Notice that hydroboration–oxidation of a 1-alkyne gives an aldehyde; hydration of any 1-alkyne (other than acetylene itself) gives a ketone.

**PROBLEM**

14.12 Compare the results of hydroboration–oxidation and mercuric ion-catalyzed hydration for (a) cyclohexylacetylene and (b) 2-butyne.

### 14.6 REDUCTION OF ALKYNES

#### A. Catalytic Hydrogenation of Alkynes

Alkynes, like alkenes (Sec. 4.9A), undergo catalytic hydrogenation. The first addition of hydrogen yields an alkene; a second addition of hydrogen gives an alkane.

\[
\begin{align*}
R - \text{C} \equiv \text{C} - R & \quad \text{H}_2, \text{catalyst} \quad R - \text{CH} - \text{CH} - R & \quad \text{H}_2, \text{catalyst} \quad R - \text{CH}_2 - \text{CH}_2 - R
\end{align*}
\]  \hspace{1cm} (14.12)

The utility of catalytic hydrogenation is enhanced considerably by the fact that hydrogenation of an alkyne may be stopped at the alkene stage if the reaction mixture contains a catalyst poison: a compound that disrupts the action of a catalyst. Among the useful catalyst poisons are salts of Pb\(^{2+}\), and certain nitrogen compounds, such as pyridine, quinoline, or other amines.

![Pyridine and Quinoline](image)

These compounds selectively block the hydrogenation of alkenes without preventing the hydrogenation of alkynes to alkenes. For example, a Pd/CaCO\(_3\) catalyst can be washed with Pb(OAc)\(_2\) to give a poisoned catalyst known as Lindlar catalyst. In the presence of Lindlar catalyst, an alkyne is hydrogenated to the corresponding alkene:

\[
\text{H}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_3 \quad \text{Lindlar catalyst or Pd/C, pyridine} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

\[
\text{cis-4-octyne}
\]  \hspace{1cm} (14.13)
As Eq. 14.13 shows, the hydrogenation of alkynes, like the hydrogenation of alkenes (Sec. 7.9E), is a stereoselective syn-addition. Thus, in the presence of a poisoned catalyst, hydrogenation of appropriate alkynes gives cis alkenes. In fact, catalytic hydrogenation of alkynes is one of the best ways to prepare cis alkenes.

In the absence of a catalyst poison, two equivalents of $H_2$ are added to the triple bond.

$$\text{2H}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{CCH}_2\text{CH}_3 \xrightarrow{\text{Pd/C \ no\ poison}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

The catalytic hydrogenation of alkynes can therefore be used to prepare alkenes or alkanes by either including or omitting the catalyst poison. How catalyst poisons exert their inhibitory effect on the hydrogenation of alkenes is not well understood.

**PROBLEM 14.13** Give the principal organic product formed in each of the following reactions.

(a) $\text{CH}_3(\text{CH}_2)_5\text{C}≡\text{CH} + \text{H}_2 \xrightarrow{\text{Lindlar catalyst}} \text{1-octyne}$

(b) Same as part (a) with no poison

(c) $\text{C}≡\text{CH} + \text{H}_2 \xrightarrow{\text{Pd/C}} \text{H}_2\text{C}≡\text{C}≡\text{CH}_2\text{CH}_3 + \text{D}_2 \xrightarrow{\text{Lindlar catalyst}} \text{2-pentyne}$

**B. Reduction of Alkynes with Sodium in Liquid Ammonia**

Reaction of an alkyne with a solution of an alkali metal (usually sodium) in liquid ammonia gives a trans alkene.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{C}≡\text{CCH}_2\text{CH}_3 + 2\text{Na} + 2\text{N}_3\text{H}_3 \xrightarrow{} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{C}≡\text{CCH}_2\text{CH}_3 + 2\text{Na}^+ \cdot \text{N}_3\text{H}_2 \\ (97\% \text{ yield}) \end{array}$$

The reduction of alkynes with sodium in liquid ammonia is complementary to the catalytic hydrogenation of alkynes, which is used to prepare cis alkenes (Sec. 14.6A).

$$\text{R}≡\text{C}≡\text{C}−\text{R}$$

$$\text{Na/NH}_3$$

$$\text{H}_2/\text{poisoned catalyst}$$

$$\begin{array}{ll}
\text{trans alkene} & \text{cis alkene} \\
\text{R}−\text{C}≡\text{C}−\text{R} & \text{R}−\text{C}≡\text{C}−\text{R} \\
\text{H} & \text{H}
\end{array}$$

(14.16)

The stereochemistry of the Na/NH$_3$ reduction follows from its mechanism. If sodium or other alkali metals are dissolved in pure liquid ammonia, a deep blue solution forms that contains electrons complexed with ammonia (solvated electrons).
The solvated electron can be thought of as the simplest free radical. Remember that free radicals add to triple bonds (Eq. 14.2, p. 653). The reaction of solvated electrons with the alkynes begins with the addition of an electron to the triple bond. The resulting species has both an unpaired electron and a negative charge. Such a species is called a **radical anion**:

\[ \text{solvated electron} \]

\[ \text{Na}^+ + n \text{NH}_3 \text{(liq)} \longrightarrow \text{Na}^+ + e^- (\text{NH}_3)_n \]  \hspace{1cm} (14.17)

The radical anion is such a strong base that it readily removes a proton from ammonia to give a **vinyllic radical**—a radical in which the unpaired electron is associated with one carbon of a double bond. The destruction of the radical anion in this manner pulls the unfavorable equilibrium in Eq. 14.18a to the right:

\[ \text{a radical anion} \]

\[ R - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - R \]

\[ \text{Na}^+ \]

\[ \text{H} \text{-NH}_2 \]

\[ \text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - R \]

\[ \text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - R \text{Na}^+ + \text{H} \text{-NH}_2 \]  \hspace{1cm} (14.18b)

The vinyllic radical, like the unshared electron pair of an amine (Sec. 6.10B), rapidly undergoes inversion, and the equilibrium between the cis and trans radicals favors the trans radical for the same reason that trans alkenes are more stable than cis alkenes: repulsions between the R groups are reduced.

\[ \text{cis vinyllic radical} \]

\[ \text{trans vinyllic radical} \]

\[ \text{(strongly favored at equilibrium)} \]

\[ \text{trans vinyllic radical} \]

\[ \text{cis vinyllic radical} \]

\[ \text{transition state for inversion} \]

\[ \overset{\ddagger}{\text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - \text{R}} \]

Next, the vinyllic radical accepts an electron to form an anion:

\[ \text{solvated electron} \]

\[ e^- \]

\[ \text{Na}^+ \]

\[ \text{Na}^+ \]

\[ \overset{\circ}{\text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - \text{R}} \]

\[ \overset{\circ}{\text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - \text{R}} \]

\[ \text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - \text{R} \]

\[ \text{R} - \overset{\cdot}{C} \equiv \overset{\cdot}{C} - \text{R} \text{Na}^+ \]  \hspace{1cm} (14.18d)

This step of the mechanism is the **product-determining step** of the reaction (Sec. 9.6B). The **rate constants** for the reactions of the cis and trans vinyllic radicals with the solvated electron are probably the same. However, the actual *rate* of the reaction of each radical is determined by the product of the rate constant and the concentration of the radical. Because the trans
vinyllic radical is present in much higher concentration, the ultimate product of the reaction, the trans alkene, is derived from this radical.

The anion formed in Eq. 14.18d is also more basic than the amide anion and readily removes a proton from ammonia to complete the addition.

Because ordinary alkenes do not react with the solvated electron (the initial equilibrium analogous to Eq. 14.18a is too unfavorable), the reaction stops at the trans alkene stage.

The Na/NH$_3$ reduction of alkynes does not work well on 1-alkynes unless certain modifications are made in the reaction conditions. (This is explored in Problem 14.39.) However, this is not a serious limitation for the reaction, because the reduction of 1-alkynes to 1-alkenes is easily accomplished by catalytic hydrogenation (Sec. 14.6A).

PROBLEM 14.14 What product is obtained in each case when 3-hexyne is treated in each of the following ways? (Hint: The products of the two reactions are stereoisomers.)
(a) with sodium in liquid ammonia and the product of that reaction with D$_2$ over Pd/C
(b) with H$_2$ over Pd/C and quinoline and the product of that reaction with D$_2$ over Pd/C

14.7 ACIDITY OF 1-ALKYNES

A. Acetylenic Anions

Most hydrocarbons do not react as Brønsted acids. Nevertheless, let’s imagine such a reaction in which a proton is removed from a hydrocarbon by a very strong base B:–.

$$\begin{align*} &\text{C–H} + \text{B:–} \rightarrow \text{C:–} + \text{B–H} \\
&\text{a carbanion} \end{align*}$$

In this equation, the conjugate base of the hydrocarbon is a carbon anion, or carbanion. Recall from Sec. 8.8B that a carbanion is a species with an unshared electron pair and a negative charge on carbon.

The conjugate base of an alkane, called generally an alkyl anion, has an electron pair in an $sp^3$ orbital. An example of such an ion is the 2-propanide anion:

2-propanide anion
(an alkyl anion)