Chapter 7 - Alkenes: Reactions and Synthesis

Addition of Carbenes

Carbenes are highly reactive intermediates that have an electron deficient carbon. The carbon contains a lone pair of electrons as well as an empty orbital. Overall, the formal charge is neutral, however, carbenes do not have an octet and are reactive with alkenes. Shown below are a couple of useful methods to prepare carbenes. The first takes chloroform (trichloromethane) and a strong base to affect overall the elimination of H and Cl to form dichlorocarbene. The second method utilizes Zn to carry out overall an elimination of I and I from a carbon. Carbenes have dual reactivity and will form two bonds at once when presented with an alkene. In this way, cyclopropane structures are formed.

Oxidation States of Organic Molecules

Organic chemists think about oxidation states a little bit differently. Classically, the oxidation of an element occurs when it gives up an electron and becomes an ion. Since carbon molecules have mostly covalent bonds, we need to think about oxidation states a little bit more broadly. We think about a higher oxidized carbon as one that has more bonds to atoms that are more electronegative than it. Thus, in the chart below, methane would have the lowest oxidation state while carbon dioxide would be the highest. When we call a reaction an oxidation, we are increasing the bonds to more electronegative atoms, and when we use the word reduction, we are decreasing them. In other words, we are increasing or decreasing carbon’s ownership of the shared electrons.
Hydrogenation of Alkenes (Reduction)

Alkenes can be reduced with hydrogen gas with the aid of a transition metal catalyst, usually Pd but sometimes, Pt, Rh, Ru, etc. These catalysts are placed on some type of solid support, often carbon (graphite). Hydrogenation of double bonds occurs stereospecifically to give cis addition products.

The catalyst activates hydrogen gas by splitting the H-H bond. It then transfers the H's to the alkene and this regenerates the metal catalyst to activate more hydrogen.

CIS addition of H₂

Oxidation of Alkenes

There are several oxidizing agents that will oxidize alkenes to varying levels of oxidation states. The addition of two oxygens to a double bond can be accomplished with osmium tetroxide. The result is the formation of a 1,2-diol. This reaction is stereospecific to give the cis product. Note that sodium bisulfite is required to break down the intermediate osmium complex.

[Diagram showing oxidation of alkenes with OsO₄ and NaHSO₃]
1,2-Diols are useful and can be further oxidized with periodic acid. This results in cleaving the carbon-carbon bond between the two alcohols and forming aldehydes on the end.

\[ \text{HIO}_4 \rightarrow \text{carbon-carbon bond broken} \]

The cleavage of a carbon-carbon bond is useful for breaking apart molecules. A more straightforward method exists to break a double bond directly to give carbonyl functional groups on either end. This reaction involves the highly reactive ozone molecule. This reaction forms intermediates that must be broken down with zinc in acetic acid.

Potassium permanganate is one of the strongest oxidizing agents. Not only will it cleave apart a carbon-carbon double bond, but it will continue to oxidize any bonds to hydrogens that were present on the alkene carbons. Note that if there are no hydrogens, a ketone is produced, if one hydrogen, it will form a carboxylic acid, and if the alkene is terminal, possessing two hydrogens, it will become carbon dioxide.