18.2 ELIMINATION REACTIONS OF VINYLIC HALIDES

Although $S_N2$ reactions of vinylic halides are unknown, base-promoted $\beta$-elimination reactions of vinylic halides do occur and can be useful in the synthesis of alkynes.

In Eq. 18.5, two successive eliminations take place. The first gives a vinylic halide and the second gives the alkyne.

Many vinylic eliminations require rather harsh conditions (heat or very strong bases), and some of the more useful examples of this reaction involve elimination of $\beta$-hydrogens with enhanced acidity. Notice, for example, that the hydrogens which are eliminated in Eqs. 18.4 and 18.5 are benzylic (Sec. 17.3B).

Can aryl halides undergo $\beta$-elimination? Try to answer this question by constructing a model of the alkyne that would be formed in such an elimination. We’ll return to this issue in Sec. 18.4B.
**PROBLEM 18.2** Arrange the following compounds according to increasing rate of elimination with \( \text{NaOC}_2\text{H}_5 \) in \( \text{C}_2\text{H}_5\text{OH} \). What is the product in each case?

\[
\begin{align*}
A &: \text{Ph} = \text{C} = \text{C} = \text{Br} \\
B &: \text{Ph} = \text{C} = \text{C} = \text{Ph} \\
C &: \text{Ph} = \text{C} = \text{C} = \text{Cl} \\
D &: \text{Ph} = \text{C} = \text{C} = \text{H}
\end{align*}
\]

**18.3 LACK OF REACTIVITY OF VINYLIC AND ARYL HALIDES UNDER S\(_{\text{N}}\)1 CONDITIONS**

Recall that tertiary and some secondary alkyl halides undergo nucleophilic substitution and elimination reactions by the \( S_{\text{N}}1 \) and \( E1 \) mechanisms (Sec. 9.6). For example, \( \text{tert}-\text{butyl bro} \)}

\[
\begin{align*}
\text{H}_3\text{C} &- \text{C} - \text{Br}: \xrightarrow{\text{C}_2\text{H}_5\text{OH} \ 55^\circ \text{C}} \left[ \text{H}_3\text{C} - \text{C}^{+} - \text{Br}^- \right] \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{H}_3\text{C} - \text{C} - \text{OC}_2\text{H}_5 + \text{H}_3\text{C} - \text{C} = \text{CH}_2 + \text{HBr}^+: \\
(72\%) &\quad (28\%)
\end{align*}
\]

Vinylic and aryl halides, however, are virtually inert to the conditions that promote \( S_{\text{N}}1 \) or \( E1 \) reactions of alkyl halides. Certain vinyl halides can be forced to react by the \( S_{\text{N}}1–E1 \) mechanism under extreme conditions, but such reactions are relatively uncommon.

\[
\begin{align*}
\text{H}_2\text{C} &- \text{C} - \text{Br} + \text{C}_2\text{H}_5\text{OH} \ 55^\circ \text{C} \quad \text{no reaction} \\
\text{Ph} - \text{Br} + \text{C}_2\text{H}_5\text{OH} \ 55^\circ \text{C} \quad \text{no reaction}
\end{align*}
\]

To understand why vinylic and aryl halides are inert under \( S_{\text{N}}1 \) conditions, consider what would happen if they were to undergo the \( S_{\text{N}}1 \) reaction. If a vinyl halide undergoes an \( S_{\text{N}}1 \) reaction, it must ionize to form a *vinyl cation*.

\[
\begin{align*}
\text{R} - \text{C} = \text{CH}_2 &\xrightarrow{+} \text{R} = \text{C} = \text{CH}_2 + \text{Br}^-: \\
\text{a vinyl cation}
\end{align*}
\]

A *vinyl cation* is a carbocation in which the electron-deficient carbon is also part of a double bond. An orbital diagram of a vinyl cation is shown in Fig. 18.2a. The electron-deficient carbon is connected to two groups, the \( R \) group and the other carbon of the double bond. Hence, the geometry at this carbon is *linear* (Sec. 1.3B) and the electron-deficient carbon is therefore \( sp \)-hybridized. Notice that the vacant \( 2p \) orbital is not conjugated with the \( \pi \)-electron system of the double bond; in order to be conjugated, it would have to be coplanar with the double-bond \( \pi \) system. Vinyl cations are considerably less stable than alkyl carbocations because their \( sp \) hybridization has a higher energy than the \( sp^2 \) hybridization of alkyl cations (the...