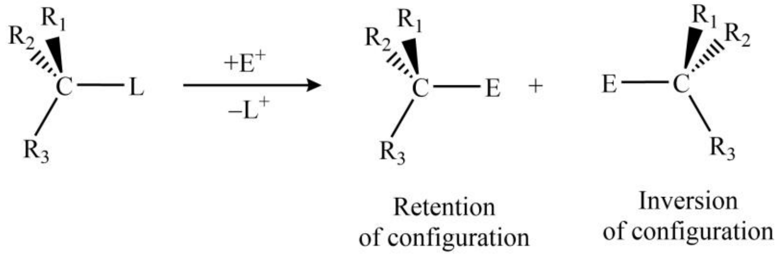
❖ The SE$_1$ Mechanism

The unimolecular electrophilic substitution (SE$_1$) reactions may simply be defined as the chemical change in which a stronger electrophile displaces a weaker one in an aliphatic substrate via the formation of a carbanion.

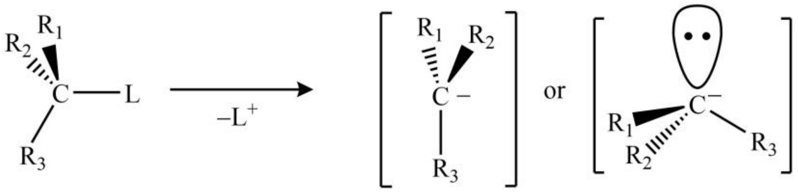
This mechanism is quite analogous with the SN$_1$ route excepting the nature of intermediate. In the SN$_1$ mechanism, a stronger nucleophile replaces a weaker one via the formation of a carbocation intermediate; however, in the SE$_1$ route, before the attacking electrophile attack, the intermediate formed after the dissociation of electrofuge is a carbanion.

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

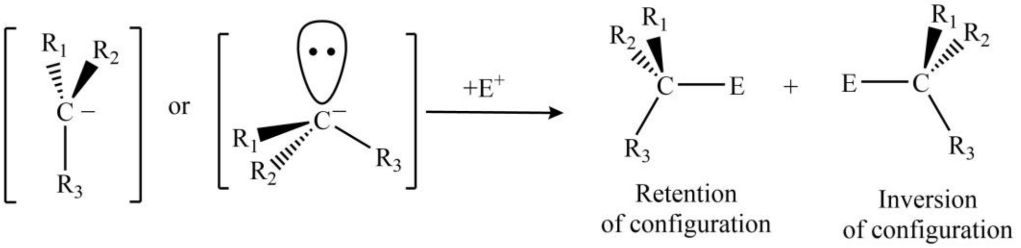


Mechanism involved: The proposed mechanism for the reaction given above involves a three-step route which must be discussed before we give the salient features of the same.

i) Heterolysis in substrate: This is the slowest, and therefore, is the rate-determining step that gives rise to a carbanion.



ii) Electrophilic attack: This is a very fast step and involves the combination of attacking electrophile with the carbanion produced in the previous step.



The stereochemistry of SE_1 reactions is quite complicated to rationalize because of the configuration of intermediatory carbanions obtained via the first step of heterolysis. Generally, we consider carbanions planar (*sp*^{2} hybridization) or pyramidal (*sp*^{3} hybridization), or an in-between configuration. As far as the energy is concerned, pyramidal geometry is more advantageous because lone pair will stay in *sp*^{3} hybridized orbital. Furthermore, a pyramidal carbanion can retain its structure in the course of substitution to result in the retention of the final configuration. However, it does not always go this way because a pyramidal carbanion has been shown to results in racemization due to 'pyramidal inversion'; amines and R_3C^- carbanions are typical examples.

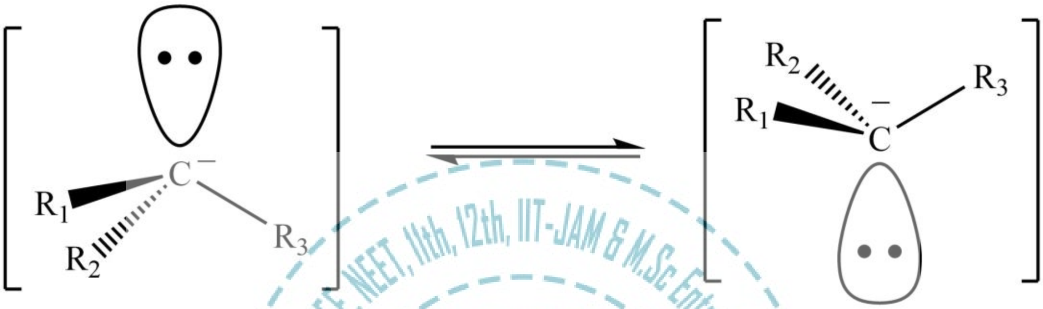


Figure 1. The pyramidal inversion of carbanion.

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On the other hand, if the carbanion is of trigonal planar geometry, the electrophile can attack from both sides to give rise to racemized yield. So, we can conclude that racemization is the characteristic feature of the SE_1 route. However, it is quite tedious to determine how the racemization actually occurred; via pyramidal inversion or planar carbanions.

Salient Features: The main features of the mechanism involved in electrophilic substitution unimolecular or SE_1 type reactions are given below.

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

$$Rate = k[RX]$$

Where *k* is the rate constant. The symbol $[RX]$ represents the molar concentration of the substrate.

ii) If the substrate is chiral, then this always leads to the racemization of the final product.

iii) Unlike SN_1-type, SE_1 reaction can also occur at bridgehead carbon because the intermediate (carbanion in this case) need not to be planar.

iv) The rate of the substitution increases as the steric bulk around the carbon center decreases.

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

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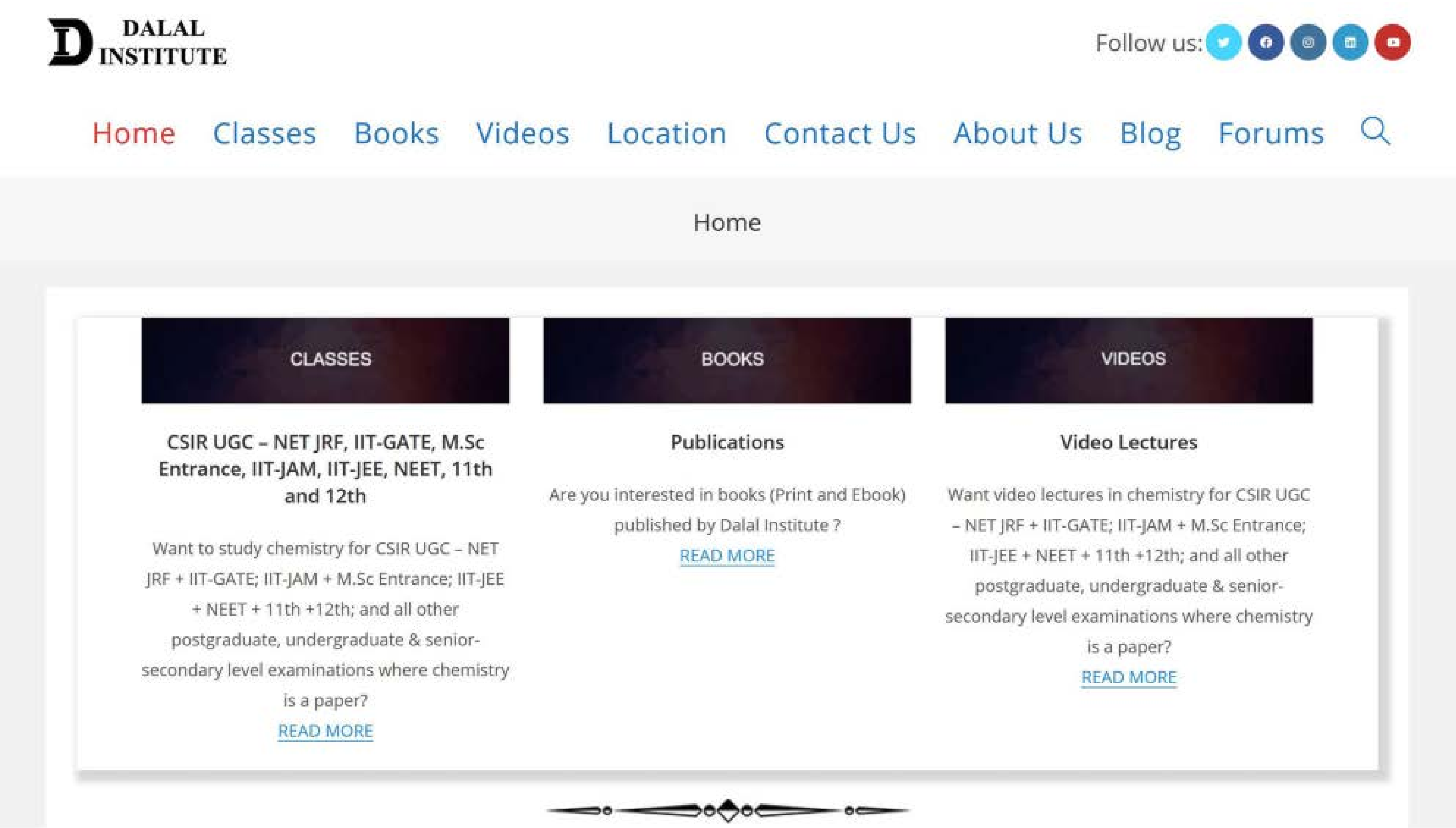

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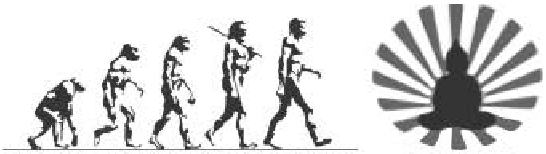

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