CHAPTER 6

♦ The addition of H-X to an alkene is regiospecific

♦ Markovnikov's Rule - In the addition of H-X to a double bond, the H attaches to the carbon with less alkyl substituents and the X attaches to the carbon with more alkyl substituents

♦ Stated another way, the electrophile adds to the double bond to form the most stable carbocation intermediate

♦ Carbocations are more stable with more alkyl groups attached - tertiary carbocations are more stable than secondary, which are more stable than primary, which are more stable than methyl carbocations

♦ Hammond Postulate - The structure of the transition state will resemble the structure of the closest stable species - for an endergonic reaction, the TS resembles the product, and for an exergonic reaction, the TS resembles the starting material - for electrophilic addition to alkenes, the first step forms a carbocation and the TS resembles the carbocation - therefore, more stable carbocations will be formed faster

♦ Carbocations can rearrange IF they form more stable carbocations - neighboring H's and methyl's will migrate. Occasionally larger alkyl groups migrate, but this is not common. Hydrogens will always migrate in preference to an alkyl group – so, methyl will only move if there are no H’s that can move.
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\[ \text{CH}_3\text{C-CH=CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{C-CH-CH}_2 + \text{CH}_3\text{C-CH-CH}_2 \]

- a 2º carbocation
- a 3º carbocation

♦ Carbocations are planar and lead to a mixture of stereoisomers if possible

\[ \text{CH}_3\text{C-CH=CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{C-CH-CH}_2 + \text{CH}_3\text{C-CH-CH}_2 \]

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