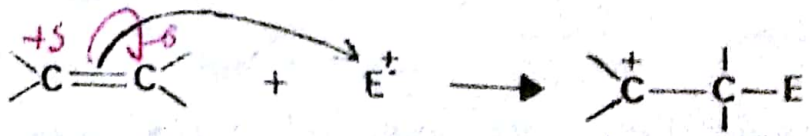
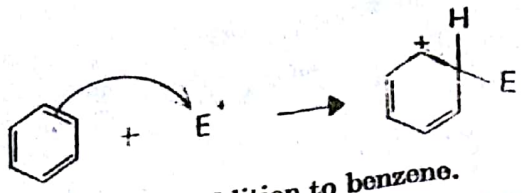
Question 13. Explain why benzene undergoes electrophilic substitution reactions whereas alkenes undergo addition reactions.

(Aligarh BSc, 1980 ; Panjab BSc, 1980 ; Punjabi BSc, 1980 : Osmania BSc, 1981 ; Bangalore BSc, 1982 ; Aligarh BSc 1982)

ANSWER. Benzene and alkenes are susceptible to electrophilic attack because of their exposed π electrons. The first step in both is the additon of an electrophile to an unsaturated carbon to give a carbonium ion.

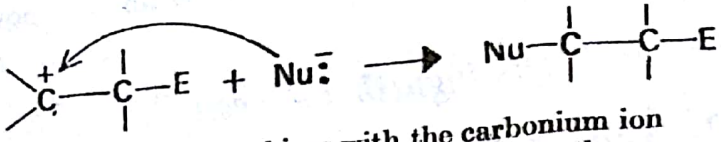


Electrophilic additioon to an alkene



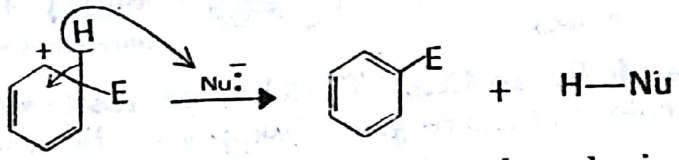
Electrophilic addition to benzene.

But similarity ends at this point. The carbonium ion produced from the alkene usually combines with a nucleophile to give the overall addition product.



Nucleophile combines with the carbonium ion intermediate from an alkene to give the addition product.

If this happend to benzene, the product would no longer be aromatic. The special stabilising energy (resonance energy) of benzene would be lost. Instead, the nucleophile removes a proton from the carbonium ion intermediate. The loss of proton allows the electrons from the C—H bond to go back into the ring and reproduce the aromatic system. Net change is the replacement of a hydrogen by an electrophile.



Nucleophile removes a proton from the carbonium ion intermediate from benzene to give the substitution product.

Question 14. Give the general mechanism of electrophilic aromatic substitution.

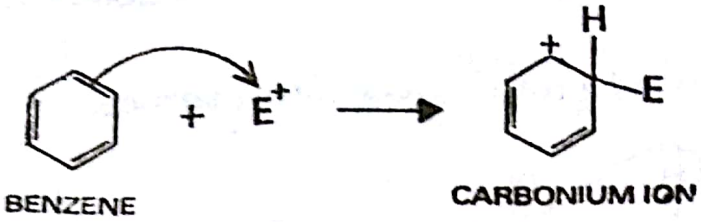
(*Annamalai BSc, 1980 ; Banaras BSc, 1980 ; Jammu BSc, 1980 ; Madurai BSc, 1980 ; Delhi BSc, 1981 ; Jabalpur BSc, 1981 ; Madras BSc, 1981 ; Rajasthan BSc, 1981 ; Saugar BSc, 1981 ; Andhra BSc, 1982 ; Burdwan BSc, 1982 ; Jabalpur BSc, 1982 ; Panjab BSc, 1982 ; Shivaji BSc, 1982*)

ANSWER. The electrophilic aromatic substitution reactions involve the replacement of a hydrogen on an aromatic ring with an electrophile.

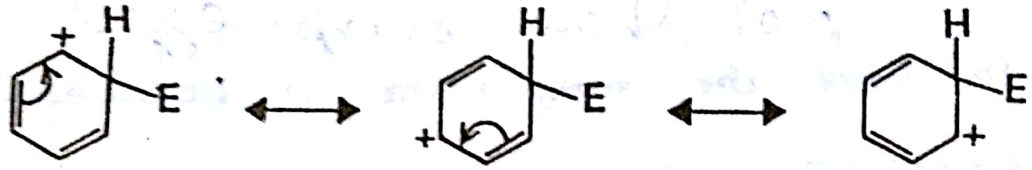
All electrophilic substitution reactions follow the same three-step mechanism :

Step 1. Formation of an electrophile.

Step 2. The electrophile attacks the aromatic ring to give a carbonium ion.



Note. The intermediate carbonium ion is resonance stabilised. It is a hybrid of the following structures :



Step 3. Removal of proton gives the product.