Chapter 7 - Alkenes: Reactions and Synthesis

Electrophilic Addition of Halogen and Water - Halohydrin Formation

When alkenes are presented with both an electrophilic bromine source AND water, the water will react in the second step to form a bromohydrin. You can do this with BR$_2$ or with NBS as the electrophilic bromine source. Note that even with the bridges species, the reaction occurs with Markovnikov selectivity placing the nucleophile (water) on the more substituted carbon.

\[
\begin{align*}
\text{Br-Br} & \quad \text{or NBS} \\
\rightarrow & \\
\text{H}_2\text{O} & \\
\text{H}_2\text{O} & \\
\end{align*}
\]

Hydration of Alkenes

The electrophilic addition of water to a double bond is a more difficult reaction than halohydrin formation. By itself, water is not electrophilic enough to react and it requires a strong acid catalyst and high heat.

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \\
\rightarrow & \\
\text{H}_2\text{O} & \\
250^\circ\text{C} & \\
\end{align*}
\]

A milder method to accomplish the Markovnikov addition of water is to use a mercury salt to promote the reaction. This will add at room temperature to form an oxymercuration product and the mercury is exchanged for H in a second step using sodium borohydride. Note that, unlike H$^+$ catalyzed addition that goes through a carbocation, the mercury salt can bridge like the bromonium systems and control a selective trans addition.

\[
\begin{align*}
\text{Hg(OAc)}_2 & \\
\rightarrow & \\
\text{H}_2\text{O} & \\
25^\circ\text{C} \text{ room temp} & \\
\end{align*}
\]
Note that, unlike $H^+$ catalyzed addition that goes through a carbocation, the mercury salt can bridge like the bromonium systems and control a selective trans addition.

Anti-Markovnikov hydration of double bonds can be accomplished using borane as a reagent. The hydroboration reaction places the boron and hydrogen onto the double bond at the same time, thus they must add on the same side. This is a cis addition. Also, the boron ends up on the least substituted carbon and they hydride on the most substituted carbon. The boron can be oxidized to an alcohol upon basic hydrogen peroxide treatment.