

UNIT 6 • HALOALKANES AND HALOARENES

Preparation of Haloarenes

Master the primary synthetic pathways: Electrophilic
Substitution and Sandmeyer's Reaction.

Essential Terminology

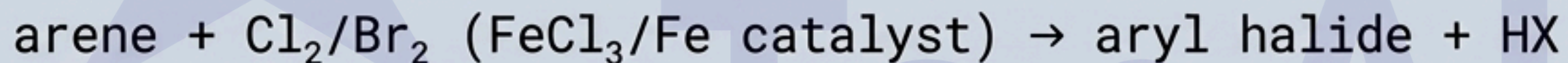
Electrophilic Substitution A reaction where an electrophile replaces a hydrogen atom on an aromatic ring, typically requiring a Lewis acid catalyst.

Sandmeyer's Reaction A radical-nucleophilic aromatic substitution synthesizing aryl halides from primary aromatic amines via a diazonium intermediate.

Diazonium Salt A highly reactive intermediate organic compound containing a characteristic $\text{-N}_2^+ \text{X}^-$ functional group.

Route A: From Hydrocarbons

Mechanism: Electrophilic Substitution of Arenes

**Catalyst Required:**

Relies on Lewis acids like iron or iron(III) chloride to generate the electrophile.

Isomer Separation:

Yields both ortho and para isomers. These are easily separated due to a large difference in their melting points.

Note on Iodine: Direct iodination is reversible and uniquely requires an oxidizing agent (HNO_3 , HIO_4) to consume the HI formed.



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Key Highlights

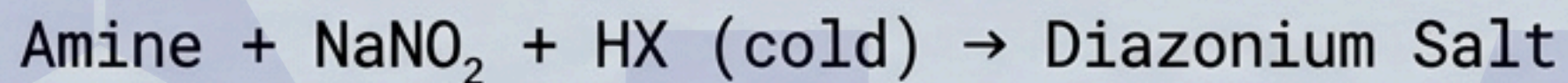
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Route B: From Amines (Sandmeyer's Reaction)

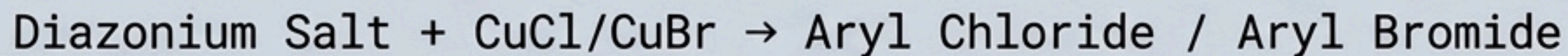
Step 1: Diazotization

Primary aromatic amine is dissolved in cold aqueous mineral acid and treated with sodium nitrite (NaNO_2) to form the unstable intermediate.



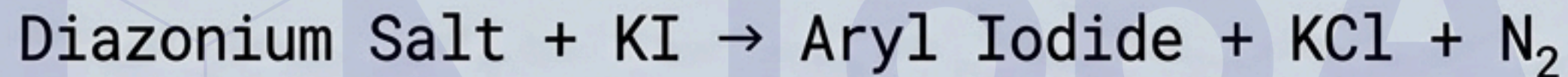
Step 2: Halogen Replacement

The freshly prepared diazonium solution is mixed with a cuprous halide catalyst.



The Iodine Pathway: No Copper Required

While Chlorine and Bromine require cuprous halides (CuCl/CuBr) to replace the diazonium group, **iodine behaves differently.**



(Notice: No Cu catalyst present)

The Mechanism:

Replacement of the diazonium group by iodine is highly efficient and is achieved simply by shaking the diazonium salt with Potassium Iodide (KI).

The Fluorine Exception

~~Direct fluorination of arenes via~~ **Electrophilic Substitution.**

Why this route is crossed out:
Fluoro-arenes **cannot** be prepared by direct electrophilic substitution methods.

The Chemical Reality:
Fluorine gas (F_2) is exceptionally reactive. Attempting direct fluorination leads to violent, uncontrolled reactions and poly-fluorinated products rather than a clean, usable aryl fluoride.

Common Exam Pitfalls

! Watch for this MCQ Trap!

Examiners love to test the specific catalyst requirements for haloarene synthesis. When evaluating reaction pathways, always verify the halogen target:

1. **The Iodine Swap Trap:** Options often falsely list CuI as the catalyst for diazonium to aryl iodide. Remember: **Iodine skips the copper catalyst entirely.** Just KI is needed.
2. **The Direct Fluorination Trap:** Options may present F_2 / Fe as a valid method. Remember: **Fluorine skips the electrophilic substitution method entirely** due to its violently high reactivity.

Chapter Summary

Key Takeaways

- **Route A (Hydrocarbons):** Electrophilic substitution uses Cl_2/Br_2 with a Lewis acid catalyst, producing easily separable ortho/para isomers due to distinct melting points.
- **Route B (Amines):** Sandmeyer's reaction utilizes a diazonium intermediate; Cl/Br targets require a copper catalyst, while I only requires KI, and F avoids these methods altogether.





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