Electrophilic addition to alkynes

The triple bond in an alkyne reacts in the same way as the double bond in an alkene. Each “multiple bond” (that is, each bond “more than single”) can undergo electrophilic addition reactions.

What trends do we observe in the reactions below?

The third bond in an alkyne is more reactive than the “extra” bond in an alkene, so that halogenation and hydrohalogenation reactions of alkynes can be stopped at a single addition if the reaction is performed with care.

In the same way, water can be added across a triple bond just as with a double bond (a hydration reaction). Since the triple bond is more sensitive, slightly different conditions must be used:

What product do you expect?
Here’s the actual product:

\[
\begin{align*}
\text{R} & - \text{C} & \text{CH} & \xrightarrow{\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}} & \text{R} & - \text{C} & \text{O} & \text{CH}_3 \\
\text{R} & - \text{C} & \text{C} & \text{CH} & \xrightarrow{\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}} & \text{R} & - \text{C} & \text{OH} & \text{CH}_2 \\
\end{align*}
\]

The product differs from the expected product not because it is something totally new, but because of a phenomenon known as tautomerism. Tautomers are isomers that interconvert so rapidly that only the more stable one can be isolated. Carbonyl groups with hydrogen atoms \( \alpha \) to the carbonyl groups are in equilibrium with their enols; the carbonyl isomer is called the keto form of the enol. Under most circumstances, the keto form is far more stable than the enol.

In the mercury-catalyzed hydration of an alkyne, the product is an enol – but the enol is swiftly converted into its keto tautomer:

\[
\begin{align*}
\text{R} & - \text{C} & \text{C} & \text{CH} & \xrightarrow{\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}} & \text{R} & - \text{C} & \text{K} & \text{OH} & \text{CH}_2 & \xrightarrow{\bigcirc} & \text{R} & - \text{C} & \text{O} & \text{CH}_3 \\
\end{align*}
\]

The brackets mean an intermediate that’s not isolated; the “arrow with a circle” means a rearrangement.

*Under strong acid conditions, what is the mechanism of the conversion of an enol to its keto form?*

Also like alkenes, alkynes can undergo hydroboration to form the anti-Markovnikov hydration product:

\[
\begin{align*}
\text{R} & - \text{C} & \text{CH}_2 & \xrightarrow{\text{BH}_3, \text{H}_2\text{O}_2, \text{NaOH}} & \text{R} & - \text{C} & \text{OH} \\
\text{R} & - \text{C} & \text{C} & \text{CH} & \xrightarrow{\text{BH}_3, \text{H}_2\text{O}_2, \text{NaOH}} & \text{R} & - \text{C} & \text{OH} & \text{OH} \\
\end{align*}
\]

But we don’t isolate the di-hydroxy product; instead, we obtain the corresponding aldehyde:

\[
\begin{align*}
\text{R} & - \text{C} & \text{C} & \text{CH} & \xrightarrow{\text{BH}_3} & \text{R} & - \text{C} & \text{BH}_2 & \text{BH}_2 & \xrightarrow{\text{H}_2\text{O}_2, \text{NaOH}} & \text{R} & - \text{C} & \text{OH} & \text{OH} & \xrightarrow{-\text{H}_2\text{O}} & \text{R} & - \text{C} & \text{O} \\
\end{align*}
\]

This is because the expected product, a carbonyl hydrate, is in rapid equilibrium with the much more stable carbonyl compound; only the aldehyde is isolated.

We will learn the mechanism of hydrate formation and decomposition when we discuss the chemistry of aldehydes and ketones. (See Chapter 17.)