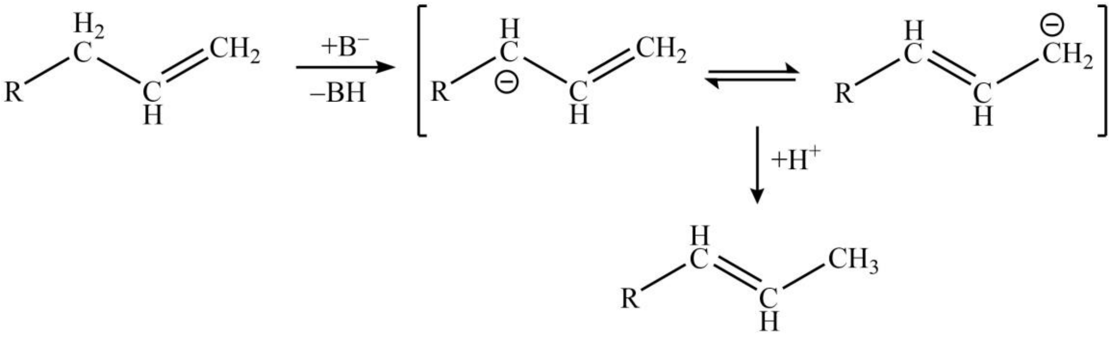
❖ Electrophilic Substitution Accompanied by Double Bond Shifts

If the substrate in electrophilic substitution is allylic in nature, the final product may undergo rearrangement, which is quite similar to the allylic rearrangements in nucleophilic substitutions. There are two main routes for this behavior to occur; one is analogous to the SE_1 pathway (leaving group is detached first) giving a resonance-stabilized allylic carbanion which attacks the electrophile E, the second one involves the initial attack on E by the π-bond to yield a carbocation which then which loses X forming new alkene unit.

➢ *Base-catalyzed Double Bond Migration*

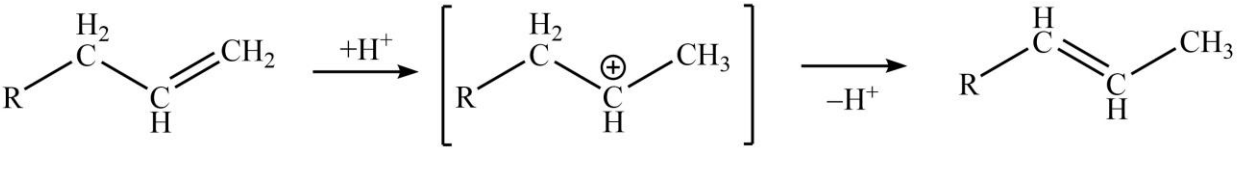
The first pathway is the base-catalyzed double bond migration, where an equilibrium mixture of isomers is obtained with stable configuration as the major product. The reaction occurs in two steps, in which the step is the abstraction of a proton by the base to yield a resonance stabilized carbanion, which in turn, is attacked by electrophile (proton in this case) to give rise to a more stable species. The typical reaction portraying mechanism is given below.



It is also worthy to note that terminal and non-conjugated alkenes can easily be converted into internal and conjugated olefins using this route, proving its significance in synthetic organic chemistry.

➢ *Acid-catalyzed Double Bond Migration*

The second pathway is the acid-catalyzed double bond migration, where an equilibrium mixture of isomers is obtained with a stable configuration as the major product. The reaction initiates with the attack of E on the π-bond to yield a carbocation which then loses L forming a new alkene unit. The typical reaction portraying mechanism is given below.



Just like base-catalyzed double bond migration, this route can also be used to convert terminal and non-conjugated alkenes into internal and conjugated olefins.

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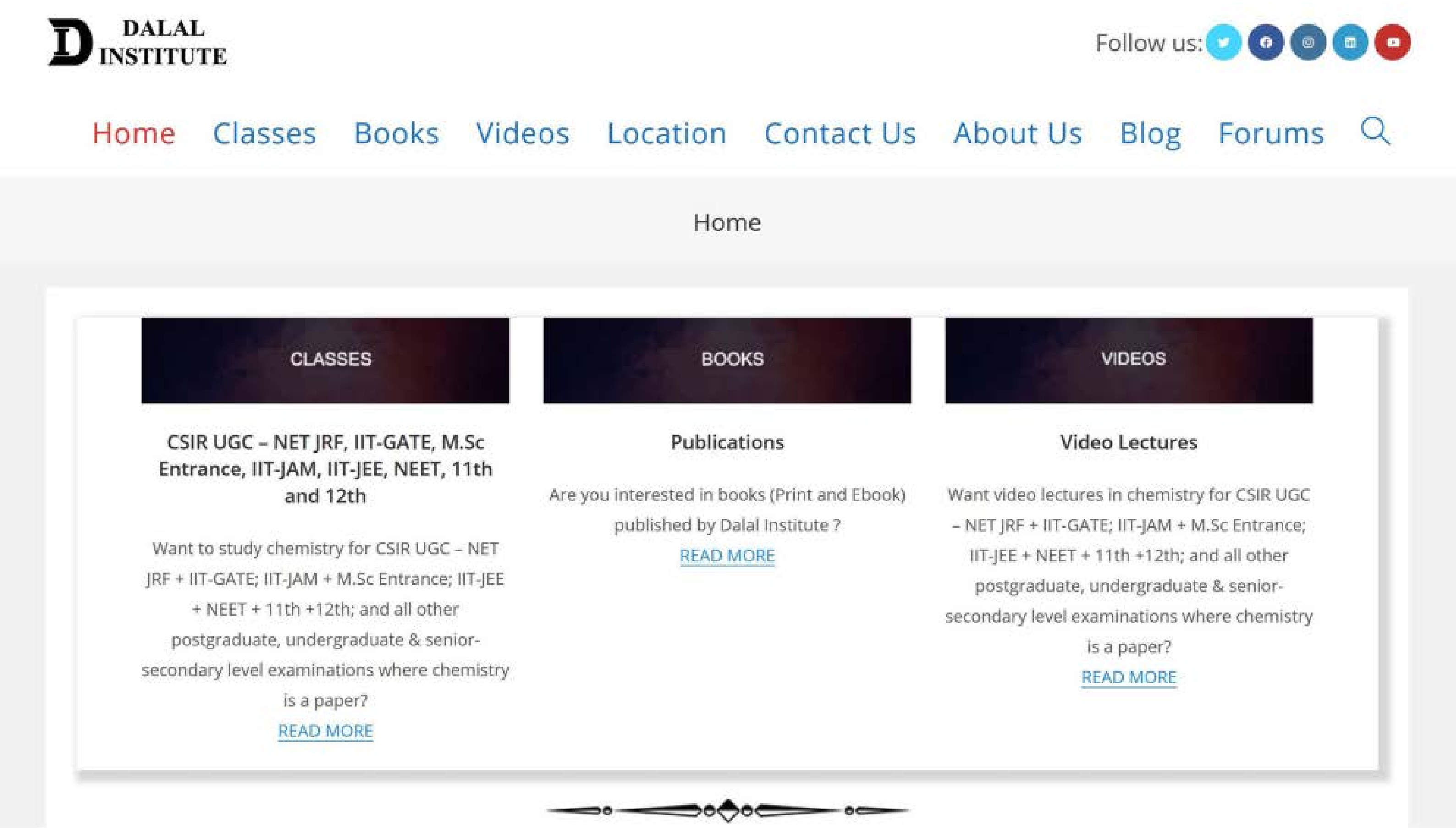

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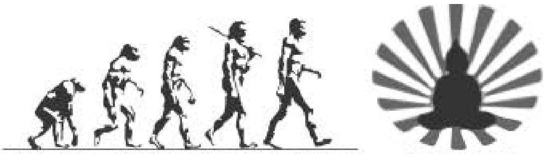

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