The most readily available alkenyl halide is chloroethene (vinyl chloride), which can be prepared by a number of routes:

\[
\begin{align*}
CH=CH + HCl & \rightarrow CH_2=CH Cl \\
CH_2=CH_2 + Cl_2 & \rightarrow \text{chloroethene} \\
\text{CH}_3+\text{Cl}_2 & \rightarrow \text{CH}_2=\text{CH}_2 + Cl_2
\end{align*}
\]

The most economical commercial preparation is high-temperature chlorination of ethene. A useful modification of this process uses hydrogen chloride in place of chlorine. An oxidizing agent is required to raise the oxidation state of chlorine in \(\text{HCl}\) to that of \(\text{Cl}_2\); molecular oxygen is used for this purpose along with cupric salts as catalysts.

General methods of preparation for alkenyl and alkynyl halides are listed in Table 14-5. By the alkynyl halides we mean 1-halo-alkynes. One interesting method by which they may be prepared employs 1-alkynes with hypohalites:

\[
\text{C}_6\text{H}_5\text{C} \equiv \text{CH} + \text{NaOBr} \rightarrow \text{C}_6\text{H}_5\text{C} \equiv \text{C} \equiv \text{Br} + \text{NaOH}
\]

This kind of reaction does not proceed with either alkanes or alkenes.

**Uses of Alkenyl Halide**

Chloroethene is produced in vast quantities for the production of polymers (polyvinyl chloride) and copolymers:

\[
n(\text{CH}_2=\text{CHCl}) \rightarrow \text{CH}_2=\text{CHCl}_n
\]

These polymers commonly are described as PVC plastics or less specifically as “vinyl.” They are materials that may be either flexible or rigid according to what they are mixed with, and they are used in the manufacture of many familiar articles such as plastic curtains, rainwear, floor tile, synthetic leather goods, upholstery, table mats, phonograph records, insulation, plastic pipes, tubing, and packaging materials.

Recently, it has been found that persons working in plants that manufacture and use chloroethene have an unusually high incidence of an unusual type of liver cancer. As a result, strict safety regulations and pollution standards have been set for plants where chloroethene is made or used. The once widespread use of chloroethene as a propellant for aerosol cans has been curtailed. Polyvinyl chloride itself seems to be quite safe, but there are possible problems with its incorporation into interior building materials, clothing, and upholstery because heat, such as fire, causes polyvinyl chloride to decompose, thereby producing hydrogen chloride as one decomposition product. In closed areas the toxicity
of hydrogen chloride gas may be as serious a hazard as the fire itself. Other polymers may give off similarly toxic products on strong heating.

14-4B Chemical Properties

The outstanding chemical characteristic of alkenyl halides is their general inertness in $S_{N1}$ and $S_{N2}$ reactions. Thus chloroethene fails to react with silver nitrate in ethanol (i.e., low $S_{N1}$ reactivity), fails to react with potassium iodide in acetone (i.e., low $S_{N2}$ reactivity), and only reacts slowly with sodium hydroxide to give ethyne (low $E2$ reactivity). The haloalkynes, such as $\text{\text{-}\text{equiv C-Cl}}$, are similarly unreactive.

It is not surprising that $\text{\text{-}\text{equiv C-X}}$ bonds are hard to break heterolytically. In general, $\text{\text{-}\text{equiv C-X}}$ bonds are strong in alkenyl halides (cf. Table 4-6) and this property tends to make them less reactive than alkyl halides. Furthermore, double- and triple-bonded carbons are more strongly electron-attracting than saturated $sp^3$ carbons, which is the reason why 1-alkynes and alkenes are stronger acids (Section 11-8) than alkanes. Consequently it is easier to break a $\text{\text{-}\text{equiv C-H}}$ bond in the sense $\text{\text{-}\text{equiv C}^\ominus \text{\text{-}\text{equiv H}^\oplus}}$ than as $\text{\text{-}\text{equiv C}^\oplus \text{\text{-}\text{equiv H}^\ominus}}$. It also will be more difficult to ionize a carbon-halogen bond to $\text{\text{-}\text{equiv C}^\oplus \text{\text{-}\text{equiv X}^\ominus}}$ if the carbon is unsaturated. Therefore ethenyl and ethynyl cations, such as $\text{\text{-}\text{equiv CH}_2=\text{\text{-}\text{equiv C}^\oplus}}$ and $\text{\text{-}\text{equiv HC}^\oplus}$, are difficult to generate from the corresponding halides. Superior leaving groups are required, such as trifluoromethanesulfonate, $\text{\text{-}\text{equiv OSO}_3\text{CF}_3}$ (Section 8-7C):

![Ethynyl cation](image)

The reason for the lack of $S_{N2}$ reactivity in ethenyl or ethynyl halides may be that the attacking nucleophile is unable to react by the concerted inversion mechanism that invariably is observed with alkyl halides:

![Backside attack with inversion is not possible](image)

Nevertheless, substitution of the halogen does occur under some circumstances. In such cases, the nucleophile first adds to the multiple bond, and in a subsequent step the halogen leaves as halide ion. This is an "addition-elimination" mechanism, of which we will have more examples later:

$$
\text{\text{-}\text{equiv CH}_2=\text{\text{-}\text{equiv C}^\oplus} + \text{\text{-}\text{equivNu}} \rightarrow \text{\text{-}\text{equiv CH}_2=\text{\text{-}\text{equiv C}^\ominus}} \rightarrow \text{\text{-}\text{equiv CH}_2=\text{\text{-}\text{equiv C}^\oplus} + \text{\text{-}\text{equivNu}}}
$$

Contributors and Attributions
