

Details of Module

Subject	Chemistry
Course Name	M. Sc. Ist Semester
Paper No.	Core Course III (Organic Chemistry-I)
Module Name/Title	Aromatic electrophilic substitution (Lect.-1)
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(1)Introduction

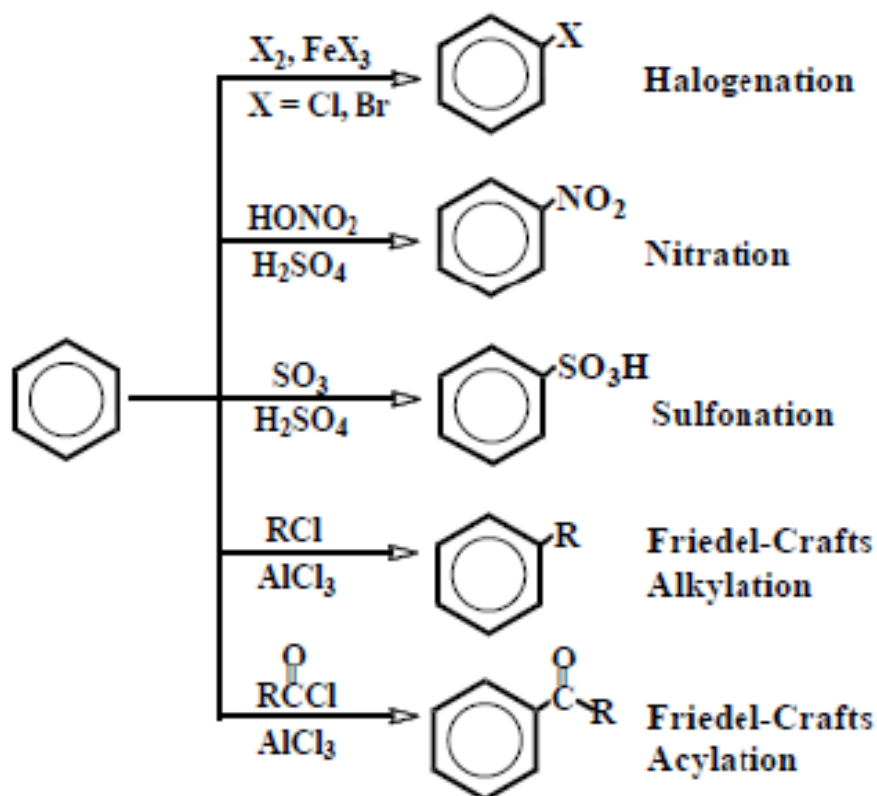
There are two main classes of aromatic substitution. One is electrophilic substitution and the other nucleophilic substitution. There are many types of aromatic systems. Among

them, the chemistry of benzene and its simple derivatives has been studied in most detail.

The attacking electrophile is a positive ion (or positive end of a dipole or induced dipole). After the reaction the “leaving group” must depart *without* its electrons. The most common departing group is the proton, H^+ .

(2) Aromatic electrophilic substitution

One of the characteristics of benzene derivatives is that they tend to undergo substitution at aromatic carbon rather than addition (to the double bonds). This property of aromatic compounds is mainly due to their ‘aromaticity’. Some common examples of electrophilic aromatic substitution reactions are shown in the given figure.



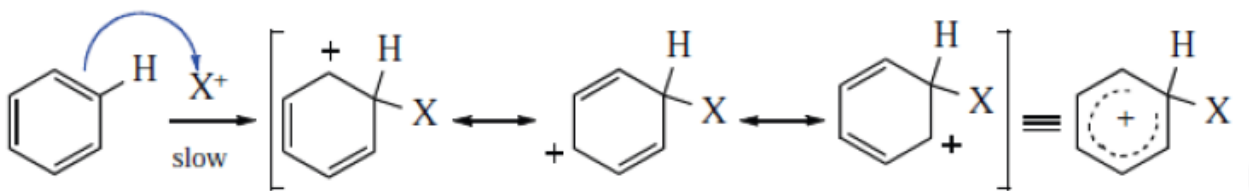
(3) Arenium ion mechanism

The mechanism of aromatic electrophilic substitution is known as the **arenium ion mechanism** and has two main steps.

Step 1:

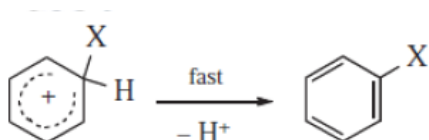
The initial step is the attack of an electrophile creating a resonance stabilized carbocation/intermediate called *arenium ion*, which is also known as the *Wheland Intermediate*. Although the *Wheland intermediate* or σ -complex or now popularly known as *arenium ion* is stabilized by resonance (with charge dispersal over the carbons *ortho* and *para* to the site of attachment of the electrophile), this step is accompanied by loss of aromaticity, so the energy of activation is high.

This is also the rate-determining step of the reaction because of the disruption of aromaticity.



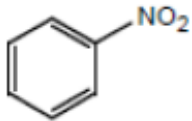
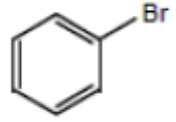
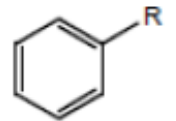
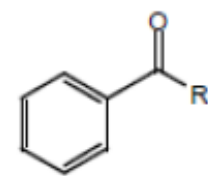
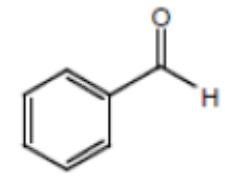
Step 2:

In the second step the leaving group departs. This leads to regeneration of aromatic stabilization. The second step is nearly always faster than the first, making the first rate determining, and the reaction is second order.



(4) Generation of Electrophiles (E⁺)

The electrophiles can be generated in various ways, examples are shown below:

Product	Electrophilic Species (boxed)	Reaction Name
	 The diagram shows the protonation of nitric acid by sulfuric acid, followed by the loss of water to form the nitronium ion (NO ₂ ⁺), which is shown in a box along with the bisulfate ion (HSO ₄ ⁻).	Nitration
	 The diagram shows the coordination of a bromine molecule to iron(III) bromide, followed by the formation of the bromonium ion (Br ⁺), which is shown in a box along with the tetrabromoferrate ion (FeBr ₄ ⁻).	Bromination
	 The diagram shows the coordination of an alkyl chloride to aluminum trichloride, followed by the formation of the alkyl cation (R ⁺), which is shown in a box along with the tetrachloroaluminate ion (AlCl ₄ ⁻).	Friedel-Crafts Alkylation
	 The diagram shows the coordination of an acyl chloride to aluminum trichloride, followed by the formation of the acylium ion (R-C ⁺ =O), which is shown in a box along with the tetrachloroaluminate ion (AlCl ₄ ⁻).	Friedel-Crafts Acylation
	 The diagram shows the reaction of N,N-dimethylformamide with phosphorus oxychloride to form the N,N-dimethyliminoyl cation (Me ₂ N ⁺ =CH-CHO), which is shown in a box along with a chloride ion (Cl ⁻).	Vilsmaier-Haack Formylation