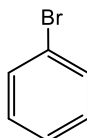
Fluorobenzene



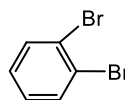
Chlorobenzene



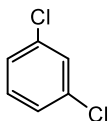
Iodobenzene



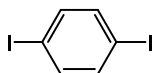
Bromobenzene



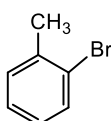
1,2-dibromobenzene
(o-dibromobenzene)



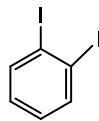
1,3-dichlorobenzene
m-dichlorobenzene



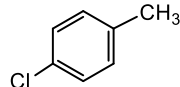
1,4-diiodobenzene
p-diiodobenzene



2-bromotoluene
o-bromotoluene

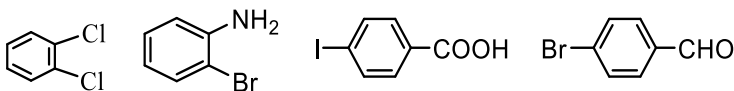


1,2-diiodobenzene
o-diiodobenzene



4-chlorotoluene
p-chlorotoluene

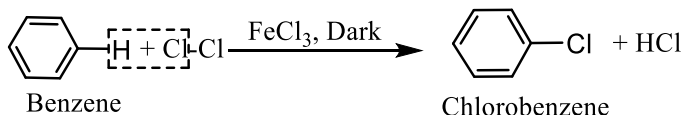
1. Write the name of the following compound according to the IUPAC rule.



Preparation

1. From benzene (by halogenation)

(Electrophilic aromatic substitution of benzene)



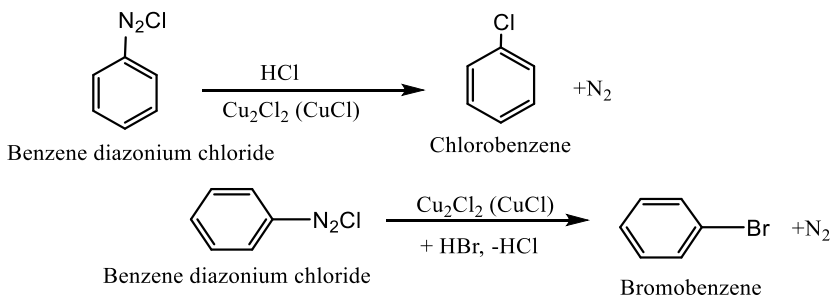
2. Give the correct chemical reaction for the preparation of chlorobenzene from benzene.

1

2. From benzene diazonium chloride

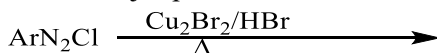
Sand-Meyer reaction

When benzene diazonium chloride is mixed with cuprous chloride or cuprous bromide dissolved in the corresponding halogen acid at room temperature or warmed, the diazo group is replaced by $-Cl$ and $-Br$, respectively. This is called the Sand Meyer reaction.



3. Give an example of the Sand-Meyer reaction.
4. Predict the major products of the following reactions:

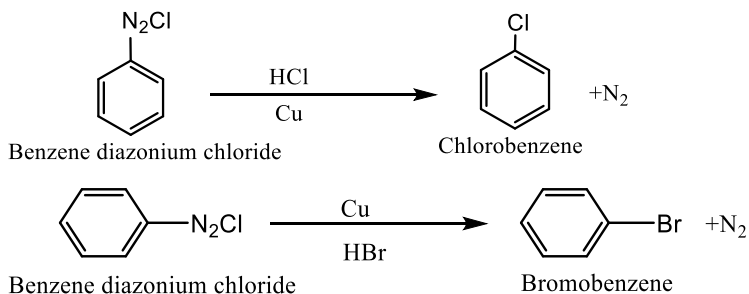
1



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Gatterman reaction

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



5. What products would you expect when benzene diazonium chloride is heated with copper powder in the presence of HCl ? 1
 6. Give the correct chemical reaction for the preparation of chlorobenzene from benzene diazonium chloride. 1
 7. Write any three methods of preparation of Chlorobenzene. 3
 8. Show your familiarity with Gattermann's reaction. 1
-
1. Chlorobenzene is formed when benzene diazonium chloride is heated with the cuprous chloride in corresponding halogen acid. The reaction is
 - a. Sandmeyer reaction
 - b. Grignard's reaction
 - c. Gattermann reaction
 - d. Fittig reaction
 2. When benzene diazonium chloride is heated with Copper and HCl , Chlorobenzene is formed, and the reaction is
 - a. Sandmeyer reaction
 - b. Fittig reaction
 - c. Gattermann reaction
 - d. All of the above
 3. Chlorobenzene is prepared commercially by
 - a. Dow's process
 - b. **Raschig process**
 - c. Deacon's process
 - d. Etard's process

[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 the preferred method for commercial production of chlorobenzene. -This is not in class 12 NEB chemistry syllabus but was asked in 2080 NEB examination]

Physical Properties

1. These are generally **oily liquids or crystalline solids**.
2. **Chlorobenzene** is a **colourless liquid** having an **aromatic odour**.
3. These are **insoluble in water** but **soluble in organic solvents**.
4. Which of the following has the highest boiling point?
a. $\text{C}_6\text{H}_5\text{F}$ b. $\text{C}_6\text{H}_5\text{Cl}$ c. $\text{C}_6\text{H}_5\text{Br}$ d. $\text{C}_6\text{H}_5\text{I}$

Chemical Properties

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

Haloarene is a resonance hybrid of the following structures, which indicates that the carbon-to-halogen bond has a partial double bond character. A double bond is shorter and stronger than the corresponding single bond. Hence it is difficult to break down the carbon halogen bond.

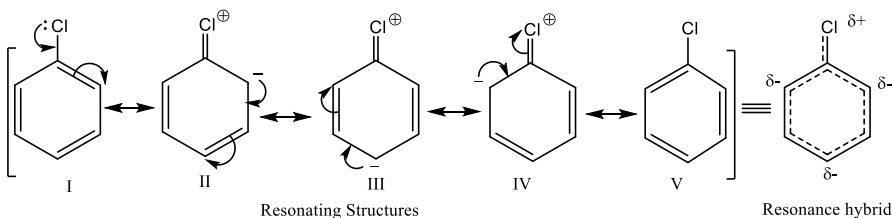
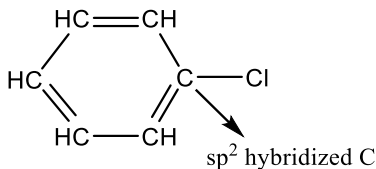
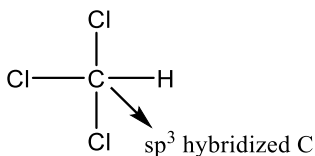


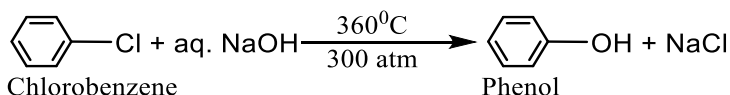
Fig: resonating structure and hybrid of Chlorobenzene

- b. Carbon to halogen bond in haloarenes is less polar:
Hybridization effect

In haloarenes, the halogen atom is bonded to sp^2 hybridized carbon, whereas in Haloalkane halogen atom is bonded to sp^3 carbon. (33.33% s-character) is more electronegative than sp^3 carbon (25% s-character). Hence carbon to halogen bond in haloarene is less polar than that of haloalkanes.



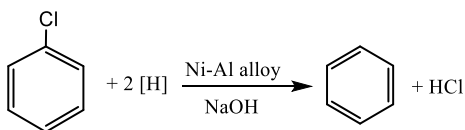
For example, Chlorobenzene reacts with aqueous NaOH only at 360°C and 300 atm producing phenol. (Dow process)

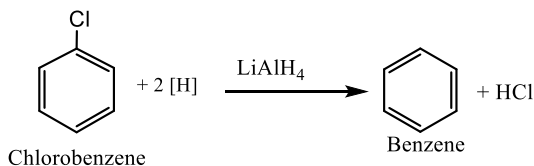


1. Why are haloarenes less reactive towards nucleophilic substitution reaction than haloalkanes? 2
2. **Why is nucleophilic substitution difficult in haloarenes?** 3
3. Why is a nucleophilic substitution reaction in Chlorobenzene difficult as compared to Chloroethane? 2
4. **Give reactions why haloalkanes are more reactive than haloarenes in nucleophilic substitution reactions.** 2
5. **What happens when Chlorobenzene is heated with alcoholic KOH?**

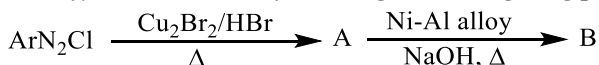
5. The C-Cl bond of Chlorobenzene, in comparison to the C-Cl bond in methyl chloride, is
 - a. Longer and weaker
 - b. Shorter and stronger
 - c. shorter and weaker
 - d. longer and stronger

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





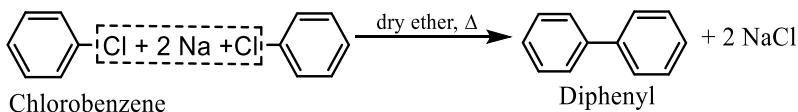
6. What happens when Chlorobenzene is treated with Ni-Al in an alkaline medium? 1
7. How would you obtain benzene from Chlorobenzene? 2
8. Identify A and B in the following reaction giving pertinent equations.



3. Action with Na

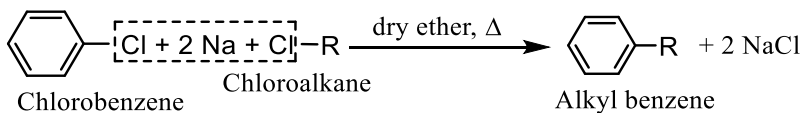
Fittig reaction

Aryl halides, when heated with sodium in the dry ether as a solvent, biphenyl compounds are obtained like 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, alkyl benzene is obtained; this is called Wurtz-Fittig reaction.

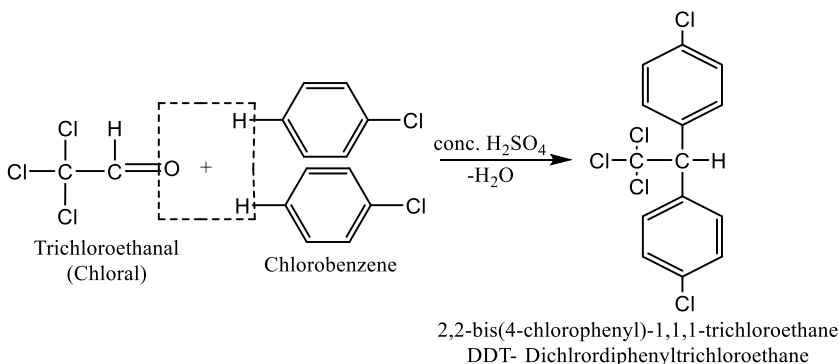


9. Write the chemical equation to illustrate Wurtz fittig reaction. 1
- 10. How would you convert Chlorobenzene into Toluene?** **1**

6. Bromobenzene and methyl bromide with sodium metal in the presence of dry ether give toluene. This reaction is called
 - a. Fittig reaction
 - b. Wurtz-Fittig reaction
 - c. Wurtz reaction
 - d. Ullman reaction

7. The name of the reaction, when halobenzene reacts with sodium metal in the presence of dry ether, is
 - a. Wurtz reaction
 - b. Fittig reaction
 - c. Friedel Craft's reaction
 - d. Cannizaro's reaction
8. Biphenyl is formed from Chlorobenzene by
 - a. Fittig reaction
 - b. Wurtz-Fittig reaction
 - c. Wurtz reaction
 - d. Grignard reagent

4. Action with chloral



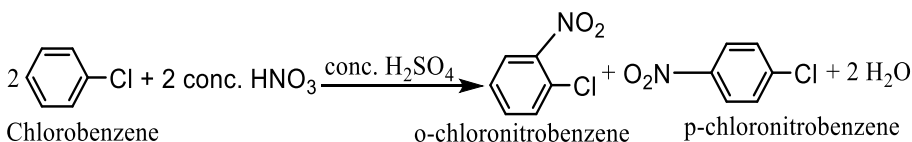
11. What happens when Chlorobenzene is treated with chloral in an acidic medium?
12. How does Chlorobenzene react with chloral? 1
13. What products would you expect when Chlorobenzene is heated with 2,2,2-trichloroethanal? 1
14. How would you convert Chlorobenzene into DDT? 1
15. How will you carry out the following conversion: phenol to DDT? 2
16. An aromatic compound (A) undergoes Sandmeyer's reaction to give (B). The compound (B) is reduced with Ni-Al in the presence of alkali to give compound (C). The compound (C) further reacts with CH₃Cl in the presence of anhydrous AlCl₃. The compound (B), when heated with chloral in an acidic medium, gives a common insecticide. Identify (A), (B), (C) and (D), giving a complete reactions. 4

9. When Chlorobenzene is heated with chloral in the presence of conc. H₂SO₄, the compound formed, is
 - a. BHC
 - b. DDT
 - c. Chloropicrin
 - d. Chloretone

10. Chloral is needed for the preparation of
 a. Mischler's Ketone b. DDT c. Aldrin d. Gammexane
11. DDT is used as
 a. Analgesic b. Antipyretic d. Insecticide c. Antiseptic
12. Which of the following compounds reacts with chlorobenzene to form DDT?
 a. Carbonyl chloride c. acetone
 b. Chloral d. chloroform

5. Electrophilic substitution reaction

a. nitration



Similarly, sulphonation, halogenation, Friedel-Craft's acylation and alkylation also occur slowly in either ortho or para positions. [practice these reactions]

17. Why does Chlorobenzene give ortho and para products during electrophilic substitution?# 2
18. Why is haloarene less reactive than benzene in electrophilic substitution reaction?# 2

Refer to class XI

13. Which of the following is o,p-director but a deactivating group towards electrophilic substitution reaction?
 a. -CH₃ b. -Cl c. -NO₂ d. -COOH

Uses of Chlorobenzene

- As starting material to prepare Chlorotoluene, Aniline, Phenol etc.
- To prepare DDT.

****This is an incomplete note- study thoroughly from books and class notes too****