Further chemistry of alkenes and alkynes is described in this chapter, with emphasis on addition reactions that lead to reduction and oxidation of carbon–carbon multiple bonds. First we explain what is meant by the terms reduction and oxidation as applied to carbon compounds. Then we emphasize hydrogenation, which is reduction through addition of hydrogen, and oxidative addition reactions with reagents such as ozone, peroxides, permanganate, and osmium tetroxide. We conclude with a section on the special nature of 1-alkynes—their acidic behavior and how the conjugate bases of alkynes can be used in synthesis to form carbon–carbon bonds.

11-1 OXIDATION–REDUCTION OF ORGANIC COMPOUNDS

An organic compound commonly is said to be “reduced” if reaction leads to an increase in its hydrogen content or a decrease in its oxygen content. The
compound would be “oxidized” if the reverse change took place:

\[
\text{CH}_2\text{=CH}_2 + \text{H}_2 \xrightarrow{\text{reduction}} \text{CH}_3\text{CH}_3
\]

\[
\text{H}_2 + \text{H}_2\text{C} = \text{CH}_2 \xrightarrow{\text{reduction}} \text{CH}_2\text{=CH}_2 + [\text{H}_2\text{O}]
\]

This is a very unsatisfactory definition because many oxidation-reduction or \textit{redox} reactions do not involve changes in hydrogen or oxygen content, as the following example illustrates:

\[
\text{CH}_3\text{Cl} + \text{Mg} \rightarrow \text{CH}_3\text{MgCl}
\]

(carbon is reduced; magnesium is oxidized)

Redox reactions are better defined in terms of the concept of electron transfer. Thus \textit{an atom is said to be oxidized if, as the result of a reaction, it experiences a net loss of electrons; and is reduced if it experiences a net gain of electrons}. This simple definition can be used to identify oxidation or reduction processes at carbon in terms of a scale of oxidation states for carbon based on the electronegativities of the atoms attached to carbon. The idea is to find out whether in a given reaction carbon becomes more, or less, electron-rich. We will use the following somewhat arbitrary rules:

1. Elementary carbon is assigned the zero oxidation state.
2. The oxidation state of any chemically bonded carbon may be assigned by adding \(-1\) for each more electropositive atom and \(+1\) for each more electronegative atom, and 0 for each carbon atom bonded directly to the carbon of interest (see Figure 10-11 for the Pauling electronegativity scale). That is,

\(-1\) for electropositive atoms, H, B, Na, Li, Mg

\(+1\) for electronegative atoms, halogens, O, N, S

0 for carbon.

The rationale for this mode of operation can be seen if we look more closely at the example of \text{CH}_3\text{Cl} + \text{Mg} \rightarrow \text{CH}_3\text{MgCl}. Chlorine is more electronegative than either carbon or magnesium. Carbon is more electronegative than magnesium. Thus \text{CH}_3\text{Cl} is written properly with a polar bond as \(\text{CH}_3\cdot\cdot\cdot\text{Cl}\), whereas the C–Mg bond is oppositely polarized, \(\text{CH}_3\cdot\cdot\cdot\text{Mg}\). If all of the bonds were ionized completely, we could write

\[
\text{CH}_3^{\oplus} + \text{Cl}^{\ominus} + \text{Mg}^{\ominus} \rightarrow \text{CH}_3\cdot^{\ominus} + \text{Mg}^{2\oplus} + \text{Cl}^{\ominus}
\]

and it would be completely clear that carbon gains two electrons (is reduced), while magnesium loses two electrons (is oxidized). But because covalent, or at most polar, bonds actually are involved, it is much more difficult to determine whether oxidation or reduction occurs.
3. In compounds with multiple bonds (\(\text{C} = \text{O}, -\text{C} \equiv \text{N}\)), the attached heteroatom is counted twice or three times, depending on whether the bond is double or triple.

4. A formal positive charge on carbon changes the oxidation state by +1, and a formal negative charge by −1; an odd electron on carbon leaves the oxidation state unchanged.

To illustrate, the oxidation state of carbon in four representative examples is determined as follows:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H}-\text{C}-\text{H} & \quad \text{H} \\
\text{Oxidation state:} & \quad 4 \times (-1) = -4 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H}-\text{C} & \quad \text{Cl} \\
\text{Oxidation state:} & \quad 2 \times (-1) + 2 \times (+1) = 0 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{C} = \text{C} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
2 \times (-1) + 2 \times (0) & = -2 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{H} \\
(-1) + (+1) + (+2) & = +2 \\
\end{align*}
\]

Using this approach, we can construct a carbon oxidation scale, as in Table 11-1. Any reaction that increases the degree of oxidation of carbon corresponds to a loss of electrons (oxidation), and a reaction that decreases the oxidation level corresponds to a gain of electrons (reduction). Two examples follow:

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \text{H}_2 \quad \text{H}_2 \quad \text{CH}_3=\text{CH}_3 \\
\text{net decrease in carbon oxidation} & \quad \text{state of 2 per molecule (reduction)} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \text{H}_2\text{O}_2 \quad \text{CH}_2=\text{CH}_2 \\
\text{net increase in carbon oxidation} & \quad \text{state of 2 per molecule (oxidation)} \\
\end{align*}
\]

We recommend this scheme of oxidation states only as an aid to identify and balance redox reactions. Also, the terminology "redox" should not be confused with the mechanism of a reaction, as there is no connection between them. A moment's reflection also will show that virtually all reactions theoretically can be regarded as redox reactions, because in almost every reaction the reacting atoms experience some change in their electronic environments. Traditionally, however, reactions are described as redox reactions of carbon only when there is a net change in the oxidation state of the carbon atoms involved. An indication of just how arbitrary this is can be seen by the example.
Table 11-1
Carbon Oxidation States of Representative Organic Compounds (R = alkyl)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>O=C=O</td>
<td>+4</td>
</tr>
<tr>
<td>tetrachloromethane</td>
<td>CCl₄</td>
<td>+4</td>
</tr>
<tr>
<td>isocyanates</td>
<td>RN=C=O</td>
<td>+4</td>
</tr>
<tr>
<td>carboxylic acids</td>
<td>R-C-OH</td>
<td>+3</td>
</tr>
<tr>
<td>nitriles</td>
<td>RC≡N</td>
<td>+3</td>
</tr>
<tr>
<td>ketones</td>
<td>R₂C=O</td>
<td>+2</td>
</tr>
<tr>
<td>trichloromethane</td>
<td>CHCl₃</td>
<td>+2</td>
</tr>
<tr>
<td>ketenes</td>
<td>R₂C≡C=O</td>
<td>+2(*)</td>
</tr>
<tr>
<td>tert-alcohols</td>
<td>R₃COH</td>
<td>+1</td>
</tr>
<tr>
<td>aldehydes</td>
<td>RCH=O</td>
<td>+1</td>
</tr>
<tr>
<td>methanal</td>
<td>H₂C=O</td>
<td>0</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>CH₂Cl₂</td>
<td>0</td>
</tr>
<tr>
<td>alkanes</td>
<td>R₄C</td>
<td>0</td>
</tr>
<tr>
<td>benzene</td>
<td>C₆H₆</td>
<td>-1 (per carbon)</td>
</tr>
<tr>
<td>alkanes</td>
<td>R₃CH</td>
<td>-1</td>
</tr>
<tr>
<td>ethyne</td>
<td>HC≡CH</td>
<td>-1 (per carbon)</td>
</tr>
<tr>
<td>alkanes</td>
<td>R₂CH₂</td>
<td>-2</td>
</tr>
<tr>
<td>ethene</td>
<td>CH₂=CH₂</td>
<td>-2 (per carbon)</td>
</tr>
<tr>
<td>chloromethane</td>
<td>CH₃Cl</td>
<td>-2</td>
</tr>
<tr>
<td>methanol</td>
<td>CH₃OH</td>
<td>-2</td>
</tr>
<tr>
<td>methyl cation</td>
<td>CH₃⁺</td>
<td>-2</td>
</tr>
<tr>
<td>methyl radical</td>
<td>CH₃⁻</td>
<td>-3</td>
</tr>
<tr>
<td>alkanes</td>
<td>RCH₃</td>
<td>-3</td>
</tr>
<tr>
<td>methyl anion</td>
<td>CH₃⁻</td>
<td>-4</td>
</tr>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>-4</td>
</tr>
</tbody>
</table>

of addition of water to ethene. This reaction usually is not regarded as an oxidation-reduction reaction because there is no net change in the oxidation state of the ethene carbons, despite the fact that, by our rules, one carbon is oxidized and the other reduced:

\[ \begin{array}{cccc}
-2 & -2 & -3 & -1 \\
\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} & \longrightarrow & \text{CH}_3\text{CH}_2\text{OH} \\
\end{array} \]
Apart from indicating when oxidation or reduction occurs, the oxidation scale is useful in balancing redox equations. For example, consider the following oxidation of ethenylbenzene (styrene) with potassium permanganate:

\[ \text{C}_8\text{H}_8\text{CHCH}_2 + \text{KMnO}_4 \rightarrow \text{C}_8\text{H}_5\text{C}-\text{CO}_2\text{H} + \text{MnO}_2 \]

To determine how many moles of permanganate ion are required to oxidize one mole of styrene in this reaction, first determine the net change in oxidation state of the reacting carbons:

\[
\begin{array}{cccc}
\text{C}_8\text{H}_8\text{CHCH}_2 & \rightarrow & \text{C}_8\text{H}_5\text{C}-\text{CO}_2\text{H} \\
+2 & +3 \\
\end{array}
\]

net change = 8

Second, determine the net change in oxidation state of manganese for \( \text{MnO}_4^- \) → \( \text{MnO}_2 \):

\[
\text{Mn}^{(\text{VII})} \rightarrow \text{Mn}^{(\text{IV})} \text{ net change } = 3
\]

Therefore we need three moles of styrene for every eight moles of permanganate:

\[ 3\text{C}_8\text{H}_8\text{CHCH}_2 + 8\text{KMnO}_4 \rightarrow 3\text{C}_8\text{H}_5\text{C}-\text{CO}_2\text{H} + 8\text{MnO}_2 + 8\text{KOH} \]

To get the overall atom and electrical balance for Equation 11-1, the requisite amounts of \( \text{H}_2\text{O} \) must be added, but the 3:8 ratio will remain unchanged:

\[ 3\text{C}_8\text{H}_8\text{CHCH}_2 + 8\text{KMnO}_4 + 8\text{H}_2\text{O} \rightarrow 3\text{C}_8\text{H}_5\text{C}-\text{CO}_2\text{H} + 8\text{MnO}_2 + 8\text{KOH} \]

Because \( \text{KOH} \) reacts in a nonoxidative way with carboxylic acids to form carboxylate salts (\( \text{RCO}_2\text{H} + \text{KOH} \rightarrow \text{RCO}_2\text{K} + \text{H}_2\text{O} \)), the final equation is

\[ 3\text{C}_8\text{H}_8\text{CHCH}_2 + 8\text{KMnO}_4 \rightarrow 3\text{C}_8\text{H}_5\text{C}-\text{CO}_2\text{K} + 8\text{MnO}_2 + 5\text{KOH} + 8\text{H}_2\text{O} \]

**Exercise 11-1** For each of the following reactions determine the oxidation state of the carbons in the reactants and products and decide whether the overall changes involve oxidation, reduction, or neither.

a. \( \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \)

b. \( \text{CH}_3\text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CHCH}_3 \)

\[ \text{Cl} \]
11-2 HYDROGENATION WITH HETEROGENEOUS CATALYSTS

Addition of hydrogen to a multiple bond is hydrogenation. It is applicable to almost all types of multiple bonds and is of great importance in synthetic chemistry, particularly in the chemical industry. Probably the most important technical example is production of ammonia by the hydrogenation of nitrogen:

$$3H_2 + N\equiv N \rightleftharpoons 2NH_3 \quad \Delta H^0 = -22.0 \text{ kcal (25°)}$$

$$\Delta G^0 = - 8.0 \text{ kcal (25°)}$$

This may appear to be a simple process, but in fact it is difficult to carry out because the equilibrium is not very favorable. High pressures (150–200 atm) are required to get a reasonable conversion, and high temperatures (430–510°) are necessary to get reasonable reaction rates. A catalyst, usually iron oxide, also is required. The reaction is very important because ammonia is used in ever-increasing amounts as a fertilizer either directly or through conversion to urea or ammonium salts.

Production of ammonia requires large quantities of hydrogen, most of which comes from the partial oxidation of hydrocarbons with water or oxygen. A simple and important example is the so-called “methane-steam gas” reaction, which is favorable only at very high temperatures because of the entropy effect in the formation of H2 (see Section 4-4B):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0 = +51.0 \text{ kcal (25°)}$$

$$\Delta G^0 = +33.9 \text{ kcal (25°)}$$
Therefore the fertilizer industry is allied closely with the natural gas and petroleum industries, and for obvious reasons ammonia and hydrogen often are produced at the same locations.

Alkenes and alkynes add hydrogen much more readily than does nitrogen. For example, ethene reacts rapidly and completely with hydrogen at ordinary pressures and temperatures in the presence of metal catalysts such as nickel, platinum, palladium, copper, and chromium:

\[
\text{CH}_2\text{CH}_2 + H_2 \xrightarrow{\text{metal catalyst}} \text{CH}_3\text{CH}_3 \quad \Delta H^0 = -32.7 \text{ kcal (25°)}
\]

These reactions are unlike any we have encountered so far. They are heterogeneous reactions, which means that the reacting system consists of two or more phases. Usually, the metal catalyst is present as a finely divided solid suspension in the liquid or solution to be reduced. Alternatively, the metal is deposited on an inert solid support such as carbon, barium sulfate, alumina (Al$_2$O$_3$), or calcium carbonate. Then the mixture of the liquid substrate and solid catalyst is shaken or stirred in a hydrogen atmosphere. However, the actual reaction takes place at the surface of the metal catalyst and is an example of heterogeneous or surface catalysis.

11-2A Mechanism of Hydrogenation

The exact mechanisms of heterogeneous reactions are difficult to determine, but much interesting and helpful information has been obtained for catalytic hydrogenation. The metal catalyst is believed to act by binding the reactants at the surface of a crystal lattice. As an example, consider the surface of a nickel crystal (Figure 11-1). The nickel atoms at the surface have fewer neighbors (lower covalency) than the atoms in the interior of the crystal. The surface atoms therefore have residual bonding capacity and might be expected to combine with a variety of substances.

![Figure 11-1](image)

Left: Schematic representation of a nickel crystal in cross section showing residual valences at the surface atoms. Right: Adsorption of ethene on the surface of the nickel crystal with formation of C–Ni bonds.
It has been shown experimentally that ethene combines exothermically \((\Delta H^0 = -60 \text{ kcal mole}^{-1})\) and reversibly with a metal surface. Although the precise structure of the ethene-nickel complex is unknown, the bonding to nickel must involve the electrons of the double bond because saturated hydrocarbons, such as ethane, combine only weakly with the nickel surface. A possible structure with carbon-nickel \(\sigma\) bonds is shown in Figure 11-1.

Hydrogen gas combines with nickel quite readily with dissociation of the H–H bonds and formation of Ni–H bonds (nickel hydride bonds). The overall hydrogenation process is viewed as a series of reversible and sequential steps, as summarized in Figure 11-2. First the reactants, hydrogen and ethene, are adsorbed on the surface of the metal catalyst. The energies of the metal–hydrogen and metal–carbon bonds are such that, in a second step, a hydrogen is transferred to carbon to give an ethyl attached to nickel. This is the halfway point. In the next step, the nickel–carbon bond is broken and the second carbon–hydrogen bond is formed. Hydrogenation is now complete and the product is desorbed from the catalyst surface.

Ethane has a low affinity for the metal surface and, when desorbed, creates a vacant space for the adsorption of new ethene and hydrogen molecules. The cycle continues until one of the reagents is consumed or some material is adsorbed that “poisons” the surface and makes it incapable of further catalytic activity. Because the reaction occurs only on the surface, small amounts of a catalyst poison can completely stop the reaction.

As might be expected for the postulated mechanism, the spacings of the metal atoms in the crystal lattice are quite important in determining the hydrogenation rates. The mechanism also accounts for the observation that

![Figure 11-2](https://example.com/figure11-2.png)
hydrogen usually adds to an alkene in the suprafacial manner. To illustrate, 1,2-dimethylcyclohexene is reduced to cis-1,2-dimethylcyclohexane:

1,2-dimethylcyclohexene  \( \xrightarrow{\text{Pt, H}_2} \) cis-1,2-dimethylcyclohexane

11-2B Catalyst Activity and Selectivity

For maximum catalytic activity, the metal usually is prepared in a finely divided state. This is achieved for platinum and palladium by reducing the metal oxides with hydrogen prior to hydrogenation of the alkene. A specially active form of nickel ("Raney nickel") is prepared from a nickel–aluminum alloy. Sodium hydroxide is added to the alloy to dissolve the aluminum. The nickel remains as a black powder which is pyrophoric (burns in air) if not kept moist:

\[
2\text{Ni} - \text{Al} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 2\text{Ni} + 2\text{AlO}_2^- + 3\text{H}_2
\]

Highly active platinum, palladium, and nickel catalysts also can be obtained by reduction of metal salts with sodium borohydride (NaBH₄).

As mentioned previously, multiple bonds are not hydrogenated with equal facility. This fact can be used to advantage in carrying out selective reactions. For instance, hydrogenation of a carbon–carbon double bond can be achieved without simultaneously reducing a carbonyl bond in the same molecule. For example the carbon–carbon double bond of the following aldehyde can be reduced selectively:

Alkynes are hydrogenated more easily than alkenes mainly because alkynes are adsorbed more readily on the catalyst surface. Hydrogenation proceeds in stages, first to the cis-alkene and then to the alkane. For example,
Normally, it is not possible to stop the hydrogenation of an alkyne at the alkene stage, but if the catalyst is suitably deactivated, addition to the triple bond can be achieved without further addition occurring to the resulting double bond. The preferred catalyst for selective hydrogenation of alkynes is palladium partially “poisoned” with a lead salt (Lindlar catalyst). This catalyst shows little affinity for adsorbing alkenes and hence is ineffective in bringing about hydrogenation to the alkane stage:

\[
\text{CH}_3\text{C}≡\text{CCH}_3 + \text{H}_2 \xrightarrow{\text{Lindlar catalyst}} \text{CH}_3\text{C}=\text{CCH}_3
\]

\[
\begin{array}{c}
\text{2-butyne} \\
\text{cis-2-butene}
\end{array}
\]

Aromatic hydrocarbons are hydrogenated with considerable difficulty, requiring higher temperatures, higher pressures, and longer reaction times than for alkenes or alkynes:

\[
\text{H}_2, \text{Ni} \quad 40 \text{ atm, 170–230°}
\]

**Exercise 11-3** Draw structures for the products expected from the following reactions. Show configurations where significant.

a. \[
\begin{array}{c}
\text{CH}_3\text{C}≡\text{CH}_2 \\
\text{H}_2, \text{Pt} \quad 25°
\end{array}
\]

b. \[
\begin{array}{c}
\text{cis-2-butene} \\
\text{D}_2, \text{Pt} \quad 25°
\end{array}
\]

c. \[
\begin{array}{c}
\text{CH}_2=\text{CH}–\text{C}–\text{CH}_3 \\
\text{H}_2, \text{Pt} \quad 25°
\end{array}
\]

d. \[
\begin{array}{c}
\text{1-penten-3-yne} \\
\text{H}_2, \text{Pd–Pb}
\end{array}
\]

e. \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{C}≡\text{CC}_6\text{H}_5 \\
\text{H}_2, \text{Pd–Pb}
\end{array}
\]

f. \[
\begin{array}{c}
\text{1,3-dimethylcyclopentene} \\
\text{H}_2, \text{Pt} \quad 25°
\end{array}
\]

**Exercise 11-4** The conditions of catalytic hydrogenation sometimes lead to rearrangement of a double bond from one location to another. Using 1-butene as an example, show how operation of the equilibria shown in the mechanism of Figure 11-2 could lead to rearrangement of 1-butene to 2-butene over a hydrogenation catalyst in the presence of \( \text{H}_2 \). If \( \text{D}_2 \) were used for reduction of 1-butene under these circumstances, suggest where and how much deuterium might be introduced into the butane formed.
In addition to having synthetic applications, catalytic hydrogenation is useful for analytical and thermochemical purposes. The analysis of a substance for the number of carbon–carbon double bonds it contains is carried out by measuring the uptake of hydrogen for a known amount of sample. Measurement of the heat evolved in the hydrogenation of alkenes gives information as to the relative stabilities of alkenes, provided that the differences in $\Delta S^0$ values are small (see Exercise 11-7).

The experimental values of $\Delta H^0$ for hydrogenation of a number of alkenes and alkynes are listed in Table 11-2. The $\Delta H^0$ calculated from average bond energies is $-30$ kcal mole$^{-1}$ for a double bond and $-69$ kcal mole$^{-1}$ for a triple bond. The divergences from these values reflect the influence of structure on the strengths of multiple bonds. Some important generalizations can be made:

1. The more alkyl groups or other substituents there are on the multiple bond, the less heat is evolved on hydrogenation. Because less heat evolved signifies a stronger, more stable bond, it appears that alkyl substitution increases the stability (strength) of the multiple bond.

### Table 11-2
Heats of Hydrogenation of Gaseous Alkenes and Alkynes (kcal mole$^{-1}$, 1 atm, 25°)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$-\Delta H^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethene</td>
<td>$\text{CH}_2=\text{CH}_2$</td>
<td>32.8</td>
</tr>
<tr>
<td>propene</td>
<td>$\text{CH}_3\text{CH}=\text{CH}_2$</td>
<td>30.1</td>
</tr>
<tr>
<td>1-butene</td>
<td>$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$</td>
<td>30.3</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_3$</td>
<td>28.6</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_3$</td>
<td>27.6</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$</td>
<td>26.9</td>
</tr>
<tr>
<td>2,3-dimethyl-2-butene</td>
<td>$(\text{CH}_3)_2\text{C}=\text{C(CH}_3)_2$</td>
<td>26.6</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_2\text{H}_5$</td>
<td>28.6</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_2\text{H}_5$</td>
<td>27.6</td>
</tr>
<tr>
<td>cis-2,2,5,5-tetramethyl-3-hexene</td>
<td>$(\text{CH}_3)_2\text{C}=\text{CH}=\text{CH}=\text{C(CH}_3)_3$</td>
<td>36.2</td>
</tr>
<tr>
<td>trans-2,2,5,5-tetramethyl-3-hexene</td>
<td>$(\text{CH}_3)_2\text{C}=\text{CH}=\text{CH}=\text{C(CH}_3)_3$</td>
<td>26.9</td>
</tr>
<tr>
<td>ethyne</td>
<td>$\text{CH}=\text{CH}$</td>
<td>74.4</td>
</tr>
<tr>
<td>propyne</td>
<td>$\text{CH}_3\text{C}=\text{CH}$</td>
<td>69.1</td>
</tr>
<tr>
<td>1,2-propadiene</td>
<td>$\text{CH}_2=\text{C}=\text{CH}_2$</td>
<td>71.3</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>$\text{CH}_2=\text{CH}=\text{CH}=\text{CH}_2$</td>
<td>57.1</td>
</tr>
<tr>
<td>1,3-pentadiene</td>
<td>$\text{CH}_3\text{CH}=\text{CH}=\text{CH}=\text{CH}_2$</td>
<td>54.1</td>
</tr>
<tr>
<td>1,4-pentadiene</td>
<td>$\text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2$</td>
<td>60.8</td>
</tr>
</tbody>
</table>
2. Trans isomers of 1,2-dialkyl-substituted ethenes evolve less heat (are more stable) than the corresponding cis isomers. This is the result of molecular overcrowding in the cis isomers from nonbonded interactions between two alkyl groups on the same side of the double bond. The effect amounts to almost 10 kcal mol⁻¹ with two cis-tert-butyl groups. This effect is another manifestation of steric hindrance and can be seen most clearly with space-filling models (Figure 11-3).

3. Conjugated dienes are more stable than isolated dienes (compare 1,3- and 1,4-pentadiene).

4. Cumulated dienes appear to be less stable than conjugated or isolated dienes (see 1,2-propadiene).

**Exercise 11-5** Use bond energies to explain the following facts:

a. Ethyne is more easily hydrogenated catalytically than nitrogen.

b. Ethyne is more easily hydrogenated catalytically than ethene.

c. Ethene is more easily hydrogenated catalytically than methanal (CH₂O).

d. In the hydrogenation of nitrogen, ammonia is formed; in contrast, the hydrogenation of ethyne leads to ethane, not methane.
Exercise 11-6  

**a.** Would you expect a carbon–nitrogen triple bond to be hydrogenated more, or less, easily than a carbon–carbon triple bond? 

**b.** Why is it difficult to hydrogenate a tetrasubstituted alkene such as 2,3-dimethyl-2-butene?

Exercise 11-7* Accurate $\Delta H^\circ$ and $\Delta G^\circ$ values in kcal mole$^{-1}$ for hydrogen addition to 1-butene, cis- and trans-2-butene in the gas phase at 25° follow:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta G^\circ$ (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2=\text{CHCH}_2\text{CH}_3$</td>
<td>-30.12</td>
<td>-12.94</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)</td>
<td>-28.48</td>
<td>-11.64</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)</td>
<td>-27.48</td>
<td>-10.95</td>
</tr>
</tbody>
</table>

**a.** From the data (and after reviewing Section 4-4B), calculate $\Delta S^\circ$ for each of these reactions at 25° (298°K). Why is $\Delta S^\circ$ so large for these reactions? 

**b.** Calculate $\Delta H^\circ$, $\Delta G^\circ$, and $\Delta S^\circ$ for $\text{CH}_2=\text{CHCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3$ (trans) and for $\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis) $\rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3$ (trans). Are the $\Delta S^\circ$ values in accord with your expectations? What can you conclude as to how good a qualitative measure heats of hydrogenation are of relative alkene stabilities?

---

11-4 HYDROGENATION WITH HOMOGENEOUS CATALYSTS

Hydrogen addition to multiple bonds is catalyzed by certain complex metal salts *in solution*. This may be described as *homogeneous* catalysis and, compared to heterogeneous catalysis, is a relatively new development in the area of hydrogenation reactions. Rhodium and ruthenium salts appear to be generally useful catalysts:

\[
\text{H}_2 + \text{C} \equiv \text{C} \xrightarrow{\text{RH}(I) \text{ or Ru}(II)} \text{C} \equiv \text{C} 
\]

At present, homogeneous catalysis for routine hydrogenation reactions offers little advantage over the convenience and simplicity of heterogeneous catalysis. Suprafacial addition of hydrogen is observed with both types of catalytic systems. However, greater selectivity can be achieved with homogeneous catalysts because they appear to be more sensitive to steric hindrance and are less likely to cause rearrangement, dissociation, and hydrogenation of other bonds (e.g., $\text{-NO}_2$ and $\text{C} \equiv \text{O}$).

The most thoroughly investigated homogeneous hydrogenation catalyst is the four-coordinate rhodium complex $\text{Rh}[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cl}$. This catalyst is called...
Wilkinson's catalyst after its discoverer, G. Wilkinson. In 1973, the Nobel Prize in chemistry was awarded jointly to Wilkinson and E. O. H. Fischer for their respective contributions to the field of organometallic chemistry. As you will see in this and later chapters, compounds with carbon-metal bonds (organometallic compounds) are extremely useful reagents, reactive intermediates, or catalysts in organic reactions. To a very large extent, the work of Fischer and Wilkinson created the current interest and developments in the field of transition-metal organic chemistry, which will be discussed in Chapter 31.

11-5 HYDROGENATION WITH DIIMIDE

There are alternative ways to add hydrogen to a multiple bond besides the catalytic methods described in the previous sections. The most useful of these are homogeneous reactions utilizing diimide, HN=NH, and diborane, B₂H₆.

The behavior and reactivity of diimide can be understood best by considering the thermochemistry of hydrogenation of nitrogen:

\[
\begin{align*}
N≡N + H₂ &\longrightarrow HN=NH & \Delta H^0 = +43.2 \text{ kcal} \\
HN=NH + H₂ &\longrightarrow H₂NNH₂ & \Delta H^0 = -21.6 \text{ kcal} \\
H₂NNH₂ + H₂ &\longrightarrow 2 \text{ NH₃} & \Delta H^0 = -43.6 \text{ kcal}
\end{align*}
\]

The first step is strongly endothermic and is the main hurdle to overcome in the hydrogenation of nitrogen to ammonia. Conversely, the reverse reaction, which is the dehydrogenation of diimide, is strongly exothermic. Therefore we may expect that diimide will have a pronounced tendency to revert to molecular nitrogen. This is in fact so and, at normal temperatures, diimide exists only as a transient intermediate that cannot be isolated. It is extremely reactive and readily transfers hydrogen to carbon–carbon multiple bonds:

\[
\begin{align*}
\text{C=CH} &\xrightarrow{\text{HN=NH}} \text{C=CH} + N₂ \\
\text{C≡C} &\xrightarrow{\text{HN=NH}} \text{HC=CH} + N₂
\end{align*}
\]

In practice, diimide is generated as it is needed in the presence of the compound to be hydrogenated. There are various ways to do this, but one of the
simplest methods is dehydrogenation of hydrazine with oxidizing agents such as atmospheric oxygen or hydrogen peroxide:

\[
\text{H}_2\text{N—NH}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HN=NH} + 2\text{H}^\oplus + 2\text{e}^\ominus
\]

Hydrazine actually has been used as a hydrogenating agent for over sixty years, but it was not until the 1960's that the diimide intermediate in such reactions was recognized.

The hydrogenation step is stereospecific and transfers hydrogen in the suprafacial manner. For example, alkynes are converted to cis-alkenes:

\[
\begin{align*}
\text{diphenylethyne} & \quad \text{H}_2\text{NNH}_2 + \text{oxidant} \quad \text{cis-1,2-diphenylethene} \\
\text{cis-stilbene} & 
\end{align*}
\]

There are no detectable intermediate stages or rearrangements in diimide hydrogenation. The reaction is visualized as a six-center (pericyclic) process in which the bonds are broken and made in a concerted fashion:

An important difference between diimide hydrogenation and catalytic hydrogenation is that diimide will react only with symmetrical or nonpolar bonds (C=C, C≡C, N=N), whereas hydrogen can add, albeit reluctantly, to polar bonds (C=O, C=N). Diimide does not attack the stronger polar bonds probably because it does not survive long enough to do so. It self-destructs in the absence of a reactive substrate to give nitrogen and hydrazine:
Exercise 11-8 Consider that it is necessary to synthesize pure samples of $\text{D,L-hexane-3,4-D}_2$ and $\text{meso-hexane-3,4-D}_2$. Show how this might be done both with diimide and catalytic-type reductions, assuming that any necessary deuterium-labeled reagents and six-carbon organic compounds are available.

11-6 ADDITION OF BORON HYDRIDES TO ALKENES. ORGANOBORANES

An especially valuable group of intermediates can be prepared by addition of an $\text{H—B}$ compound to carbon–carbon double or triple bonds:

\[
\begin{align*}
\text{C}═\text{C} + \text{H—B} & \rightarrow \text{H—C—C—BR}_2 \\
\text{C}≡\text{C} + \text{H—B} & \rightarrow \text{C≡C}
\end{align*}
\]

The reaction is called hydroboration and is a versatile synthesis of organoboron compounds. One example is the addition of diborane, $\text{B}_2\text{H}_6$, to ethene. Diborane behaves as though it is in equilibrium with $\text{BH}_3$ ($\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$), and addition proceeds in three stages:

\[
\begin{align*}
\text{CH}_2═\text{CH}_2 + \text{BH}_3 \text{ (from } \text{B}_2\text{H}_6) & \rightarrow \text{CH}_3\text{CH}_2\text{BH}_2 \quad \text{ethylborane} \\
\text{CH}_2═\text{CH}_2 + \text{CH}_3\text{CH}_2\text{BH}_3 & \rightarrow (\text{CH}_3\text{CH}_2)_2\text{BH} \quad \text{diethylborane} \\
\text{CH}_2═\text{CH}_2 + (\text{CH}_3\text{CH}_2)_2\text{BH} & \rightarrow (\text{CH}_3\text{CH}_2)_3\text{B} \quad \text{triethylborane}
\end{align*}
\]

The monoalkylborane, $\text{RBH}_2$, and the dialkylborane, $\text{R}_2\text{BH}$, seldom are isolated because they rapidly add to the alkene. These additions amount to reduction of both carbons of the double bond:

\[
\begin{align*}
\text{CH}_2═\text{CH}_2 + \text{B—H} & \rightarrow \text{CH}_3—\text{CH}_2—\text{B}
\end{align*}
\]

Organoboranes can be considered to be organometallic compounds. Elemental boron does not have the properties of a metal, and boron–carbon
bonds are more covalent than ionic. However, boron is more electropositive than either carbon or hydrogen and when bonded to carbon behaves like most metals in the sense that \( R-B \) bonds are polarized with R negative and boron positive:

\[
\delta^+ \quad \delta^+
\]

R → B

Hydroboration and the many uses of organoboranes in synthesis were developed largely by H. C. Brown and co-workers. In our discussion, we shall give more detail on hydroboration itself, and then describe several useful transformations of organoboranes.

11-6A Hydroboration

The simplest borane, \( \text{BH}_3 \), exists as the dimer, \( \text{B}_2\text{H}_6 \), or in complexed form with certain ethers or sulfides:

\[
\begin{aligned}
\text{B}_2\text{H}_6 & \quad \text{H}_3\text{B} \quad \text{O} \\
\text{borane} & \quad \text{borane-oxacyclopentane} \\
& \quad \text{(borane-tetrahydrofuran)}
\end{aligned}
\]

Any of these \( \text{BH}_3 \) compounds adds readily to most alkenes at room temperature or lower temperatures. The reactions usually are carried out in ether solvents, although hydrocarbon solvents can be used with the borane-dimethyl sulfide complex. When diborane is the reagent, it can be generated either in situ or externally through the reaction of boron trifluoride with sodium borohydride:

\[
\text{NaBH}_4 + 4\text{BF}_3 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{NaBF}_4
\]

Hydroborations have to be carried out with some care, because diborane and many alkylboranes are highly reactive and toxic substances; many are spontaneously flammable in air.

With unsymmetrical alkenes, hydroboration occurs so that boron becomes attached to the less-substituted end of the double bond:

\[
\begin{aligned}
\text{RCH} = \text{CH}_2 & \quad \text{H} \rightarrow \text{B} \\
\text{preferred orientation}
\end{aligned}
\]

\[
\text{RCH} = \text{CH}_2 \quad \rightarrow \quad \text{RCH}_2\text{CH}_2\text{B}
\]
These additions are *suprafacial additions*:

Furthermore, when there is a choice, addition occurs preferentially from the less crowded side of the double bond:

If the alkene is a bulky molecule, borane may add only one or two alkene molecules to give either mono- or dialkylborane, RBH₂ or R₂BH, respectively, as the following reactions show:

These bulky boranes still possess B–H bonds and can add further to a multiple bond, but they are highly selective reagents and add only if the alkene or alkyne is unhindered. This selectivity can be useful, particularly in additions
to 1-alkynes, which are difficult to stop at the alkenylborane stage when using diborane:

\[
\text{CH}_3(\text{CH}_2)_3\text{C} \equiv \text{CH} + \text{R}_2\text{BH} \rightarrow \text{CH}_3(\text{CH}_2)_3\text{C} = \text{C} \quad \text{R} = (\text{CH}_3)_2\text{CHCH}\_\_\_\_ \quad \text{H} \quad \text{H} \quad \text{BR}_2
\]

With a bulky dialkylborane, such as di-(1,2-dimethylpropyl)borane, further addition to the alkenylborane does not occur.

An especially selective hydroborating reagent is prepared from 1,5-cyclooctadiene and borane. The product is a bicyclic compound of structure 1 (often abbreviated as 9-BBN), in which the residual B–H bond adds to unhindered alkenes with much greater selectivity than is observed with other hydroborating reagents. It is also one of the few boranes that reacts sufficiently slowly with oxygen that it can be manipulated in air.

An example of the difference in selectivity in the hydroboration of cis-4-methyl-2-pentene with \( \text{B}_2\text{H}_6 \) and 1 follows:

\[
\begin{align*}
\text{CH}_3-\text{C} \equiv \text{C} & \quad \text{orientation of addition with } \text{BH}_3 (\text{B}_2\text{H}_6) \\
\text{CH}_3-\text{CH} & \quad \text{orientation of addition with 9-BBN}
\end{align*}
\]

Exercise 11-9 a. Show how 1 is formed by hydroboration of 1,5-cyclooctadiene.

b. What product would you anticipate from the hydroboration of 2,4-dimethyl-1,4-pentadiene with BH\(_3\)?

c. Explain why diborane adds to methylcyclohexene to give tris-(trans-2-methyl-cyclohexyl)borane in preference to the cis isomer.
11-6B Mechanism of Hydroboration

According to the electronegativity chart (Figure 10-1), the boron–hydrogen bond is polarized in the sense \( \text{B} \rightarrow \text{H} \). Therefore the direction of addition of \( \text{B}_2\text{H}_6 \) to propene is that expected of a polar mechanism whereby the electrophilic boron atom becomes bonded to the less-substituted carbon of the double bond.

**Stepwise mechanism**

\[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{B} \rightarrow \text{H} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 \text{B} \rightarrow \text{R}
\]

However, there is no firm evidence to suggest that a carbocation intermediate is formed through a stepwise electrophilic addition reaction. For this reason, the reaction often is considered to be a four-center concerted addition.

**Concerted mechanism**

\[
\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{B} \rightarrow \text{R}} \text{CH}_3\text{CH} = \text{CH}_2 \text{B} \rightarrow \text{R}
\]

The stepwise formulation explains why boron becomes attached to the less-substituted carbon, but does not account for the fact that the reactions show no other characteristics of carbocation reactions. This could be because of an expected, extraordinarily fast rate of hydride-ion transfer to the carbocation. A more serious objection to the stepwise mechanism is that alkynes react more rapidly than alkenes, something which normally is not observed for stepwise electrophilic additions (cf. Section 10-5).

11-6C Isomerization of Alkylboranes

Some alkylboranes rearrange at elevated temperatures \((160^\circ)\) to form more stable isomers. For example, the alkylborane 2, produced by hydroboration
of 3-ethyl-2-pentene, rearranges to 3 on heating:

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad \text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{C}≡\text{CHCH}_3 & \quad \stackrel{\text{R}_2\text{BH}}{\text{25}°} \quad \text{CH}_3\text{CH}_2\text{CHCHCH}_2 \\
\text{CH}_2\text{CH}_3 & \quad \text{160}° \\
\end{align*}
\]

In general, the boron in alkylboranes prefers to be at the end of a hydrocarbon chain so it is bonded to a primary carbon where steric crowding around boron is least severe. Thus rearrangement tends to proceed in the direction

\[
\begin{align*}
\text{C—C—C—C—C} & \quad \rightarrow \quad \text{C—C—C—C—B} \\
\text{R—B—R} & \\
\end{align*}
\]

Rearrangement is associated with the fact that hydroboration is reversible at elevated temperatures. This makes possible a sequence of elimination-addition reactions in which boron becomes attached to different carbons and ultimately leads to the most stable product that has boron bonded to the carbon at the end of the chain:

\[
\begin{align*}
\text{C—C—C—C—C} & \quad \Leftrightarrow \quad \text{C—C—C≡C—C} & \quad \Leftrightarrow \quad \text{C—C—C—C—C} \\
\text{R—B—H} & \quad \text{H—B—R} & \quad \text{R—B—H} \\
\end{align*}
\]

Rearrangement of alkylboranes can be used to transform alkenes with double bonds in the middle of the chain into less stable 1-alkenes; for
example, RCH═CHCH₃ → RCH₂→CH=CH₂. The procedure involves hydroboration of the starting alkene in the usual manner; the borane then is isomerized by heating. An excess of 1-decene (bp 170°) then is added to the rearranged borane and the mixture is reheated. Heating causes the alkylborane to dissociate into 1-alkene and HBR₂; the 1-decene “scavenges” the HBR₂ as it forms, thereby allowing a more volatile 1-alkene (bp < 170°) to be removed by simple distillation. Thus, for the rearrangement of 3-ethyl-2-pentene to 3-ethyl-1-pentene,

\[
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \rightarrow \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \quad 160°
\]

\[
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{B} \equiv \text{R} \rightarrow \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \quad 160°
\]

Exercise 11-10 What products would you expect from hydroboration of the following alkenes with a dialkylborane, R₂BH, followed by isomerization at 160°?

a. CH₃CH=CHCH₃

b. CH₃CH₃CH=CH=CH₂CH₃

c. CH₃CH₃CH=CHCH₃

d. \[
\text{CH}_3.\text{CH}_3\text{CH}_3\text{CH}_3
\]

11-6D Synthetic Reactions of Organoboranes

Alkylboranes formed in the hydroboration of alkenes and alkynes seldom are isolated; for the most part they are used as reactive intermediates for the synthesis of other substances. In the reactions of alkylboranes, the B−C bond
is cleaved in the sense $\text{B}^\ominus - \text{C}^\ominus$ so that carbon is transferred to other atoms, such as H, O, N, and C, with its bonding electron pair:

$$\text{R}_3\text{B} \xrightarrow{\text{H}^\ominus, \text{H}_2\text{O}} 3\text{RH} + \text{B(OH)}_3$$  \hspace{1cm} (11-2)
$$\text{R}_3\text{B} \xrightarrow{\text{H}_2\text{O}_2, \text{OH}} 3\text{ROH} + \text{B(OH)}_3$$  \hspace{1cm} (11-3)
$$\text{R}_3\text{B} \xrightarrow{\text{H}_2\text{N} - \text{OSO}_3\text{H}} 3\text{RNH}_2 + \text{B(OH)}_3 + \text{H}_2\text{SO}_4$$  \hspace{1cm} (11-4)

In the first of these reactions (Equation 11-2), a hydrocarbon is produced by the cleavage of a borane, $\text{R}_3\text{B}$, with aqueous acid, or better, with anhydrous propanoic acid, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$. The overall sequence of hydroboration–acid hydrolysis achieves the reduction of a carbon-carbon multiple bond without using hydrogen and a metal catalyst or diimide (Table 11-3):

The second reaction (Equation 11-3) achieves the synthesis of a primary alcohol by the oxidation of the alkylborane with hydrogen peroxide in basic solution. Starting with a 1-alkene, one can prepare a primary alcohol in two steps:

$$\text{R'}\text{CH}=\text{CH}_2 \xrightarrow{\text{R}^\ominus, \text{HB}} \text{R'}\text{CH}_2\text{CH}_2\text{B} \xrightarrow{\text{R}^\ominus, \text{H}_2\text{O}} \text{R'}\text{CH}_2\text{CH}_3$$

This sequence complements the direct hydration of 1-alkenes, which gives secondary alcohols:

$$\text{R'}\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^\ominus} \text{R'}\text{CHCH}_3$$

Hydroboration of an alkene and subsequent reactions of the product trialkylborane, either with hydrogen peroxide or with acid, appear to be highly stereospecific. For example, 1-methylcyclopentene gives exclusively trans-2-methylcyclopentanol on hydroboration followed by reaction with alkaline
### Table 11-3
Some Methods of Hydrogenation of Carbon–Carbon Multiple Bonds

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>Heterogeneous catalytic hydrogenation</strong></td>
<td></td>
</tr>
</tbody>
</table>
| \[
\begin{align*}
    &\text{C} = \text{C} + \text{H}_2 \xrightarrow{\text{Pt}} \text{C} - \text{C} \\
    &\text{C} = \text{C} + \text{H}_2 \xrightarrow{\text{Pd-Pb}} \text{C} - \text{C} \\
\end{align*}
\] |
| Requires a transition metal catalyst, Pt, Pd, Ni, etc. Addition is suprafacial from least hindered side. Rearrangements can occur. Alkynes are reduced to cis-alkenes over Lindlar catalyst, Pd–Pb (Section 11-2). |

2. **Homogeneous catalytic hydrogenation** |
| \[
\begin{align*}
    &\text{C} = \text{C} + \text{H}_2 \xrightarrow{\text{RhL}_3\text{Cl}} \text{C} - \text{C} \\
    &\text{L}=\text{triphenylphosphine}
\end{align*}
\] |
| Catalyst is a soluble complex salt of rhodium or ruthenium; suprafacial addition occurs to the least hindered double bond (Section 11-4). |

3. **Diimide reduction** |
| \[
\begin{align*}
    &\text{C} = \text{C} + \text{HN} = \text{NH} \rightarrow \text{C} - \text{C} + \text{N}_2 \\
\end{align*}
\] |
| Diimide is generated *in situ* by oxidation of H$_2$NNH$_2$; suprafacial addition occurs (Section 11-5). |

4. **Hydroboration–Protolysis** |
| \[
\begin{align*}
    &\text{C} = \text{C} + \text{R}_2\text{BH} \rightarrow \text{C} - \text{C} \xrightarrow{\text{H}^\circ} \text{C} - \text{C} \\
\end{align*}
\] |
| Hydroboration is suprafacial; protolysis occurs with retention (Section 11-6). |

hydrogen peroxide. This indicates that, overall, *the reactions result in suprafacial addition of water to the double bond*:

\[
\begin{align*}
\text{1-methylcyclopentene} & \quad 1. \quad \text{B}_2\text{H}_6 \\
\text{2.} & \quad \text{H}_2\text{O}_2,\text{OH} \\
\end{align*}
\]

Hydroboration of an alkyne followed by treatment of the alkenylborane with basic peroxide provides a method of synthesis of aldehydes and ketones.
Thus hydroboration of 1-hexyne and oxidation of the 1-hexenylborane, 4, with hydrogen peroxide gives hexanal by way of the enol:

\[
\begin{align*}
C_4H_9C≡CH & \xrightarrow{R_2BH} C_4H_9\overset{C}{\xrightarrow{\text{H}}} C & \xrightarrow{\text{H}_2\text{O}_2, \overset{\text{OH}}{\text{OH}}} \\
& & \text{4} \\
& & \left[ C_4H_9\text{CH}=\overset{\text{CHOH}}{\text{CHOH}} \right] \rightarrow C_4H_9\text{CH}_2\text{CHO} \\
& & \text{hexanal}
\end{align*}
\]

If 4 is treated with deuteriopropanoic acid, replacement of —BR_2 by deuterium occurs with retention of configuration, forming trans-hexene-1-D_1:

\[
\begin{align*}
\text{4} & \xrightarrow{\text{CH}_3\text{CH}_2\text{CO}_2\text{D}} \text{trans-hexene-1-D}_1
\end{align*}
\]

**Exercise 11-11** Predict the products in each step of the following reaction sequences:

**a.**

\[
\quad \xrightarrow{\text{B}_2\text{H}_6} \xrightarrow{\text{H}_2\text{O}_2, \overset{\text{OH}}{\text{OH}}}
\]

**b.** (CH_3)_2C≡CHCH_3 \xrightarrow{\text{B}_2\text{H}_6} C_2\text{H}_5\text{C≡CC}_2\text{H}_5 \xrightarrow{\text{H}_2\text{O}_2, \overset{\text{OH}}{\text{OH}}}

**c.** (CH_3)_2C≡CHCH_3 \xrightarrow{\text{B}_2\text{H}_6} C_2\text{H}_5\text{C≡CC}_2\text{H}_5 \xrightarrow{\text{CH}_3\text{CH}_2\text{CO}_2\text{D}}

**11-6E Mechanism of Oxidation of Alkylboranes**

The stereospecific oxidation of alkylboranes occurs with hydrogen peroxide by an interesting and important general type of rearrangement which, for these reactions, involves migration of an organic group from boron to oxygen. The first step in the oxidation depends on the fact that tricoordinate boron has only six electrons in its valence shell and therefore behaves as if it were electron-deficient. The first step is bond formation at boron by the strongly nucleophilic
perroxide anion (from $\text{H}_2\text{O}_2 + \text{OH}^- \leftrightarrow \text{OOH} + \text{H}_2\text{O}$) to give a tetracovalent boron intermediate:

\[
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{OOH} \\
\text{R}
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{R}
\end{array}
\]

In the second step, an alkyl group moves with its bonding electron pair from boron to the neighboring oxygen and, in so doing, displaces hydroxide ion. *The stereochemical configuration of the migrating R group is retained:*

\[
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{O} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{OH} \\
\text{R}
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{O} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{OH} \\
\text{R}
\end{array}
\]

(11-5)

Reaction is completed by hydrolysis of the B–O bond:

\[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{R}_2\text{B}=-\text{OR} + \text{OH}^- \\
\rightarrow \\
\text{R}_2\text{B} \rightarrow \text{OR} \\
\rightarrow \\
\text{R}_2\text{B} \rightarrow \text{O}^- + \text{HOR}
\end{array}
\]

All three groups on boron are replaced in this manner.

The rearrangement step (Equation 11-5) is an example of many related rearrangements in which a group, R, migrates with its bonding electrons from one atom to an adjacent atom. We already have encountered an example in the rearrangement of carbocations (Section 8-9B):

The difference between the carbocation rearrangement and the rearrangement of Equation 11-5 is that R migrates from boron to oxygen as HO$^-$ departs in what might be considered an internal S$_\text{N}$2 reaction. We can generalize this kind of reaction of boron with a substance, X–Y, as in Equation 11-6:

\[
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{X} \\
\text{Y}
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{X} \\
\text{Y}
\end{array}
\begin{array}{c}
\text{R} \\
\text{Y} \\
\text{R}
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \\
\text{B} \\
\text{X} \\
\text{Y}
\end{array}
\begin{array}{c}
\text{R} \\
\text{X} \\
\text{R}
\end{array}
\]

(11-6)

An example of the use of an X–Y reagent is conversion of alkylboranes to primary amines with hydroxylaminesulfonic acid, $\text{H}_2\text{NOSO}_3\text{H}$ (Equation 11-4). The key steps are attack of the nucleophilic nitrogen at boron,
followed by rearrangement,

\[
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{N} \quad \text{H} \quad \text{Y} \\
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\end{array}
\xrightarrow{\text{O}}
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{N} \quad \text{H} \\
\text{R} \quad \text{R} \quad \text{R} \\
\end{array}
\xrightarrow{\text{Y}}
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{N} \quad \text{H} \\
\text{R} \quad \text{R} \\
\end{array}
\xrightarrow{\text{HY}}
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{N} \quad \text{H} \\
\text{R} \\
\end{array}
\]

and hydrolysis,

\[
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{N} \quad \text{H} \\
\text{R} \\
\end{array}
\xrightarrow{\text{H}_2\text{O}}
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{O} \\
\text{R} \\
\end{array}
\xrightarrow{\text{RNH}_2}
\begin{array}{c}
\text{R} \quad \text{B} \quad \text{O} \\
\text{R} \\
\end{array}
\]

**Exercise 11-12**

a. Draw the structure and configuration of the product expected of the reaction between 1-bromo-1-hexyne and diethylborane, \((\text{C}_2\text{H}_5)_2\text{BH}\).

b. When the product is treated with sodium methoxide, \(\text{NaOCH}_3\), then with propanoic acid, trans-3-octene is formed. Show the steps involved in forming this trans-alkene.

---

**11-7 OXIDATION REACTIONS**

**11-7A Ozonization**

Most alkenes react readily with ozone \((O_3)\), even at low temperatures, to yield cyclic peroxidic derivatives known as **ozonides**. For example,

\[
\text{CH}_3\text{CH=CHCH}_3 \xrightarrow{\text{O}_3, 80^\circ} \text{CH}_3\text{CH}_2\text{CHCH}_3
\]

2-butene ozonide

These substances, like most compounds with peroxide \((O=O)\) bonds, may explode violently and unpredictably. Therefore ozonizations must be carried out with appropriate caution. The general importance of these reactions derives not from the ozonides, which usually are not isolated, but from their subsequent products. The ozonides can be converted by hydrolysis with water and reduction, with hydrogen (palladium catalyst) or with zinc and acid, to carbonyl compounds that can be isolated and identified. For example, 2-butene
gives ethanal on ozonization, provided the ozonide is destroyed with water and a reducing agent which is effective for hydrogen peroxide:

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{H}_2\text{O}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C} = \text{O} + \text{CH}_3\text{CH} + \text{H}_2\text{O}_2 + \text{Zn, } \text{H}^\circ \quad (\text{or } \text{H}_2, \text{ Pd}) \quad 2\text{H}_2\text{O}
\]

An alternative procedure for decomposing ozonides from di- or trisubstituted alkenes is to treat them with methanol (CH₃OH). The use of this reagent results in the formation of an aldehyde or ketone and a carboxylic acid:

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{C} = \text{O} + \text{CH}_3\text{COCH}_3
\]

The overall ozonization reaction sequence provides an excellent means for locating the positions of double bonds in alkenes. The potentialities of the method may be illustrated by the difference in reaction products from the 1- and 2-butenes:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 & \xrightarrow{1. \text{ O}_3} \text{CH}_3\text{CH}_2\text{C} = \text{O} \\
& \text{(propanal)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CHCH}_3 & \xrightarrow{1. \text{ O}_3} \xrightarrow{2. \text{H}_2, \text{ Pd}} 2\text{CH}_3\text{C} = \text{O} \\
& \text{(ethanal)}
\end{align*}
\]

**Exercise 11-13** A hydrocarbon of formula C₁₁H₁₈ on reaction with ozone in dichloromethane gave, after the addition of water and finely divided zinc, three products in equimolar amounts that were identified as 2-butanone (CH₃COCH₂CH₃), methanal (CH₂O), and cyclohexane-1,4-dione (O=\(\text{C}\)-\(\text{C}\)=O). Draw the structure of the hydrocarbon C₁₁H₁₈.

**11-7B Mechanism of Ozonization**

Ozonization of alkenes has been studied extensively for many years, but there still is disagreement about the mechanism (or mechanisms) involved because
some alkenes react with ozone to give oxidation products other than ozonides. It is clear that the ozonide is not formed directly, but by way of an unstable intermediate called a molozonide. The molozonide then either isomerizes to the “normal” ozonide or participates in other oxidation reactions. Although the structure of normal ozonides has been established beyond question, that of the molozonide, which is very unstable even at $-100^\circ$, is much less certain.

The simplest and most widely accepted mechanism involves formation of a molozonide by a direct cycloaddition of ozone to the double bond.\(^1\)

\[
\text{CH}_3\text{CH}═\text{CHCH}_3 \rightarrow \text{CH}_3\text{CH}—\text{CHCH}_3 \text{ molozonide}
\]

Isomerization of the molozonide appears to occur by a fragmentation-recombination reaction, as shown in Equations 11-7 and 11-8:

\[
\text{CH}_3\text{CH}═\text{CHCH}_3 \rightarrow \text{CH}_3—\text{C} + \text{C—CH}_3 \quad (11-7)
\]

\[
\text{CH}_3\text{O} —\text{O} \text{C—H} \rightarrow \text{CH}_3\text{CH}—\text{HCHCH}_3 \text{ normal ozonide} \quad (11-8)
\]

**Exercise 11-14** When 2-butene reacts with ozone in the presence of 2-propanone, two structurally different ozonides are obtained, as well as ethanal:

\[
\text{CH}_3\text{CH}═\text{CHCH}_3 + \text{CH}_3—\text{C—CH}_3 \rightarrow \text{O}_3
\]

\[
\text{CH}_3—\text{C—CHCH}_3 + \text{CH}_3\text{C—CH—CHCH}_3 + \text{CH}_3—\text{CH}
\]

Suggest how these products can be formed from the molozonide(s) of 2-butene.

\(^1\)The ozone structure shown here with single electrons having paired spins on the terminal oxygens accords both with the best available quantum mechanical calculations and the low dipole moment of ozone, which is not consonant with the conventional $\text{O}═\text{O}—\text{O}$ structure. See W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Accounts of Chemical Research* 6, 368 (1973).
11-7C Hydroxylation of Alkenes

Several oxidizing reagents react with alkenes under mild conditions to give, as the overall result, addition of hydrogen peroxide as HO—OH. Of particular importance are alkaline permanganate (MnO₄⁻) and osmium tetroxide (OsO₄), both of which react in an initial step by a suprafacial cycloaddition mechanism like that postulated for ozone.

Each of these reagents produces cis-1,2-dihydroxy compounds (diols) with cycloalkenes:

![Chemical structures](image)

Osmium tetroxide is superior to permanganate in giving good yields of diol, but its use is restricted because it is a very costly and very toxic reagent.

**Exercise 11-15** Alkynes react more slowly than alkenes with permanganate and usually give dicarbonyl compounds. An example follows:
11-7D Oxidation with Peroxidic Compounds. Oxacyclopropane (Oxirane) Formation

Alkenes can be oxidized with peroxycarboxylic acids, \( \text{RCO}_2\text{H} \), to give oxacyclopropanes (oxiranes, epoxides), which are three-membered cyclic ethers:

\[
\begin{align*}
\text{C} &= \text{C}^- + \text{R}^-\text{C}^- \\
\text{O} - \text{OH} &\quad\rightarrow\quad \text{C} = \text{C}^- + \text{R}^-\text{C}^- \\
\text{O} \quad \text{O} - \text{OH} &\quad\text{an oxacyclopropane (oxirane, epoxide)}
\end{align*}
\]

The reaction, known as epoxidation, is valuable because the oxacyclopropane ring is cleaved easily, thereby providing a route to the introduction of many kinds of functional groups. In fact, oxidation of alkenes with peroxymethanoic acid (peroxyformic acid), prepared by mixing methanoic acid and hydrogen peroxide, usually does not stop at the oxacyclopropane stage, but leads to ring-opening and the subsequent formation of a diol:

\[
\begin{align*}
\text{C} &= \text{C}^- + \text{H}_2\text{O}_2 \text{HCO}_2\text{H} &\quad\rightarrow\quad \text{C} = \text{C}^- + \text{H}_2\text{O} \\
\text{O} \quad \text{OH} &\quad\text{not stable under the reaction conditions}
\end{align*}
\]

This is an alternative scheme for the hydroxylation of alkenes (see Section 11-7C). However, the overall stereochemistry is opposite to that in permanganate hydroxylation. For instance, cyclopentene gives \( \text{trans-1,2-cyclopentanediol} \). First the oxirane forms by suprafacial addition and then undergoes ring opening to give the trans product:
The ring opening is a type of $S_{N}2$ reaction. Methanoic acid is sufficiently acidic to protonate the ring oxygen, which makes it a better leaving group, thus facilitating nucleophilic attack by water. The nucleophile always attacks from the side remote from the leaving group:

Exercise 11-16 Starting with cyclohexene, show how you could prepare each of the following compounds: a. the epoxide of cyclohexene, b. cis-cyclohexane-1,2-diol, and c. trans-cyclohexane-1,2-diol.

The peroxyacids that are used in the formation of oxacyclopropanes include peroxyethanoic ($\text{CH}_3\text{C}_2\text{O}_2\text{H}$), peroxybenzoic ($\text{C}_6\text{H}_5\text{C}_2\text{O}_2\text{H}$), and trifluoroperoxyethanoic ($\text{CF}_3\text{C}_2\text{O}_2\text{H}$) acids. A particularly useful peroxyacid is 3-chloroperoxybenzoic acid, because it is relatively stable and is handled easily as the crystalline solid. The most reactive reagent is trifluoroperoxyethanoic acid, which suggests that the peroxyacid behaves as an electrophile (the electronegativity of fluorine makes the $\text{CF}_3$ group strongly electron-attracting). The overall reaction can be viewed as a cycloaddition, in which the proton on oxygen is transferred to the neighboring carbonyl oxygen more or less simultaneously with formation of the three-membered ring:
A reaction of immense industrial importance is the formation of oxacyclopropane itself (most often called ethylene oxide) by oxidation of ethene with oxygen over a silver oxide catalyst at 300°:

\[ \text{CH}_2\text{═CH}_2 + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Ag}_2\text{O} \text{300°}} \text{H}_2\text{C}═\text{CH}_2 \quad \text{(oxirane, ethylene oxide, 1,2-epoxyethane)} \]

Oxacyclopropane is used for many purposes, but probably the most important reaction is ring opening with water to give 1,2-ethanediol (ethylene glycol, bp 197°). This diol, mixed with water, is employed widely in automotive cooling systems to provide both a higher boiling and lower freezing coolant than water alone:

\[ \text{CH}_2\text{═CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{HOCH}_2\text{CH}_2\text{OH} \quad \text{(1,2-ethanediol, ethylene glycol)} \]

A characteristic and synthetically important reaction of ethyne and 1-alkynes is salt ("acetylide") formation with very strong bases. In such reactions the alkyynes behave as acids in the sense that they give up protons to suitably strong bases:

\[ \text{R}═\text{C}═\text{CH}_2 + \text{base} \xleftrightarrow{\text{RC}═\text{C}═\text{CH}_2 + \text{H}^+} \text{RC}═\text{C}═\text{CH}_2 + \text{H}^+ + \text{base} \]

Water is too weak a base to accept protons from alkyynes; consequently no measurable concentration of \( \text{H}_3\text{O}^+ \) is expected from the ionization of alkyynes in dilute aqueous solutions. Therefore we have no quantitative measure of 1-alkyne acidity in aqueous solution other than that it probably is about \( 10^{10} \) times less acidic than water, as judged from measurements in other solvents to be discussed shortly. In the gas phase, however, the situation is reversed, and ethyne is a stronger acid than water:

\[ \text{HC}═\text{CH(aq)} + \text{K}^+\text{OH}^-\text{(aq)} \xleftarrow{\text{H}_2\text{O}} \text{HC}═\text{C}∶\text{K}^+\text{(aq)} + \text{H}_2\text{O} \quad K \ll 1 \]
\[ \text{HC}═\text{CH(g)} + \text{OH}^-(g) \xleftrightarrow{\text{g}} \text{HC}═\text{C}∶\text{H}_2\text{O(g)} \quad K \gg 1 \]
This reversal is of little practical value because organic reactions involving ions normally are not carried out in the gas phase. However, it should alert us to the tremendous role that solvents play in determining acidities by their abilities (some much more than others) to stabilize ions by the property known as solvation. (See Section 11-8A.)

Liquid ammonia is a more useful solvent than water for the preparation of 1-alkyne salts. A substantial amount of the alkyne can be converted to the conjugate base by amide anions (potassium or sodium amide) because a 1-alkyne is a stronger acid than ammonia.

\[
R\equiv C\equiv C: H + K^+ : \overset{\text{amide}}{\overset{\text{potassium}}{\text{NH}_2}} \overset{\text{potassium}}{\overset{\text{NH}_3(l)}{\text{alynide}}}} \rightarrow R\equiv C\equiv C: K^+ + \overset{\text{potassium}}{\overset{\text{amide}}{\text{NH}_3}}
\]

The acidity of the terminal hydrogen in 1-alkynes provides a simple and useful test for 1-alkynes. With silver-ammonia solution (AgNO₃ in aqueous ammonia), 1-alkynes give insoluble silver salts, whereas disubstituted alkynes do not:

\[
R\equiv C\equiv C\equiv H + Ag(NH_3)_2 \rightarrow R\equiv C\equiv C\equiv Ag + NH_3 + NH_4^+
\]

(R = H, alkyl, or aryl)

The silver “acetylides” appear to have substantially covalent carbon-metal bonds and are less ionic than sodium and potassium alkynides. Silver-ammonia solution may be used to precipitate 1-alkynes from mixtures with other hydrocarbons. The 1-alkynes are regenerated easily from the silver precipitates by treatment with strong inorganic acids. It should be noted, however, that silver alkynides may be shock sensitive and can decompose explosively, especially when dry.

---

**Exercise 11-17** Suppose you were given four unlabeled bottles, each of which is known to contain one of the following compounds: pentane, 1-pentene, 2-pentyne, or 1-pentyne. Explain how you could use simple chemical tests (preferably test-tube reactions) to identify the contents of each bottle. (Notice that all four compounds are low-boiling liquids.)

---

**11-8A Thermodynamics of Solvation of Ions and Its Importance**

Some idea of the importance of solvation can be gained from the calculated \(\Delta H\) for the following process:

\[
Na^\ominus(g) + Cl^\ominus(g) \rightarrow Na^\ominus(aq) + Cl^\ominus(aq) \quad \Delta H^0 = -187 \text{ kcal}
\]
The solvation energies of ions are so large that relatively small differences for
different ions can have a very large effect on equilibrium constants. Thus, the
ratio between the relative acidities of ethyne and water in the gas phase and
in water of $10^{15}$ corresponds at $25^\circ$ to an overall $\Delta G^\circ$ difference in solvation
energies of approximately 16 kcal, which is less than 10% of the total solvation
energies of the ions. Further difficulties arise because of differences between
solvation energies and interactions between the ions in different solvents. Thus
the acidities of 1-alkynes relative to other acids have been found to change by
a factor of $10^{11}$ in different solvents. For this reason, we must be particularly
careful in comparing the rates and equilibrium constants of ionic reactions to
take proper account of solvation and ion interaction effects.

An excellent rule of thumb is that, other things being equal, large ions are
more stable than small ions in the gas phase, with the opposite being true in
polar solvents, where small ions are more strongly solvated (thus more stable)
than large ions. For comparison,

1. $\text{Li}^\circ(g) + \text{F}^\circ(g) \rightarrow \text{Li}^\circ(aq) + \text{F}^\circ(aq) \quad \Delta H^\circ = -246 \text{ kcal}$
2. $\text{Li}^\circ(g) + \text{I}^\circ(g) \rightarrow \text{Li}^\circ(aq) + \text{I}^\circ(aq) \quad \Delta H^\circ = -211 \text{ kcal}$
3. $\text{K}^\circ(g) + \text{F}^\circ(g) \rightarrow \text{K}^\circ(aq) + \text{F}^\circ(aq) \quad \Delta H^\circ = -199 \text{ kcal}$
4. $\text{K}^\circ(g) + \text{I}^\circ(g) \rightarrow \text{K}^\circ(aq) + \text{I}^\circ(aq) \quad \Delta H^\circ = -165 \text{ kcal}$

From (1) minus (3), the solvation energy of gaseous $\text{Li}^\circ$ is 47 kcal mole$^{-1}$
greater than $\text{K}^\circ$; and from (1) minus (2), that of $\text{F}^\circ$ is 35 kcal mole$^{-1}$ greater
than of $\text{I}^\circ$. Such differences in solvation energies can have considerable effects
on reactivity, and you may remember from Section 8-7E that $\text{F}^\circ$ is a weaker
nucleophile than $\text{I}^\circ$, largely because of its greater solvation energy. Further
understanding of the energy differences between ions in the gas phase and in
water solution can be gained from Exercise 11-18.

Exercise 11-18* Show how the $\Delta H$ values of the following processes can be com-
bined to calculate the heat of solution of $\text{Na}^\circ(g) + \text{Cl}^\circ(g)$ at 298$^\circ$K.

$$
\begin{align*}
\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) & \rightarrow \text{Na}^\circ(aq) + \text{Cl}^\circ(aq) \quad \Delta H^\circ = -97 \text{ kcal} \\
\text{Na}(g) & \rightarrow \text{Na}^\circ(g) + e^- \quad \Delta H^\circ = +118 \text{ kcal} \\
\text{Cl}^\circ(g) & \rightarrow \text{Cl}^-(g) + e^- \quad \Delta H^\circ = +83 \text{ kcal} \\
\frac{1}{2}\text{Cl}_2(g) & \rightarrow \text{Cl}^-(g) \quad \Delta H^\circ = +29 \text{ kcal} \\
\text{Na}(s) & \rightarrow \text{Na}(g) \quad \Delta H^\circ = +26 \text{ kcal}
\end{align*}
$$

11-8B Why is Ethyne a Stronger Acid than Ethane or Ethene?

If we compare acid strengths of the simple hydrocarbons, we find that ethyne
is substantially more acidic than ethene or ethane in the gas phase or in solu-
tion. Why is this? The simplest explanation is that there is a direct connection
between C—H acidity and the amount of $s$ character associated with the $\sigma$-
bonding carbon orbital. Other things being equal, acidity increases with increasing $s$ character in the carbon orbital.

order of acid strength: \[ \text{HC≡CH} \gg \text{H}_2\text{C}≡\text{CH}_2 \gg \text{H}_3\text{C}—\text{CH}_3 \]

hybrid carbon $\sigma$ orbital: \[ sp \quad sp^2 \quad sp^3 \]

On the average the $s$ electrons are closer to the carbon nucleus than are $p$ electrons. Therefore, the more $s$ character there is to the $\text{C—H}$ bond, the closer the electrons of the bond are, on the average, to the carbon nucleus. This makes it easier to remove the hydrogens as protons. This displacement of the electrons is clearly shown by the GVB orbitals (see Section 6-6) for the hydrogen-bonding orbitals of ethane and ethyne (Figure 11-4).

11-8C Alkynide Anions as Nucleophiles

1-Alkynes are very weak acids, hence their conjugate bases, \( \text{RC≡C}:^- \), are quite strong bases. These anions also are reactive carbon nucleophiles, and it is this property that makes them useful for organic syntheses. Recall from Chapter 8 that one of the most generally useful organic reactions is a displacement reaction in which an anionic nucleophile, \( \text{Nu}^- \), attacks an alkyl de-
11-8D Coupling Reactions of Alkynes

Another reaction of 1-alkynes that extends the carbon chain is a coupling reaction in which the alkyne dimerizes under the influence of a cuprous salt, usually cuprous ammonium chloride:

\[
\text{HC} \equiv \text{CH} + \text{Cu(NH}_3\text{)}_2^+\text{Cl}^- \rightarrow \text{HC} \equiv \text{C} \equiv \text{CH} - \text{CH} 
\]

butenyne (vinylacetylene)

This addition of one molecule of alkyne to another is formally analogous to the dimerization of alkenes under the influence of sulfuric acid (see Section 10-9), but the mechanisms are quite different.

If the reaction is carried out in the presence of an oxidizing agent, such as O\(_2\), or a cupric salt dissolved in pyridine (a weak base), a different product is obtained. Under these conditions, oxidative coupling occurs to give a conjugated diyne:

\[
\text{HC} \equiv \text{CH} + 2\text{Cu}^{(II)} \rightarrow \text{HC} \equiv \text{C} \equiv \text{C} \equiv \text{CH}
\]

butadiyne

Although the details of the mechanisms of these alkyne reactions are not known, it is likely that the ability of 1-alkynes to form carbon-metal bonds with metals such as copper is a key factor.

Other oxidative coupling reactions occur with transition metals, and this will be discussed in detail in Chapter 31.

Exercise 11-19 A serious contaminant in butenyne made by dimerization of ethyne with cuprous ion is 1,5-hexadien-3-yne. Show how this substance can be formed.
Additional Reading


R. J. Kokes, “Characterization of Adsorbed Intermediates on Zinc Oxide by Infrared Spectroscopy,” Accounts of Chemical Research 6, 226 (1973). This article is rather mistitled and actually is concerned mostly with the mechanism of heterogeneous hydrogenation of alkenes.


Supplementary Exercises

11-20 The following physical properties and analytical data pertain to two isomeric hydrocarbons, A and B, isolated from a gasoline:

<table>
<thead>
<tr>
<th></th>
<th>bp, °C</th>
<th>mp, °C</th>
<th>%C</th>
<th>%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>68.6</td>
<td>-141</td>
<td>85.63</td>
<td>14.34</td>
</tr>
<tr>
<td>B</td>
<td>67.9</td>
<td>-133</td>
<td>85.63</td>
<td>14.34</td>
</tr>
</tbody>
</table>

Both A and B readily decolorize bromine and permanganate solutions and give the same products on ozonization. Suggest possible structures for A and B. What experiments would you consider necessary to further establish the structures and configurations of A and B?

11-21 It is possible to synthesize two isomeric cycloalkenes of formula C₆H₁₂. Both of these compounds react with hydrogen in the presence of platinum to give cyclooctane, and each, on ozonization followed by reduction, gives:

\[
\text{O} \quad \text{O}
\]

\[
\text{H} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{C} \quad \text{H}
\]

a. What are the structures of the two compounds?

b. Would the two substances give the same compound on hydroxylation with potassium permanganate?

11-22 When 5-decyne is heated with diborane at 160° and the product is oxidized with hydrogen peroxide in basic solution, 1,10-decanediol is obtained. Write equations to show the several reactions involved in these transformations. You need not show detailed mechanisms.
Supplementary Exercises

11-23  a. Draw the structures and configurations of the products that will be formed by the following reactions of cis-2-butene-2-D:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{D} & \quad \text{H}
\end{align*}
\]

\[
\text{aqueous KMnO}_4, \text{pH 7.5}
\]

\[
\text{H}_2\text{O}_2, \text{HCO}_2\text{H}
\]

b. What is the stereochemical relationship between the products of the two reactions in Part a?

11-24* Show the structures of the products expected in each step of the following sequences. Be sure to indicate the stereochemistry of reactions where this is important. Remember that D is the hydrogen isotope of mass 2.

a. \(\text{cis-2-butene} \xrightarrow{\text{D}_3\text{NND}_2} \)

b. \(\text{1-methylcyclohexene} \xrightarrow{\text{BH}_3} 160^\circ \xrightarrow{\text{H}_2\text{O}_2, \text{G} \text{OH}} \)

c. \(\text{CH}_3 \xrightarrow{\text{BH}_3} \text{CH}_3\text{CH}_2\text{CO}_2\text{D} \)

d. \(\text{propyne} \xrightarrow{\text{R}_2\text{BD}} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \xrightarrow{\text{O}_3} \text{H}_2\text{O}, \text{Zn} \)

e. \(\text{2-butyne} \xrightarrow{\text{R}_2\text{BH}} \text{H}_2\text{O}_2, \text{G} \text{OH} \)

f. \(\text{CH}_3\text{C}\equiv\text{CH} \xrightarrow{\text{R}_2\text{BD}} \text{CH}_3\text{CH}_2\text{CO}_2\text{D} \)

g. \(\text{3-methylcyclopentene} \xrightarrow{\text{BH}_3} 160^\circ \xrightarrow{\text{CH}_3(\text{CH}_2)\text{C}\equiv\text{CH}_2} \text{(as trapping agent)} \)

h. \(\text{1-pentene} \xrightarrow{\text{HBr, peroxides}} \text{CH}_3\text{C}\equiv\text{CNa} \xrightarrow{\text{H}_2, \text{Pd-Pb}} \text{O}_3 \xrightarrow{\text{Na}_2\text{SO}_3} \)

i. \(\text{1-pentene} \xrightarrow{\text{BH}_3} \text{H}_2\text{N}-\text{OSO}_3\text{H} \)

11-25 Two stable compounds of formula \(\text{C}_6\text{H}_8\) react with bromine and with \(\text{KMnO}_4\). On hydrogenation with a platinum catalyst at 25°, both absorb two moles of hydrogen and form cyclohexane. Write possible structures for these substances and explain how electronic spectra may be used to tell which compound is which.

11-26 Suppose one added hydrogen as \(\text{H}_2\) to the cyclopropene double bond of 1-methoxy-2-phenyl-3,3-dimethylcyclopropene. Explain how the proton nmr of the product can be used to infer whether the hydrogen added to the double bond in the suprafacial or antarafacial manner. (Review Section 9-10G and 9-10H.)
11-27 In the hydrogenation of 1,2-dimethylcyclohexene over a platinum catalyst, the suprafacial addition product is formed. Assuming that the mechanism of this hydrogenation is as shown in Figure 11-2, what conditions must be put on the stereochemistry of each of the postulated steps in order that the overall reaction be suprafacial?

11-28* When optically active 3-methylhexane is shaken with a nickel catalyst in the presence of deuterium gas (D₂ = ²H₂), it, like other alkanes, undergoes slow exchange of hydrogen for deuterium at the various carbons. The key observation is that substitution of D for H at C₃ causes racemization, (i.e., formation of equal amounts of deuterated 3-methylhexane with the two possible configurations at C₃). Assuming that racemization and deuterium exchange occur only by way of the steps shown in Figure 11-2, determine how many steps backward the reaction has to go to produce the racemized, exchanged 3-methylhexane. To work this problem you will need to determine whether, when one starts with optically active 3-methylhexane, the various possible intermediate structures in Figure 11-2 would be chiral or not and how many steps back one would have to go to get to an achiral system. If you are uncertain about chirality we suggest that you review Section 5-1B.

11-29 Calculate ΔH⁰ for the reaction \( \text{CH}_3-\text{C}≡\text{C}-\text{H} \rightarrow \text{CH}_2-\text{C}≡\text{CH}_2 \) from bond energies and also from ΔH⁰ values for the following reactions:

\[
\begin{align*}
\text{CH}_3\text{C}≡\text{CH} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 & \Delta H^0 &= -69.1 \text{ kcal} \\
\text{CH}_2-\text{C}≡\text{CH}_2 + 2\text{H}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 & \Delta H^0 &= -71.3 \text{ kcal}
\end{align*}
\]

Explain why the value of ΔH⁰ calculated from bond energies might be unreliable for the last reaction.

11-30 a. Write a mechanism for the sulfuric acid-induced dimerization of 2-methyl-2-butene, indicating the products you expect to be formed. (It will be helpful to review Section 10-8B.)

b. Ozonization of the actual alkene mixture that is formed gives (along with a mixture of aldehydes and ketones) substantial amounts of 2-butanone (\( \text{CH}_3-\text{C}≡\text{CH}_2 \)). Write a structure and reaction mechanism for formation of a \( \text{C}_10 \)-olefin that reasonably might be formed in the dimerization reaction and that, on ozonization, would yield 2-butanone and a \( \text{C}_6 \)-carbonyl compound. (Consider how sulfuric acid might cause the double bond in 2-methyl-2-butene to shift its position.)

11-31 How would you distinguish between the compounds in each of the following pairs using chemical methods (preferably test-tube reactions)?

a. \( \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \) and \( \text{CH}_2\text{C}≡\text{CCH}_3 \)

b. \( \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \) and \( \text{CH}_2-\text{C}≡\text{CH} \)

C. \( \text{C}_8\text{H}_6\text{C}≡\text{CC}_8\text{H}_5 \) and \( \text{C}_8\text{H}_6\text{CH}_2\text{CH}_2\text{C}_8\text{H}_5 \)

11-32 How could you distinguish between the compounds in the previous exercise, using spectroscopic methods?