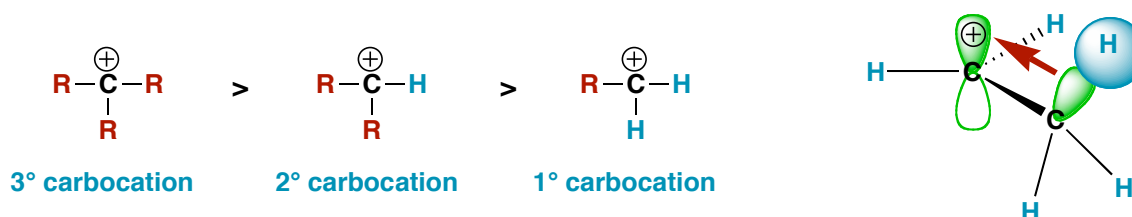


Chapter 6 - Alkenes: Structure and Reactivity

Carbocation Stability

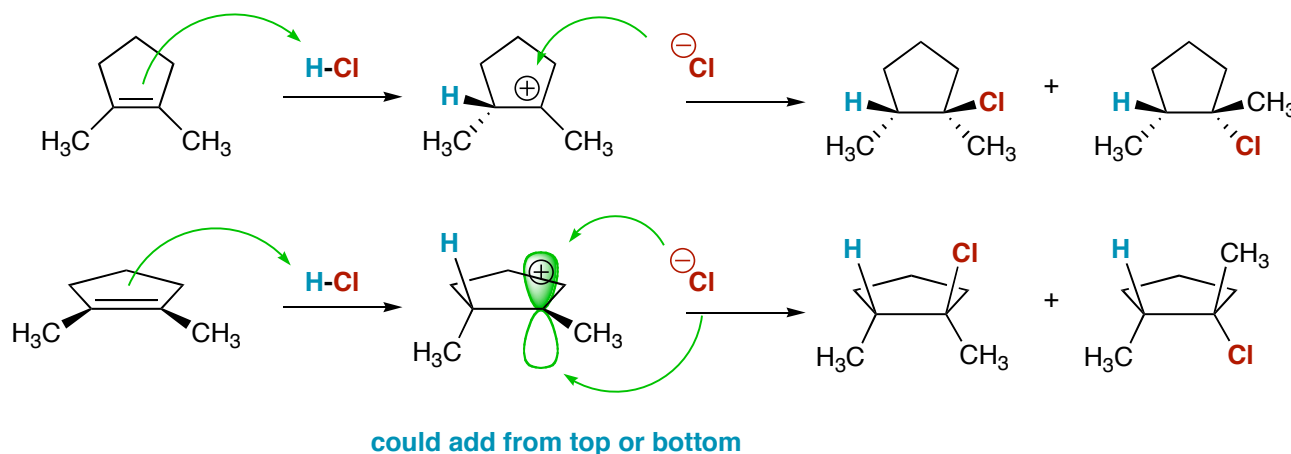
Hyperconjugation of adjacent sigma bonds also helps to stabilize a carbocation because the electron density of the bond is donating into the empty orbital. Thus, similar to alkenes, carbocations are more stable with more alkyl groups attached. A tertiary carbocation is more stable than a secondary carbocation which is more stable than a primary carbocation.



Electrophilic Addition of HX to Alkenes

Carbocation stability has a direct influence on the energy of the intermediate in the electrophilic addition of HX to alkenes. That is because the transition state resembles the structure of the carbocation intermediate (the Hammond Postulate). Thus, the more stable intermediate can be formed by a lower energy pathway than the less stable intermediate.

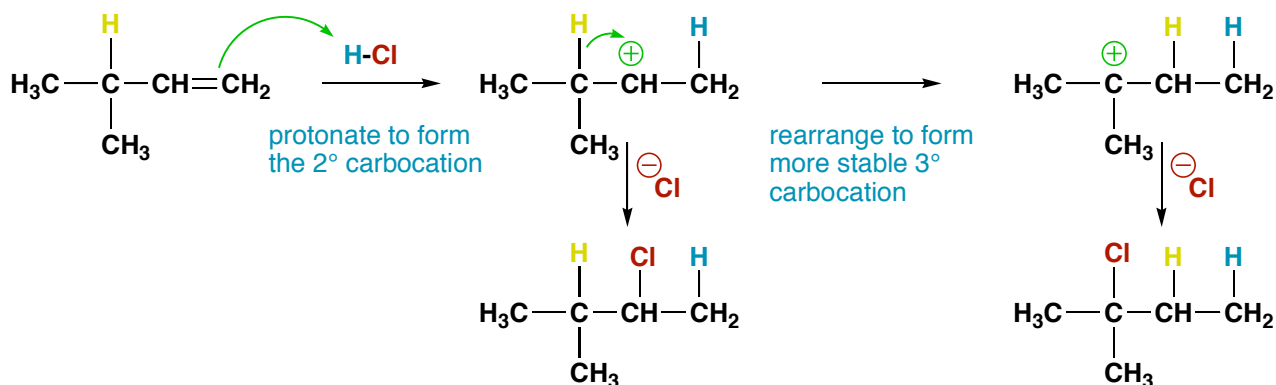
In the case of cycloalkenes, there are cases where more than one stereoisomer may be formed. These reactions are not selective due to the carbocation intermediate being sp^2 -hybridized and planar. That is, the halide can form a bond from either the top or the bottom face of the ring.



Carbocation Rearrangements

Evidence for carbocation intermediates in the electrophilic addition to alkenes is found in the fact that products of rearrangements are obtained. Hydrogen (with its electrons) or even methyl groups and other carbon groups can move one position over to an adjacent empty orbital. This shifts the carbocation to the position the migrating group just left. Carbocations will rearrange IF they form more stable carbocations in the process. For example, the 2° carbocation shown below

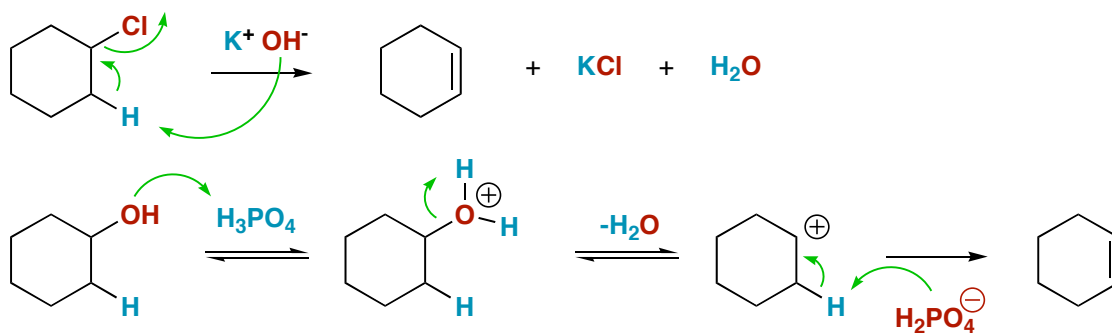
will rearrange to the more stable 3° carbocation by shifting a hydrogen over one position. In the reaction of 2-methyl-1-butene with HCl, a mixture of products is obtained.



Chapter 7 - Alkenes: Reactions and Synthesis

Preparation of Alkenes

Alkenes are most commonly prepared by elimination reactions. Note that these are the opposite of additions reactions. For example, a halogenated alkane will undergo a dehydrohalogenation reaction in the presence of a good base. Alcohols, in the presence of a strong acid, will also undergo a stepwise elimination of water (dehydration) to produce an alkene.



Electrophilic Addition of X₂ to Alkenes

Alkenes will react with many different electrophiles. Molecular bromine, chlorine or iodine is no different. You can think of these reagents as equivalent to an X⁺ and an X⁻. Unlike the addition of HX, the halogens have the ability to share one of their lone pairs to form a bridged halonium intermediate. This is more stable than a carbocation intermediate. The result of this is that one face of a ring is blocked, so the second halide addition step can only occur trans to the first halogen.

