

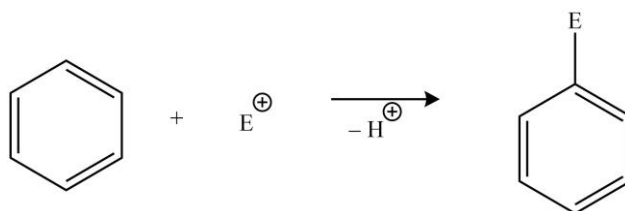
CHAPTER 8

Aromatic Electrophilic Substitution

❖ The Arenium Ion Mechanism

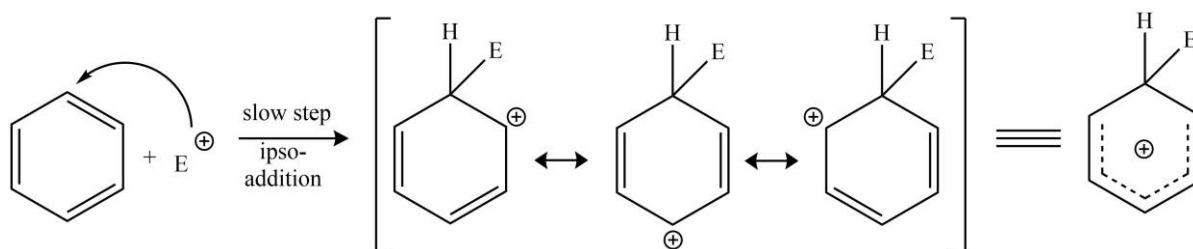
Electrophilic aromatic substitution (EAS) is the organic reaction in which an atom that is attached to an aromatic system (typically hydrogen) is replaced by an electrophile. This is quite possible in aromatic systems because there is π -electron density above and below the plane which is easily available for attacking electrophile; and nucleophilic attack is opposed because of π -cloud shields the carbon from such invasions.

Illustrative reaction: The general reaction showing the electrophilic substitution in aromatic compounds is shown below (E is electrophile).

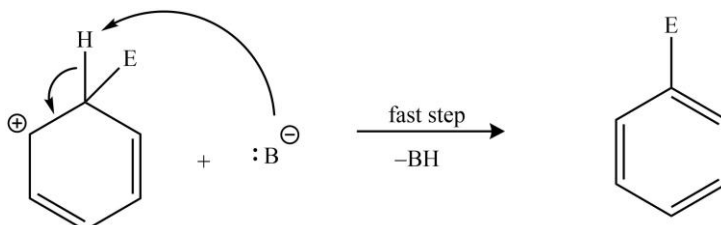


Mechanism involved: The proposed mechanism for the reaction given above involves three steps which must be discussed before we give salient features of the same.

i) *Attack of the electrophile on aromatic ring forming carbocation intermediate:* In this step, the electrophile attacks the aromatic ring to form a resonance stabilized carbocations.



iii) *Departure of the leaving group:* In this step, the leaving group detaches itself from the aromatic ring to give rise to the final product.



Salient Features: The main features of the mechanism involved in electrophilic aromatic substitution type reactions are given below.

i) The aromatic electrophilic substitution (EAS) reactions follow second-order kinetics with the rate law as given below.

$$\text{Rate} = k[\text{RX}][\text{E}]$$

Where k is the rate constant. The symbol $[\text{RX}]$ and $[\text{E}]$ represent the molar concentration of the substrate and attacking electrophiles, respectively.

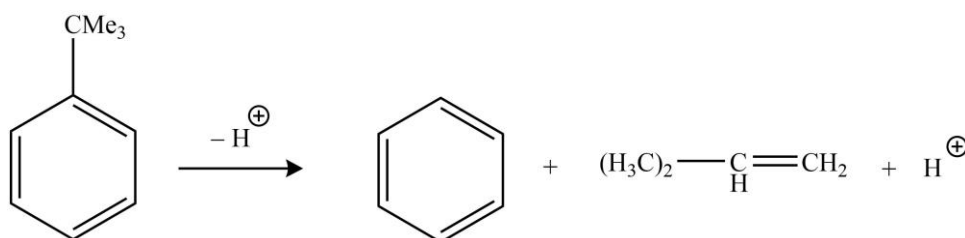
ii) The substituents like $-\text{XY}$, where X has lone pairs of electrons and no conjugated double bond in extended part (Y), increase the electron density at the ring; and therefore, are strongly activating. Furthermore, these types of groups donate those lone pair of electrons to the π -system, creating a negative charge density at para and ortho sites; and therefore, become ortho/para-directing via resonance. In other words, these groups make these positions more susceptible to an electron-deficient electrophile.

iii) The substituents like $-\text{X}=\text{Y}$, where there is conjugated double bond (w.r.t ring), decrease the electron density at the ring; and therefore, are strongly deactivating. Furthermore, these types of groups accept those electrons from the π -system, creating a positive charge density at para and ortho sites; and therefore, become meta-directing via resonance. In other words, these groups make m-positions more susceptible towards an electron-deficient electrophile.

iv) Alkyl groups as substituents increase the electron density at the ring via hyperconjugation; and therefore, are strongly activating. In other words, these groups make o- and p-positions more susceptible towards an electron-deficient electrophile.

iv) Although the halogens as substituents also have lone pairs of electrons, they decrease the electron density at the ring; and therefore, are strongly deactivating. This is because these types of groups donate those lone pair of electrons to the π -system via resonance (creating a negative charge density at para and ortho sites), but also withdraw electron density via inductive effect which is more dominant. In other words, these groups make these positions (o- and p- to the attached halogen) more susceptible towards the electron-deficient electrophile.

v) The addition of an entering group to a site in an aromatic compound that already has a substituent group (other than H), the attacking group may replace that substituent group but may also itself get expelled or moved to another position in a subsequent step, called '*ipso*-substitution'.



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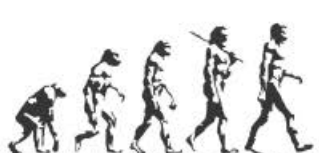
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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