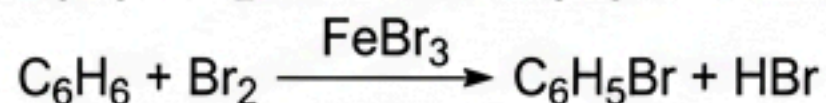
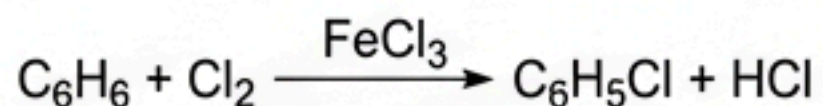
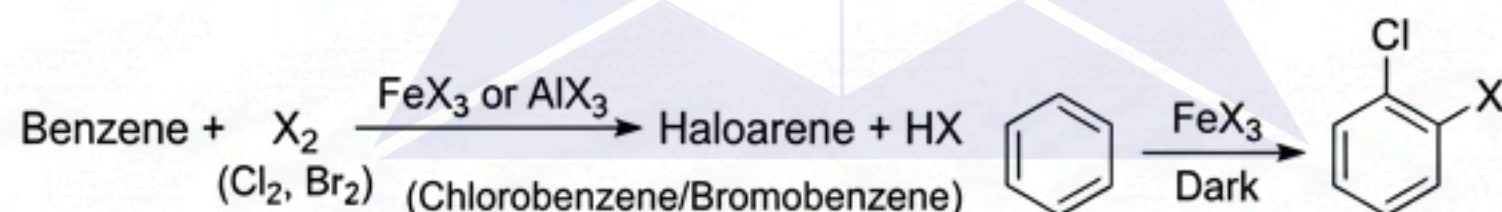


Making Haloarenes from Arenes

Preparation via Electrophilic Substitution: Mechanisms, Catalysts, and Conditions

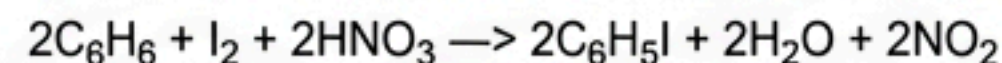
1. Chlorination and Bromination

Reaction of arenes with chlorine or bromine requires a Lewis acid catalyst (e.g., FeX_3 , AlX_3) in the absence of light. This proceeds via an electrophilic aromatic substitution mechanism.

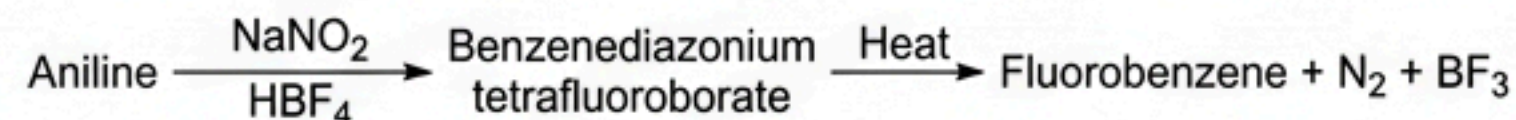


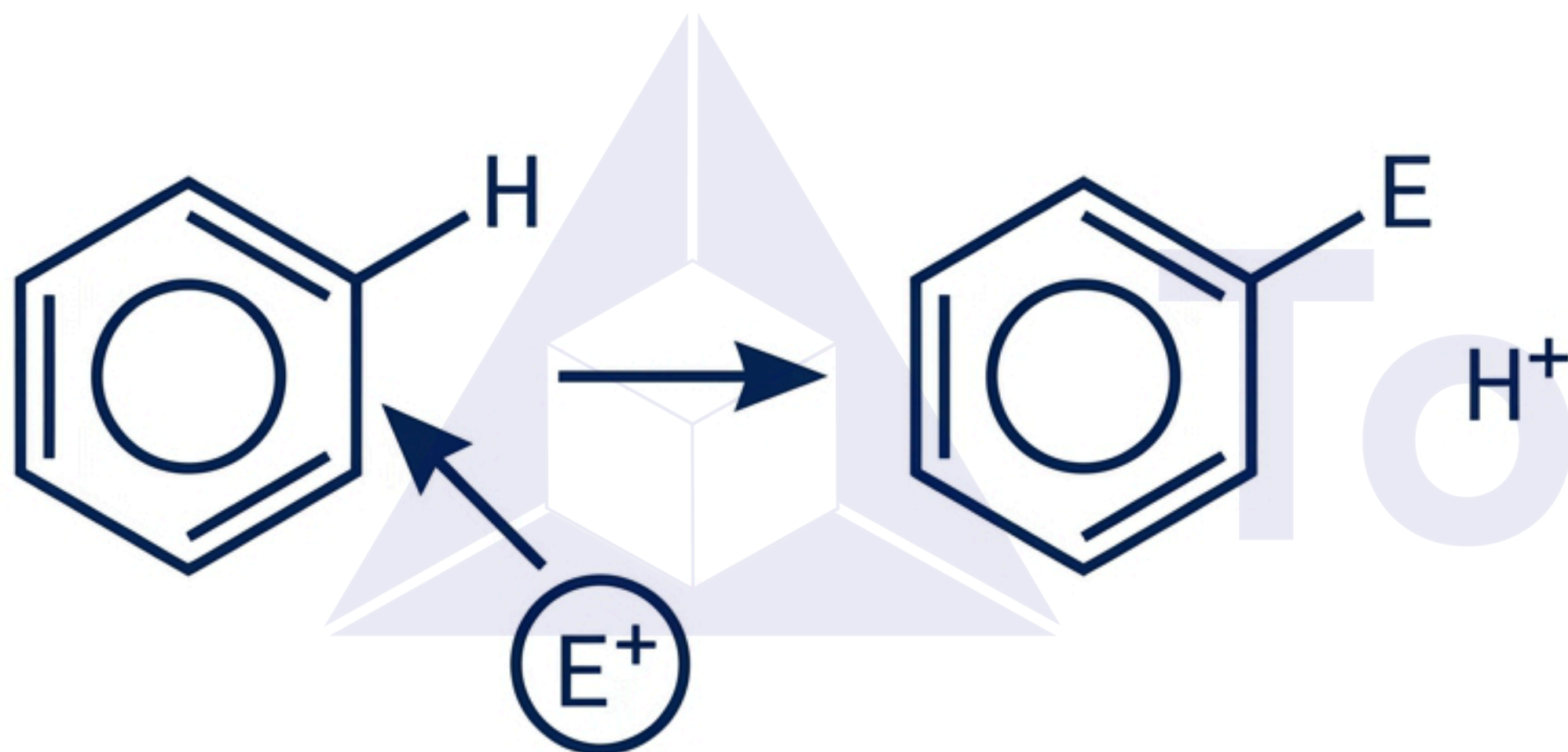
2. Iodination and Fluorination

Iodination is reversible and requires an oxidizing agent (e.g., HNO_3 , HIO_4) to remove HI . Fluorination is highly reactive and often requires indirect methods, such as the Balz-Schiemann reaction.



Fluorination: Indirect methods preferred due to high reactivity.





Benzene Ring Substitution

Aryl chlorides and bromides are prepared by directly substituting a hydrogen atom on an aromatic ring with a halogen.

- Aromatic rings are electron-rich, naturally attracting electrophiles (electron-seekers).
- The reaction strictly preserves the stable, delocalized π -electron system of the arene.
- Requires specialized conditions to overcome the exceptionally high stability of the benzene ring.

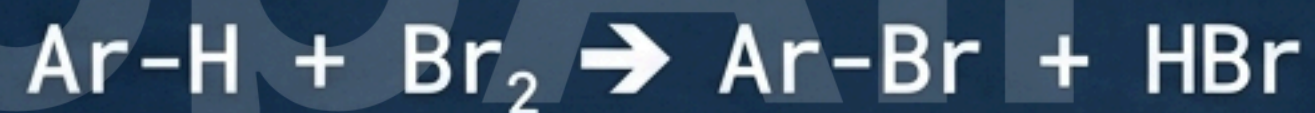
CHLORINATION PATHWAY

Direct reaction of an arene with chlorine gas yields an aryl chloride.



BROMINATION PATHWAY

Direct reaction with liquid bromine yields an aryl bromide.





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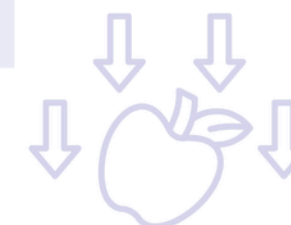
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Lewis Acid Catalyst: Fe / FeCl₃

Why standard halogens cannot react with benzene alone

The Problem

Cl₂ and Br₂ are not electrophilic enough to break the highly stable aromatic electron cloud on their own.

Catalyst Required

The Catalyst

Lewis acids like Iron (Fe) or Iron(III) chloride (FeCl₃) are added. They act as powerful electron-pair acceptors.

The Activation

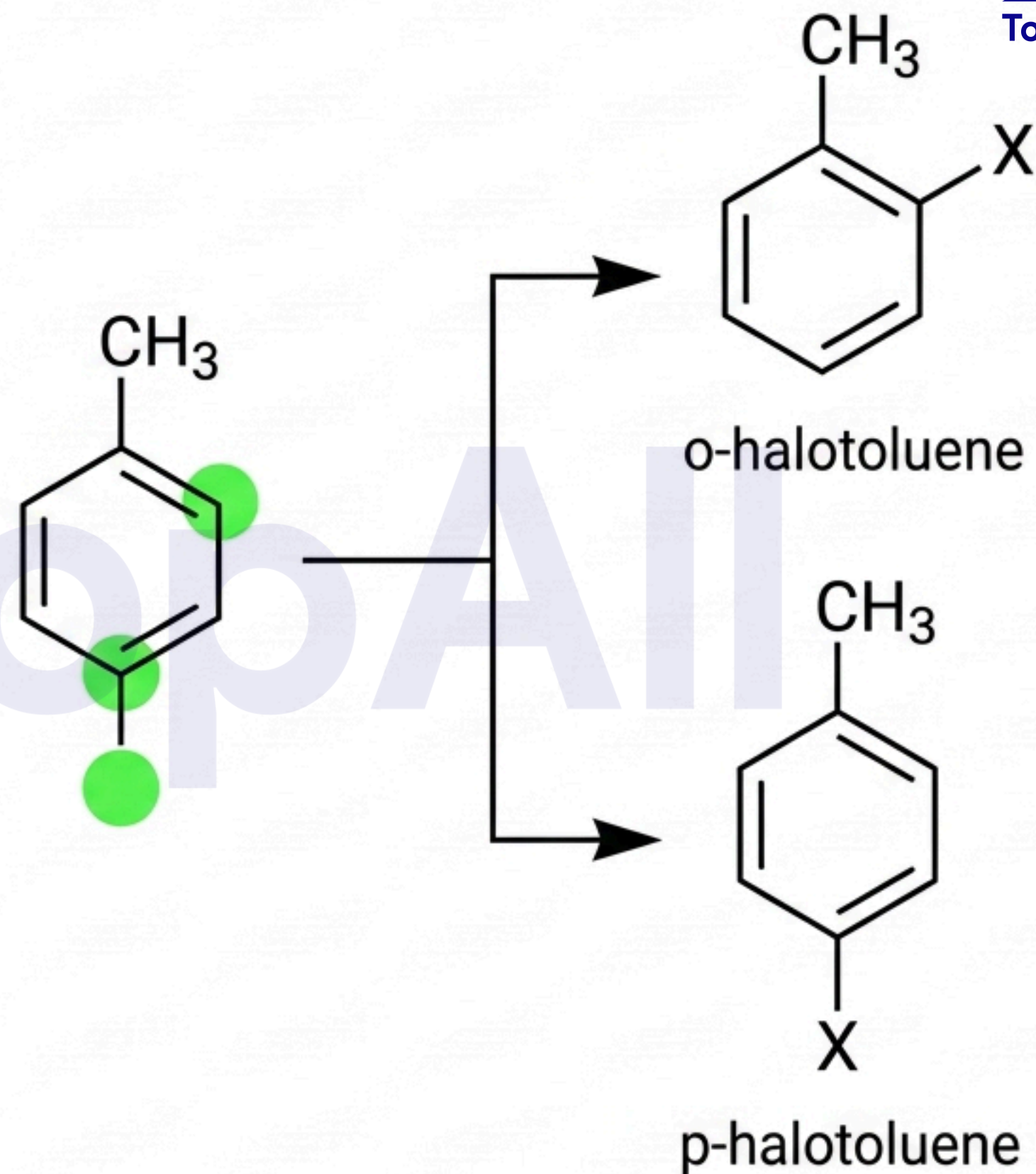
The catalyst polarizes the halogen bond, generating a highly reactive, positive halogen ion (X⁺) that attacks the ring.

Ortho and Para Products

When substituting an arene that already has an alkyl group (like toluene), the incoming halogen is directed to specific positions on the ring.

Easy Separation

The ortho and para isomers can be easily separated due to a large difference in their melting points.



Special Cases: Iodine and Fluorine

Amber Alert: Reversible Reaction

Why Iodine Needs an Oxidising Agent

Iodination is uniquely reversible. It produces HI as a byproduct, which can reverse the reaction back to the starting materials.

Solution: Oxidizing agents (like HNO_3 or HIO_4) must be added to consume the HI and drive the reaction forward.

Red Warning: Dangerously Reactive

Why Fluorine is Not Used

Fluoro compounds cannot be prepared by direct electrophilic substitution.

Reason: Fluorine gas is excessively reactive, leading to uncontrolled, often explosive reactions and total ring destruction.

Exam Summary

Electrophilic Substitution of Arenes at a Glance

Halogen	Reagents	Catalyst Required?	Viability / Notes
Chlorine (Cl ₂)	Cl ₂	Yes (Fe / FeCl ₃)	Excellent yield. Ortho/Para separated by melting point. 
Bromine (Br ₂)	Br ₂	Yes (Fe / FeBr ₃)	Excellent yield. Standard pathway. 
Iodine (I ₂)	I ₂ + HNO ₃ /HIO ₄	No (Needs Oxidizer)	Reversible. Requires oxidizer to remove HI. 
Fluorine (F ₂)	N/A	N/A	Not viable. Too highly reactive. 



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