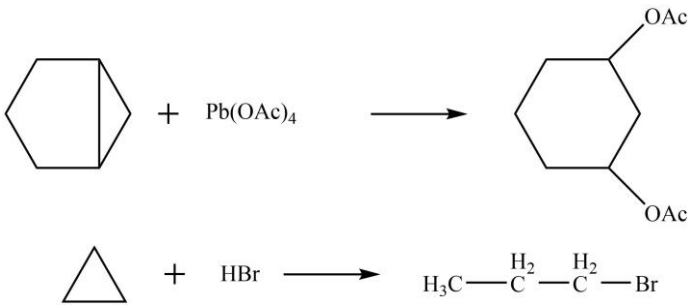
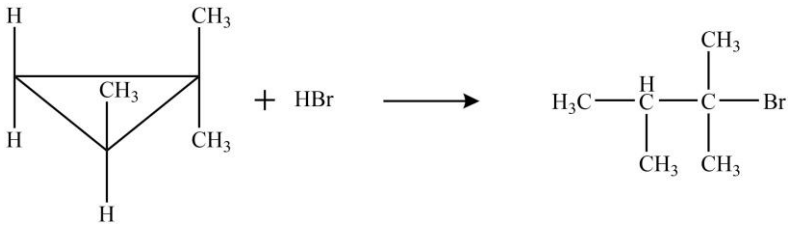
❖ Addition to Cyclopropane Ring

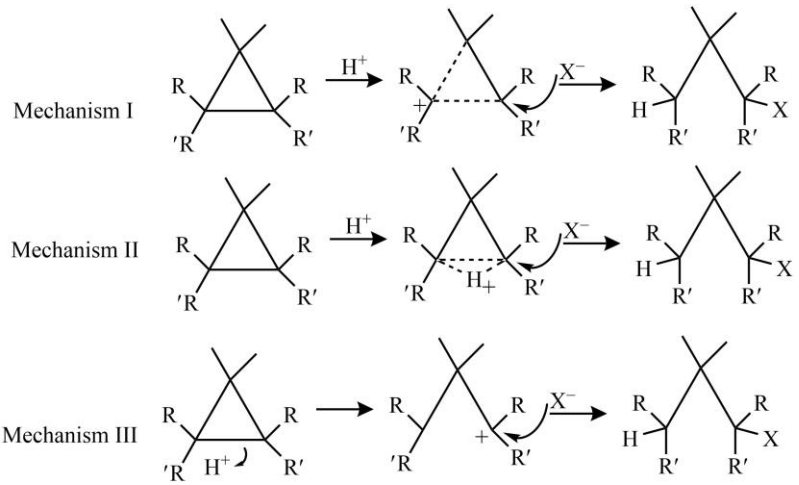
It is quite a well-known fact that cyclopropane rings behave in a similar manner as double bonds as far the reactivity is concerned. Therefore, like carbon-carbon multiple bonds, the cyclopropane ring can also undergo addition giving rise to open chain products as shown below.



Now although the attack at cyclopropanes can occur via polar as well as non-polar additions, the electrophile type is the most important to discuss. The final product of electrophilic addition to substituted cyclopropanes is primarily dictated by Markovnikov's rule with rare exceptions.



The stereochemical configuration of the final product can be analyzed in terms of the electrophilic as well as nucleophilic part of the attacking reagent. The electrophilic position can give rise to retention, inversion, or a mixture of two; whereas the nucleophilic position almost always gives rise to inversion. Three primary mechanisms that the electrophilic addition can adapt are given below.



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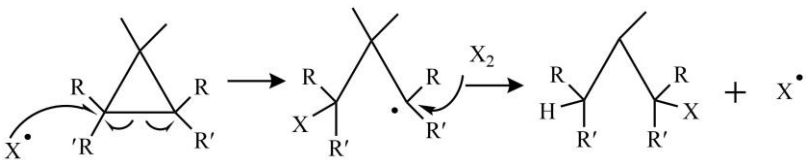
It is obvious that a cyclopropane ring system with one cornered carbon protonated is involved in the first mechanism; for instance, 7-norbornenyl and 2-norbornyl cations. On the other hand, the cyclopropane ring system with one protonate edge is involved in the second mechanism. The third mechanism involves an SE_2 type attack of H^+ to result in a classical cation, which subsequently reacts with the nucleophilic part of the attacking regent. It is also important to recall the fact that despite the depiction of configuration retention at carbon in all three cases, the 1st and 3rd routes are capable of giving inversion also. Since the cherry-picking of the mechanisms is not always possible, all or some of the cases take place at the same time. It has been found that Br^+ and Cl^+ react primarily via the second pathway; whereas D+ and Hg^{2+} react via the first pathway. Furthermore, density functional analysis has shown that edge-protonated is less stable than the corner-protonated; and the third pathway is usually opposed or less favorable. The reagents like Br_2 and Cl_2 can add to cyclopropanes via the free radical pathway (according to Markovnikov's rule) when the sample is irradiated with ultra-violet light. These free radical additions are stereospecific w.r.t only one carbon as shown below.



The addition to the cyclopropane ring may also occur in conjugated mode if the cyclopropyl ring is conjugated with a multiple bond.

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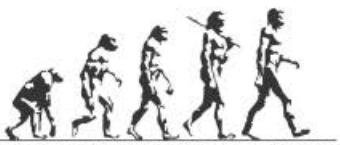

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ISBN: 978-81-952427-3-3

MRP: Rs 800.00

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