# HALOALKANES AND HALOARENES

# **METHODS & PREPARATION OF HALOARENES**

# ARYL HALIDE

When a halogen atom is directly bonded to the benzene ring, the compound is referred to as a **Haloarene**.



#### Class-12<sup>th</sup>

#### Chemistry



Raschig Process

$$2 \bigcirc + 2\text{HCl} + 0_2 \qquad \frac{\text{CuCl}}{\Delta} \qquad 2 \bigcirc + 2\text{H}_20$$

#### **CHEMICAL PROPERTIES**

(i) Chlorobenzene remains unreactive when exposed to aqueous sodium hydroxide at room temperature.

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- (ii) In nucleophilic substitution reactions, aryl halides exhibit significantly lower reactivity compared to alkyl halides.
- (iii) The carbon-halogen bonds in aryl halides are exceptionally robust, and the energy of aryl cations is too high to facilitate the easy ionization of aryl halides through an  $S_{N^1}$ -type process.
- (iv) Achieving the optimal transition state geometry required for an  $S_{N^2}$  process is unattainable.
- (v) The presence of the aromatic ring obstructs nucleophilic attacks from the side opposite to the carbon-halogen bond.

# The Elimination-Addition Mechanism of Nucleophilic Aromatic Substitution (Benzyne)

"Highly reactive bases like sodium or potassium amide can undergo a reaction with aryl halides, including those lacking electron-withdrawing substituents, leading to the formation of products resulting from the nucleophilic substitution of the halide by the base."



## MECHANISM

**Step-1**: **Elimination stage;** "The amide ion is an exceptionally potent base that triggers the dehydrohalogenation of chlorobenzene by removing a proton from the carbon atom adjacent to the one carrying the leaving group. This step results in the formation of an unstable intermediate known as benzyne."



Chlorobenzene

Benzyne

**Step-2: Beginning of addition phase;** "The amide ion functions as a nucleophile, attaching to one of the carbons within the triple bond. The outcome of this reaction is the formation of a carbanion."



**Step-3: Completion of addition phase;** The aryl anion removes a proton from the ammonia, which serves as the solvent in the reaction.

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**NOTE:** The sp<sup>2</sup> orbital within the benzene ring's plane is not correctly oriented for optimal overlap, resulting in weaker  $\pi$  bonding compared to alkynes.

(i)



(ii)



(iii)



### Nucleophilic Aromatic Substitution by the addition Elimination Mechanism

(i) The widely acknowledged mechanism for nucleophilic aromatic substitution in aryl halides with nitro substituents.



p-Chloronitrobenzene

p-Nitro anisole

- (ii) An ortho-nitro group exhibits a similar rate-enhancing influence in m-chlorinated benzyne, but it is significantly less reactive than o- or p-chloronitrobenzene, even though it is much more reactive than chlorobenzene itself.
- (iii) The cumulative effect of o- and p-nitro substituents is evident, as the rate data for methoxide ion substitution in a series of nitro-substituted chlorobenzene derivatives demonstrate a progressively increasing reaction rate.



(iv) Unlike nucleophilic substitution in alkyl halides, where alkyl fluorides exhibit very low reactivity, aryl fluorides readily undergo nucleophilic substitution when the ring features an o- or p-nitro group.



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- (v) Certainly, the reactivity order of leaving groups in nucleophilic aromatic substitution is opposite to what is observed in aliphatic substitution.
- (vi) In nucleophilic aromatic substitution, fluoride is the most reactive leaving group, while iodide is the least reactive.

Relative reactivity towards sodium methoxide in methanol X = F Cl Br I 312 1.0 0.8 0.4

(vii) Kinetic investigations of numerous reactions outlined in this section have confirmed their adherence to a second-order rate equation.
Rate = k [aryl halide] [nucleophile]

(viii) Second-order kinetics are typically explained by a rate-determining step involving a bimolecular reaction.



p-Fluor nitrobenzene Sodium methoxide



#### MECHANISM

**Step -1:** During the addition stage, the nucleophile, which is methoxide ion in this instance, attaches to the carbon atom carrying the leaving group, forming a cyclohexadienyl anion intermediate.



p-Fluor nitrobenzene Methoxide ion

Cyclohexadienyl anion interm edi at e

**Step -2:** Elimination stage. Loss of halide form the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.



(via benzyne mechanism)

Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

Reactivity Order: (Towards nucleophilic substitution)



**Fitting reaction** 



Wurtz fitting reaction

$$\bigcirc \qquad Cl + 2Na + ClCH_2CH_2CH_3 \qquad \xrightarrow{Dry \text{ ether}} \bigcirc CH_2 CH_2CH_3 + 2NaCl$$

Formation of aryl magnesium halide



Reduction





With Chloral





DDT (insecticide) p,p–Dichloro diphenyl trichloroethane

# **Electrophilic Substitution Reaction**



Cl is o- and p- directing group.

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