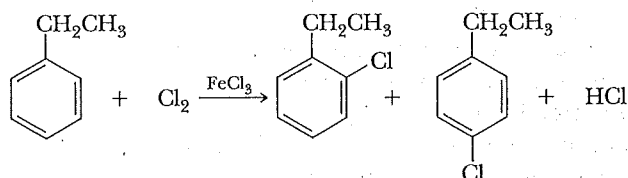
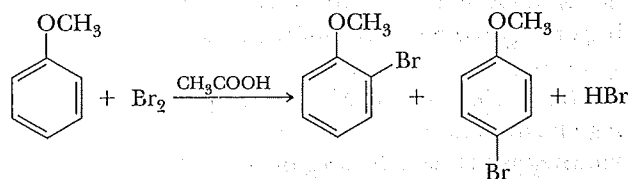


Key Reactions

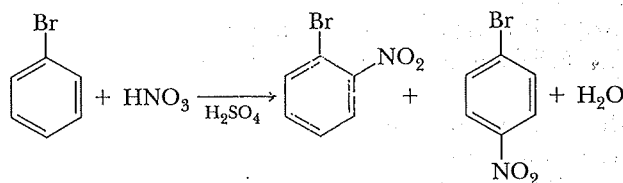
1. Halogenation (Section 22.1A) The electrophile is a halonium ion formed as an ion pair by interaction of chlorine or bromine with a Lewis acid. The mechanism involves an initial reaction between Cl_2 and FeCl_3 to generate a molecular complex that can rearrange to give a Cl^+ , FeCl_4^- ion pair. The Cl^+ reacts as a very strong electrophile with the weakly nucleophilic aromatic π cloud to form a resonance-stabilized cation intermediate that loses a proton to give the aryl chloride product.



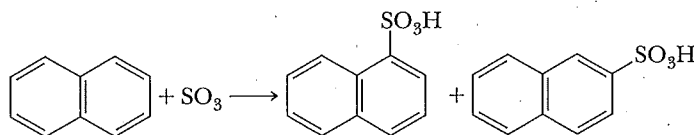
Halogenation of an aromatic ring substituted by strongly activating groups (such as $-\text{OH}$, $-\text{OR}$, and $-\text{NH}_2$) does not require a Lewis acid catalyst.



2. Nitration (Section 22.1B) The electrophile is the nitronium ion, NO_2^+ , formed by interaction of nitric acid and sulfuric acid. The mechanism involves an initial protonation of nitric acid by sulfuric acid followed by loss of water to yield the nitronium ion NO_2^+ . The nitronium ion reacts as a very strong electrophile with the weakly nucleophilic aromatic π cloud to form a resonance-stabilized cation intermediate that loses a proton to give the final product.

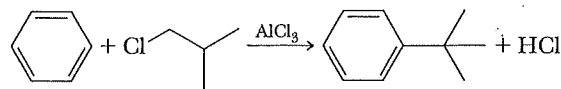


3. Sulfonation (Section 22.1B) The electrophile is either sulfur trioxide, SO_3 , or HSO_3^+ depending on experimental conditions. The mechanism involves reaction of SO_3 as a very strong electrophile with the weakly nucleophilic aromatic π cloud to form a resonance-stabilized cation intermediate that loses a proton to give the arylsulfonic acid product.



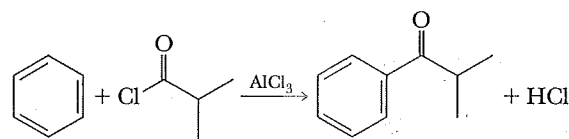
4. Friedel-Crafts Alkylation (Section 22.1C) The electrophile is a carbocation formed as an ion pair by interaction of an alkyl halide with a Lewis acid. Rearrangements from a less stable carbocation to a more stable carbocation are common. The mechanism involves an initial reaction between the alkyl halide and Lewis acid AlCl_3 to yield an intermediate that can be thought of as a carbocation, AlX_4^- ion pair. The carbocation portion of the ion pair reacts as a very strong electrophile with the weakly nucleophilic aromatic π cloud to form a resonance-stabilized cation intermediate that loses a proton to give the final product. Because carbocations are involved in the mechanism, rearrangements can be a

problem, especially with primary or secondary alkyl halides, or any other alkyl halide that will generate a carbocation prone to rearrangement.

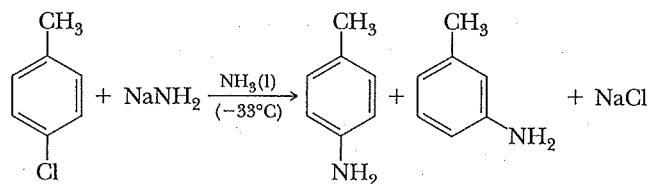


The reaction fails when there is one or more strongly electron-withdrawing groups on the ring. It can be hard to stop the reaction after a single alkylation, because the aromatic monoalkylation product is more reactive than the starting material.

5. **Friedel-Crafts Acylation (Section 22.1C)** The electrophile is an acyl cation (an acylium ion) formed as an ion pair by interaction of an acyl halide with a Lewis acid. The mechanism involves an initial reaction between the acid chloride and Lewis acid AlCl_3 to yield an intermediate that can be thought of as a resonance-stabilized acylium ion, AlCl_4^- ion pair. The acylium ion portion of the ion pair reacts as a very strong electrophile with the weakly nucleophilic aromatic π cloud to form a resonance-stabilized cation intermediate that loses a proton to give the final product. Because acylium ions do not rearrange like carbocations, no rearrangements occur. The reaction fails when there is one or more strongly electron-withdrawing groups on the ring. It is easy to stop the reaction after a single acylation because the aromatic monoacylation product is less reactive than the starting material.

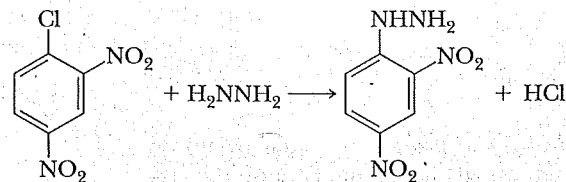


8. **Nucleophilic Aromatic Substitution: A Benzyne Intermediate (Section 22.3A)** The mechanism involves an initial elimination reaction between the aryl halide and strong base to give a benzyne intermediate, which undergoes addition at either sp hybridized carbon atom to give the products.



9. **Nucleophilic Aromatic Substitution: Addition-Elimination (Section 22.3B)** The mechanism involves a nucleophilic attack of the ring carbon containing the halogen to give a negatively charged Meisenheimer complex, followed by loss of halogen to give the substituted product. This reaction does not occur unless there are electron-withdrawing

groups ortho and/or para to the halogen, because these groups activate the ring toward nucleophilic attack.



12.10
12.11
12.12
12.13