An aryl halide is a compound in which a halogen is bound to the carbon of a benzene ring (or another aromatic ring).

In a vinylic halide, a halogen is bound to a carbon of a double bond.

Be sure to differentiate carefully between vinylic and allylic halides (p. 788). Allylic groups are on a carbon adjacent to the double bond. Likewise, be sure that the distinction between aryl and benzylic halides is clear. Benzylic groups are on a carbon adjacent to an aromatic ring.
The reactivity of aryl and vinylic halides is quite different from that of ordinary alkyl halides. In fact, one of the major points of this chapter is that aryl halides do not undergo nucleophilic substitution reactions by the $S_{N_2}$ or $S_{N_1}$ mechanisms.

In a phenol, a hydroxy (—OH) group is bound to an aromatic ring. As the following structures illustrate, phenol is also the name given to the parent compound, and a number of phenols have traditional names.

![ Phenol structures ]

Although phenols and alcohols have some reactions in common, there are also important differences in the chemical behavior of these two functional groups.

A relatively recent field of organic chemistry involves the use of transition-metal catalysts in organic reactions, particularly in reactions that involve formation of carbon–carbon bonds. The reactivity of aryl and vinylic halides in substitution reactions is dramatically increased by certain catalysts of this type, and this heightened reactivity will be the vehicle through which we can learn some of the basic principles involved in transition-metal catalysis.

The nomenclature and spectroscopy of aryl halides and phenols were discussed in Secs. 16.1 and 16.3, respectively. The nomenclature of vinylic halides follows the principles of alkene nomenclature (Sec. 4.2A), and the spectroscopy of vinylic halides, except for minor differences due to the halogen, is also similar to that of alkenes.

### 18.1 LACK OF REACTIVITY OF VINYLIC AND ARYL HALIDES UNDER $S_{N_2}$ CONDITIONS

One of the most important differences between vinylic or aryl halides and alkyl halides is their reactivity in nucleophilic substitution reactions. The two most important mechanisms for nucleophilic substitution reactions of alkyl halides are the $S_{N_2}$ (bimolecular backside substitution) mechanism, and the $S_{N_1}$ (unimolecular carbocation) mechanism (Secs. 9.4 and 9.6). What happens to vinylic and aryl halides under the conditions used for $S_{N_1}$ or $S_{N_2}$ reactions of alkyl halides?

Consider first the $S_{N_2}$ reaction. One of the most dramatic contrasts between vinylic or aryl halides and alkyl halides is that simple vinylic and aryl halides are inert under $S_{N_2}$ conditions. For example, when ethyl bromide is allowed to react with NaOH in C$_2$H$_5$OH solvent at 55 °C, the following $S_{N_2}$ reaction proceeds to completion in about an hour with excellent yield:

$$\text{CH}_3\text{CH}_2\text{--Br} + \text{Na}^+\text{CH}_3\text{CH}_2\text{--O}^— \xrightarrow{55 \degree C} \text{CH}_3\text{CH}_2\text{--O}^-\text{CH}_3\text{CH}_3 + \text{Na}^+\text{Br}^-$$  \hspace{1cm} (18.1)

Yet when vinyl bromide or bromobenzene is subjected to the same conditions, nothing happens!
Why don’t vinylic halides undergo S\textsubscript{N}2 reactions? In Sec. 9.4C (Fig. 9.2, p. 390), we learned that, in the transition state of an S\textsubscript{N}2 reaction of an alkyl halide, the carbon undergoing substitution has a 2p orbital to which the nucleophile and the leaving group are partially bound, and is therefore sp\textsuperscript{2}-hybridized. In other words, this carbon rehybridizes from sp\textsuperscript{3} in the alkyl halide to sp\textsuperscript{2} in the transition state. The carbon undergoing substitution in a vinylic halide is sp\textsuperscript{2}-hybridized in the starting material; it contains a 2p orbital involved in the double bond. If the S\textsubscript{N}2 reaction results in the development of a second 2p orbital at this carbon, then this carbon must become sp-hybridized. Therefore, an S\textsubscript{N}2 reaction at a vinylic carbon involves rehybridization from sp\textsuperscript{2} in the vinylic halide to sp in the transition state.

The sp hybridization state has such high energy (Sec. 14.2) that conversion of an sp\textsuperscript{2}-hybridized carbon into an sp-hybridized carbon requires about 21 kJ mol\textsuperscript{-1} (5 kcal mol\textsuperscript{-1}) more energy than is required for an sp\textsuperscript{3} to sp\textsuperscript{2} hybridization change. The relatively high energy of the transition state caused by sp hybridization reduces the rate of S\textsubscript{N}2 reactions of vinylic halides by almost four orders of magnitude (by Eq. 9.22a, p. 385). This means that, under the conditions in which the S\textsubscript{N}2 reaction of ethyl bromide takes an hour, transition-state hybridization alone would cause the same reaction of vinyl bromide to take almost 200 days.

Rehybridization, however, is not the only reason that vinylic halides are unreactive in the S\textsubscript{N}2 reaction. A second reason is that the nucleophile (Nuc\textsuperscript{3} in Eq. 18.2) would have to approach the vinylic halide at the back side of the halogen-bearing carbon and in the plane of the alkene. This arrangement results in significant van der Waals repulsions (steric effect) of both the nucleophile and the leaving group with the groups on the other vinylic carbon. This is shown for the S\textsubscript{N}2 reaction of vinyl bromide in Fig. 18.1. When the groups on the other vinylic carbon are larger than hydrogen, the repulsions are even greater. These repulsions raise the energy of the transition state and decrease the reaction rate even further.

In summary, both hybridization and van der Waals repulsions (steric effects) within the transition state retard the S\textsubscript{N}2 reactions of vinylic halides to such an extent that they do not occur.

S\textsubscript{N}2 reactions of aryl halides have the same problems as those of vinylic halides and two others as well. First, backside approach to the carbon of the carbon–halogen bond would place the nucleophile on a path that goes through the plane of the benzene ring—an obvious impossibility. Furthermore, because the carbon at which substitution occurs would have to undergo stereoisomerization, the reaction would necessarily yield a benzene derivative containing a twisted and highly strained double bond.

If the impossibility of this result is unclear, try to build a model of the product—but don’t break your models!
18.2 ELIMINATION REACTIONS OF VINYLIC HALIDES

Although S<sub>N</sub>2 reactions of vinylic halides are unknown, base-promoted β-elimination reactions of vinylic halides do occur and can be useful in the synthesis of alkynes.

\[
\begin{align*}
\text{Ph} & \text{CH} & \text{CH} & \text{Br} & + & \text{KOH} & \xrightarrow{200 \, ^\circ \text{C}} & \text{Ph} & \text{C} & \text{C} & \text{H} & + & \text{K}^+ & \text{Br}^- & + & \text{H}_2\text{O} \\
(E \text{ or } Z) & & & & & & & & & & & & (\text{distills from reaction mixture; } 67\% \text{ yield})
\end{align*}
\]

\[
\begin{align*}
& \text{Br} & & \text{Br} \\
\text{Ph} & \text{CH} & \text{CH} & \text{Ph} & + & 2 \text{KOH} & \xrightarrow{\text{C}_2\text{H}_5\text{OH}} & \text{Ph} & \text{C} & \text{C} & \text{Ph} & + & 2 \text{K}^+ & \text{Br}^- & + & 2 \text{H}_2\text{O} \\
& & & & & & & & & & & (67\% \text{ yield})
\end{align*}
\]

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 β-hydrogens with enhanced acidity. Notice, for example, that the hydrogens which are eliminated in Eqs. 18.4 and 18.5 are benzyllic (Sec. 17.3B).

Can aryl halides undergo β-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.