When a stepwise ionic addition reaction involves nucleophilic attack at carbon as a first step, it is described as a nucleophilic addition. Reactions of this type often are catalyzed by bases, which generate the required nucleophile. For example, consider the addition of some weakly acidic reagent \(\ce{HX}\) to an alkene. In the presence of a strong base \(\left( ^{-}\ce{OH} \right)\), \(\ce{HX}\) could give up its proton to form the conjugate base \(\ce{X}^{-}\), which is expected to be a much better nucleophile than \(\ce{HX}\):

\[
\ce{H\cdot\cdot\cdotX + ^{-}\ce{OH} \rightleftharpoons H_2O + \cdot\cdot\cdotX^{-}}
\]

What can follow with an alkene is an ionic chain reaction with the following two propagating steps. First, the nucleophile attacks at carbon to form a carbon anion (carbanion) intermediate (Equation 10-8). Second, electrophilic transfer of a proton from \(\ce{HX}\) to the carbanion forms the adduct and regenerates the nucleophile (Equation 10-9). The overall reaction is the addition of \(\ce{HX}\) to the double bond:

\[
\begin{align*}
\ce{X: + C\equiv C \rightarrow C\cdot\cdot\cdotX} & \quad \text{(10-8)} \\
\ce{C\cdot\cdot\cdotX + H: \rightarrow C\cdot\cdot\cdotX + \cdot\cdot\cdotX:} & \quad \text{(10-9)}
\end{align*}
\]

Net reaction:

\[
\ce{HX + C\equiv C \rightarrow C\cdot\cdot\cdotX}
\]

The \(\ce{HX}\) reagent can be water, an alcohol \(\left( \text{ROH} \right)\), a thiol \(\left( \text{RSH} \right)\), an amine \(\left( \text{RNH}_2 \right)\), or hydrogen cyanide \(\left( \text{HCN} \right)\) or other carbon acids (i.e., compounds with acidic \(\ce{C-H}\) bonds). However, nucleophilic addition of these reagents to simple alkenes rarely is encountered. To have nucleophilic addition the double bond must be substituted with strongly electron-withdrawing groups such as carbonyl-containing groups, \(\left( \text{NO}_2 \right)\), \(\left( \text{C \equiv N} \right)\), or positively charged ammonium or sulfonium groups. However, alkynes generally are more reactive towards nucleophiles than they are toward electrophiles. For example, with a base catalyst, 2-hexen-4-yne adds methanol across the triple bond, leaving the double bond untouched:

\[
\text{CH}_2\text{C\equiv C\equiv C\text{CH}_3 + CH}_3\text{OH }\xrightarrow{\text{KOH}} \text{CH}_2\text{C\equiv C\equiv C\equiv CH}_3
\]

(Nonetheless, the double bond seems to be necessary because a corresponding addition is not observed for 2-butyne, \(\left( \text{CH}_3\text{C \equiv C\equiv C\equiv Spike}_3 \right)\)).

Many nucleophilic addition reactions have considerable synthetic value, particularly those involving addition of carbon acids, such as \(\ce{HCN}\), because they provide ways of forming carbon-carbon bonds. More of their utility will be discussed in Chapters 14, 17, and 18.
References