

# CHAPTER 7

## Aliphatic Electrophilic Substitution

### ❖ Bimolecular Mechanisms – $SE_2$ and $SE_i$

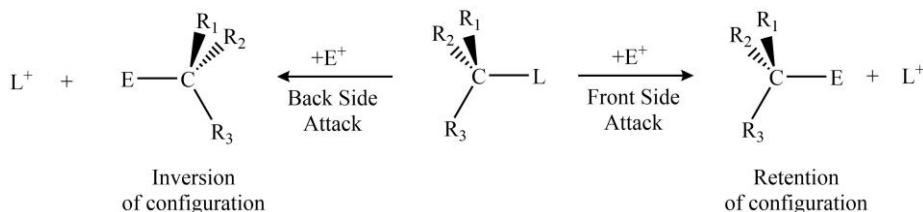
The electrophilic substitution in the aliphatic compounds is just similar to the aliphatic nucleophilic substitution, except for the fact that here an electrophile displaces a functional group rather than an electrophile. In this section, we will discuss the two major types of electrophilic substitutions;  $SE_2$  (substitution electrophilic bimolecular) and  $SE_i$  (substitution electrophilic internal) mechanisms.

#### ➤ $SE_2$ (Substitution Electrophilic Bimolecular) Mechanism

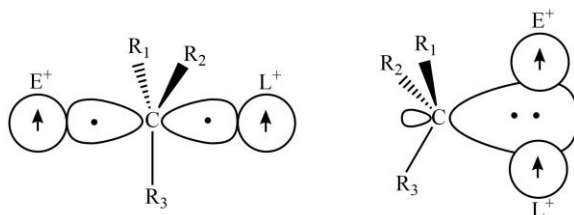
The bimolecular electrophilic substitution ( $SE_2$ ) reactions may simply be defined as the chemical changes where a stronger electrophile displaces a weaker one in an aliphatic substrate.

This mechanism is quite analogous with the  $SN_2$  route excepting the mode of attack. In the  $SN_2$  mechanism, a stronger nucleophile replaces a weaker one via the backside attack due to its inter-cloud repulsion with the leaving group; however, in the  $SE_2$  route, the attacking electrophile may come from the front, as well as from the backside because it is only using its vacant orbital towards substrates causing little to no repulsion. So, the  $SE_2$  mechanism can be divided into  $SE_2$ -front and  $SE_2$ -back based upon the front and back attacks, respectively.

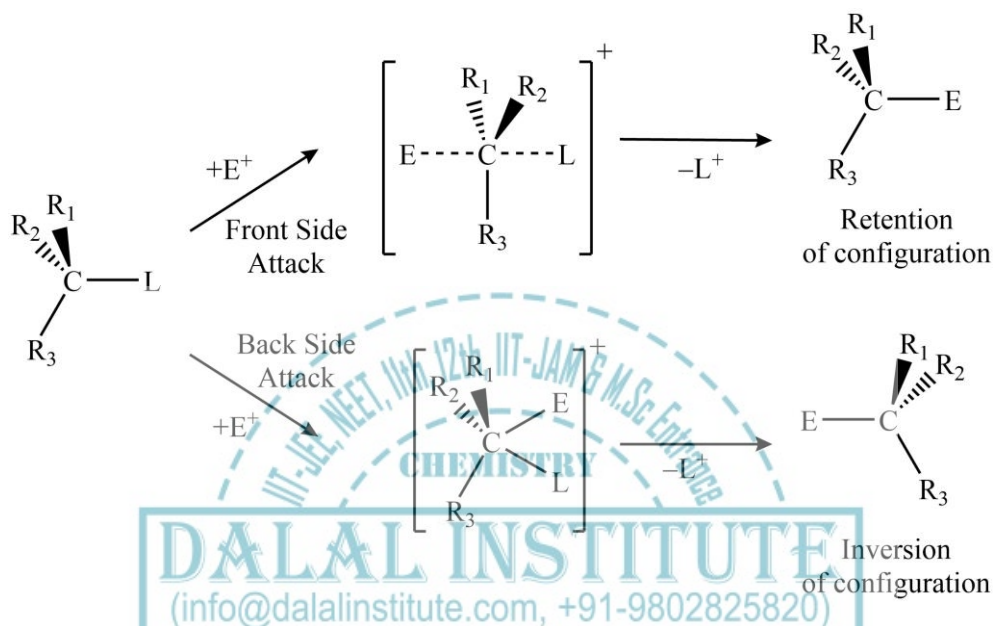
**Illustrative reaction:** The general reaction showing both types of electrophilic attacks (with their corresponding products), is shown below.



**Mechanism involved:** The proposed mechanism for the reaction given above says that the two electrons of the carbon-electrophile bond reside in the central orbital. Ingold proposed that the electronic distribution responsible for different stereochemistry of products is a function of bond-extension's magnitude and the extent of bond ionicity of the transition state.



It is obvious that the transition state needs to have high ionicity and good bond extension potential for  $SE_2$ -back reactions so that the carbon's orbital is sufficiently spread on both ends, resulting in the inverted configuration in the case of a chiral substrate. On the other hand, if there is a very little bond extension and low ionicity in the transition state, the electron-pair of the original bond pretty much retains its position and gives rise to the retention of the configuration, and we get  $SE_2$ -front case.



Where  $E^+$  is the attacking electrophile whereas  $L^+$  is the leaving group. Furthermore, it is also worthy to note that organometallic compounds have exceptional susceptibility towards electrophilic substitution.

**Salient Features:** The main features of the mechanism involved in electrophilic substitution bimolecular or  $SE_2$  type reactions are given below.

i)  $SE_2$  reactions follow second-order kinetics with the rate law

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

Where  $k$  is the rate constant. The symbol  $[RX]$  and  $[E]$  represent the molar concentration of the substrate and attacking electrophile, respectively.

ii) If the substrate is chiral, then the  $SE_2$  mechanism can lead to the inversion, as well as, retention of the configuration; depending upon the mode of attack (front or back).

iii) The rate of the substitution becomes independent of the concentration of the attacking electrophile if its concentration is extremely high in comparison to the substrate.

iv) Stereochemical studies can be employed to differentiate between  $SE_2$ -front and  $SE_2$ -back.

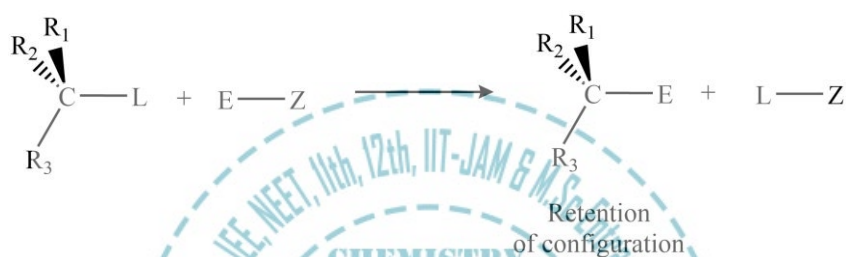
v) The  $SE_2$  reactions are favored by the more polar  $C-L$  bond.

➤ **SE<sub>i</sub> (Substitution Electrophilic Internal) Mechanism**

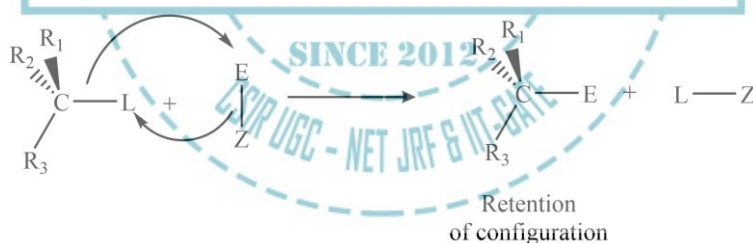
The internal electrophilic substitution (SE<sub>i</sub>) reactions may simply be defined as the chemical changes where a stronger electrophile displaces a weaker one in an aliphatic substrate by assisting its departure.

This mechanism is also very analogous with the SN<sub>2</sub> route excepting the mode of attack. In the SN<sub>2</sub> mechanism, a stronger nucleophile replaces a weaker one via the backside attack due to its inter-cloud repulsion with the leaving group; however, in the SE<sub>i</sub> route, the attacking electrophile comes from the front and assists the departure of leaving group by forming a bond with it.

**Illustrative reaction:** The general reaction showing this type of electrophilic attack (with the corresponding product) is shown below.



**Mechanism involved:** The proposed mechanism for the reaction given above says that the two electrons of the carbon-electrophile bond reside in the central orbital. It is observed that if there is a very little bond extension and low ionicity in the transition state, the electron-pair of the original bond pretty much retains its position and gives rise to the retention of the configuration, and we get SE<sub>i</sub> case (like SE<sub>2</sub>-front).



**Salient Features:** The main features of the mechanism involved in electrophilic substitution internal or SE<sub>i</sub> type reactions are given below.

i) SE<sub>i</sub> reactions follow second-order kinetics with the rate law

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

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

ii) Like SE<sub>2</sub>-front, SE<sub>i</sub> reactions result in the retention of the configuration.

iii) The SE<sub>2</sub> reactions are favored by the more polar C-L bond.

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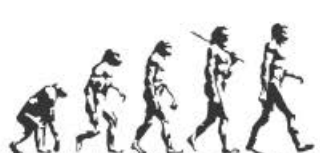
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