

# Chapter 22: Reactions of Benzene and Its Derivatives

## Lecture Guide

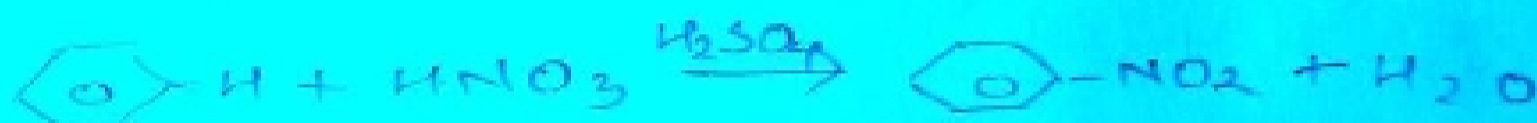
### Introduction

- A. Remember from Chapter 21 that the most characteristic reaction that aromatics undergo is substitution – in which a hydrogen from the benzene ring is replaced by another atom/group of atoms.
- B. There are five different types of substitution that we can undergo with aromatic compounds:

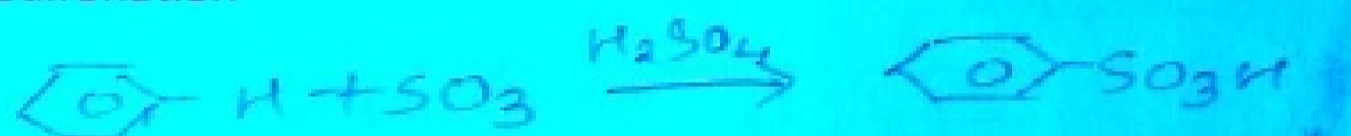
1. Halogenation



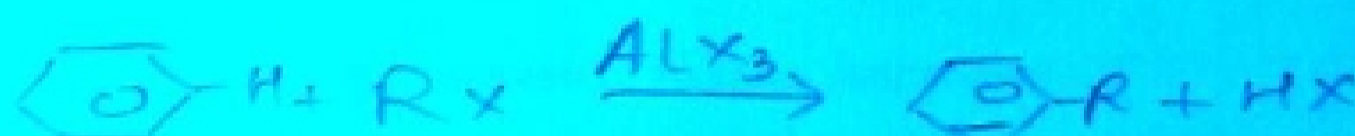
2. Nitration



3. Sulfonation



4. Alkylation



5. Acylation



### II. Electrophilic Aromatic Substitution

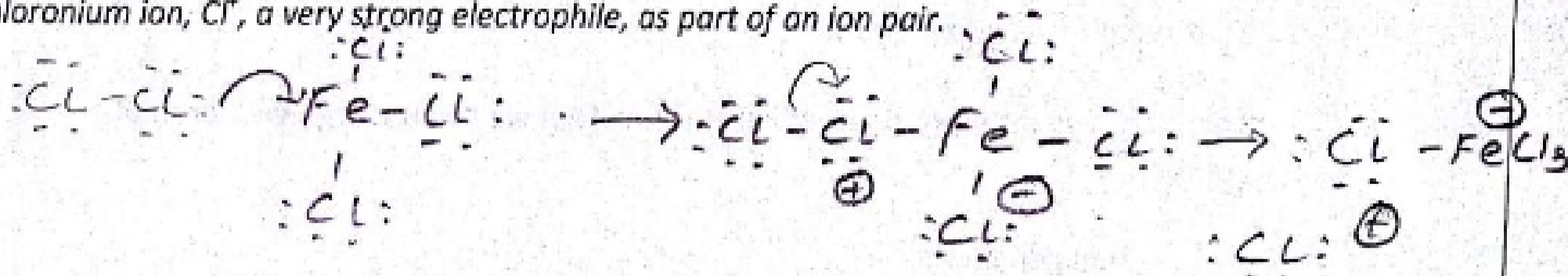
- A. In an **electrophilic aromatic substitution** reaction, a hydrogen atom of an aromatic ring is replaced by an electrophile. Let's look at different electrophiles...

B. Halogenation

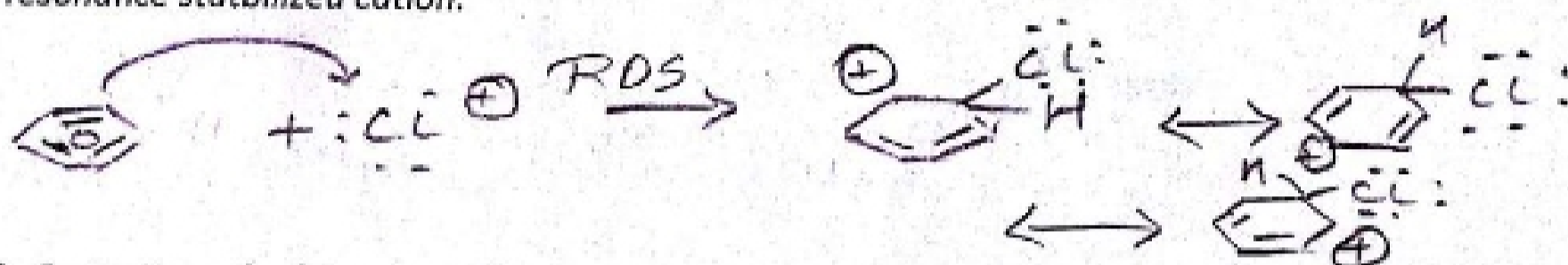
1. In the presence of a Lewis acid catalyst ( $\text{FeCl}_3$  or  $\text{AlCl}_3$ ), benzene can react with a halide ( $\text{Cl}_2$  or  $\text{Br}_2$ ) to give chloro/bromobenzene and  $\text{HCl}$  or  $\text{HBr}$ .

### Mechanism #1: Electrophilic Aromatic Substitution – Chlorination

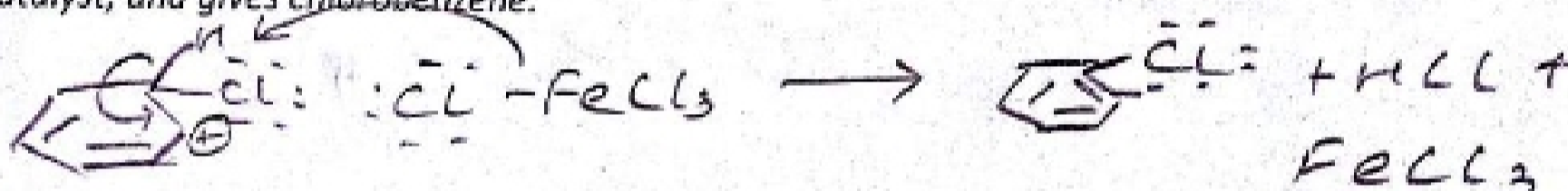
Step 1: Reaction between chlorine and the Lewis acid catalyst gives a molecular complex with a positive charge on chlorine and a negative charge on iron. Redistribution of electrons in this complex generates a chloronium ion,  $Cl^+$ , a very strong electrophile, as part of an ion pair.



Step 2: Attack of the chloronium ion on the  $\pi$  system of the aromatic ring gives a resonance-stabilized cation intermediate. Notice that the positive charge is located primarily at the ortho and para positions of the resonance-stabilized cation.



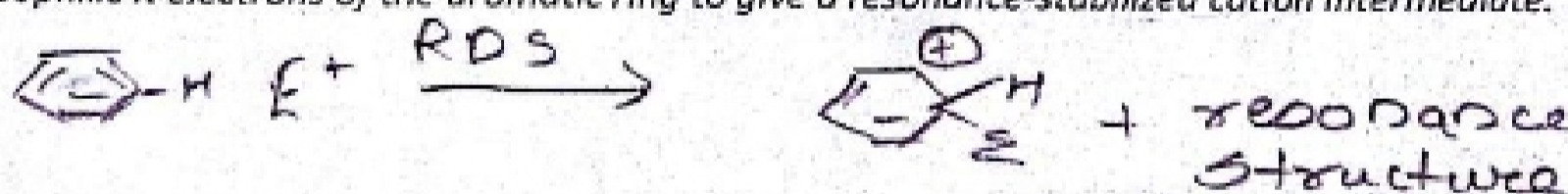
Step 3: Proton transfer from the cation intermediate to  $FeCl_4^-$  forms  $HCl$ , regenerates the Lewis acid catalyst, and gives chlorobenzene.



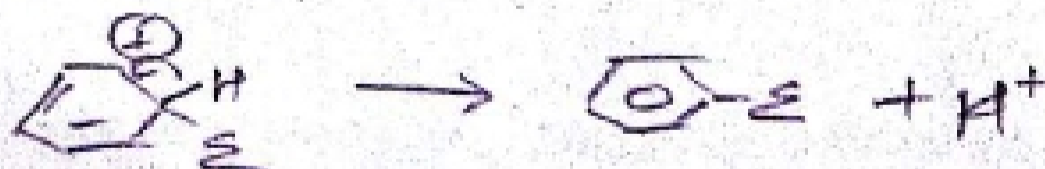
2. This mechanism leads us to develop a generic two-step mechanism for EAS.

### Mechanism #2: Generic Mechanism for Electrophilic Aromatic Substitution

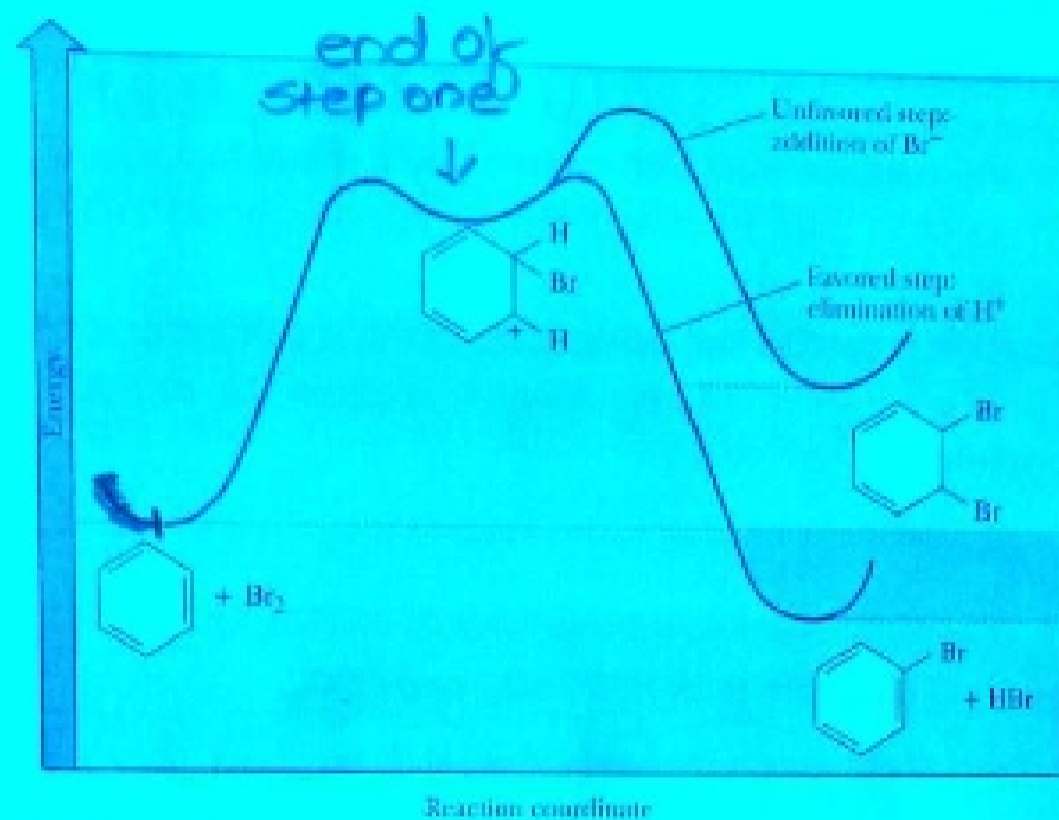
Step 1: The first – and rate determining – step is attack of the strong electrophile,  $E^+$ , by the weakly nucleophilic  $\pi$  electrons of the aromatic ring to give a resonance-stabilized cation intermediate.



Step 2: The second and faster step, loss of  $H^+$  from the cation intermediate, regenerates aromaticity in the ring and gives the product.



3. We can create a reaction coordinate diagram for electrophilic aromatic substitution.

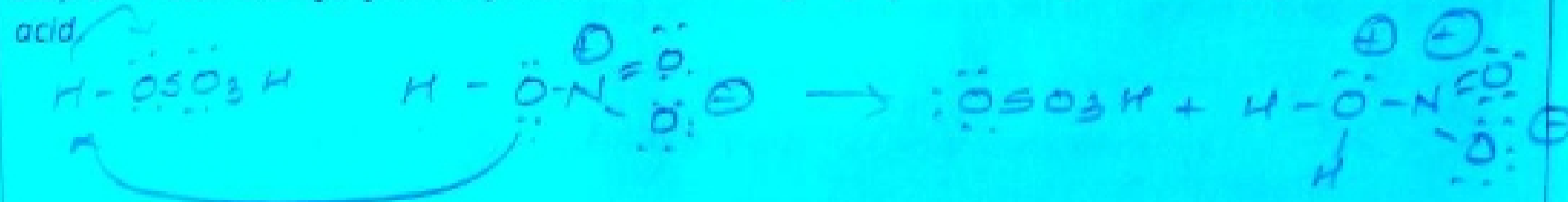


### C. Nitration and Sulfonation

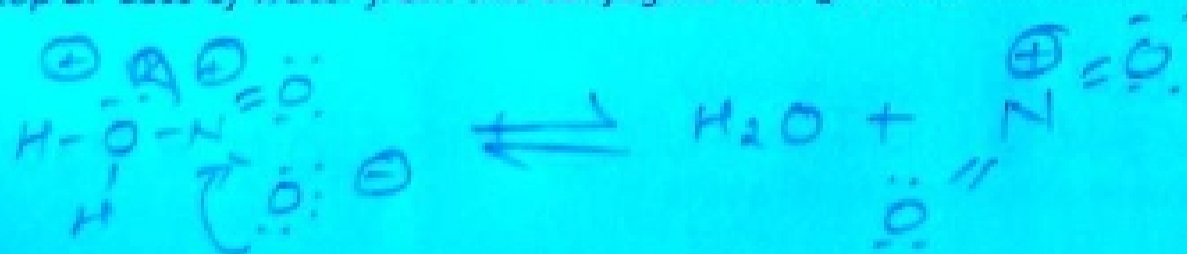
1. Nitration and sulfonation follow the same mechanism as halogenations.
2. Nitration involves the formation of the **nitronium ion**,  $\text{NO}_2^+$  from the reaction of nitric acid and sulfuric acid.

#### Mechanism #3: Formation of the Nitronium Ion

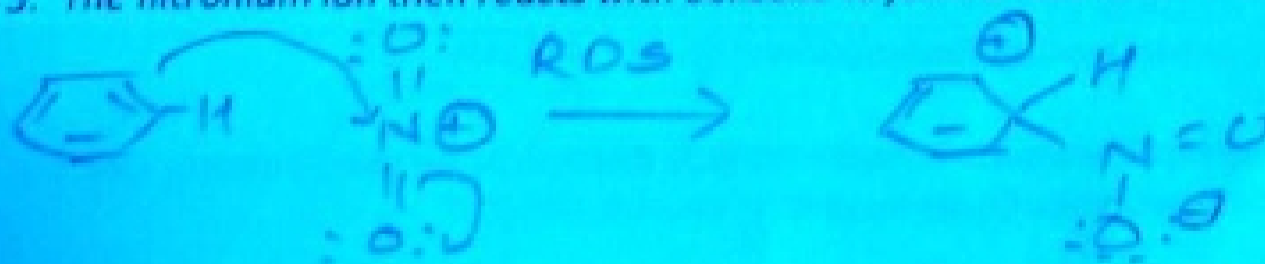
Step 1: Proton transfer from sulfuric acid to the OH group of nitric acid gives the conjugate acid of nitric acid.



Step 2: Loss of water from this conjugate acid gives the nitronium ion, a very strong electrophile.



Step 3: The nitronium ion then reacts with benzene to form a resonance-stabilized arenium ion.



Step 4: The arenium ion then loses a proton to a Lewis base to form nitrobenzene.

