PROBLEM 18
Why are Na⁺ and K⁺ unable to form covalent bonds?

PROBLEM 19
What will be the product of the addition of I⁻Cl to 1-butene? [Hint: Chlorine is more electronegative than iodine (Table 1.3).]

PROBLEM 20
What would be the major product obtained from the reaction of Br₂ with 1-butene if the reaction were carried out in
a. dichloromethane? c. ethyl alcohol?
b. water? d. methyl alcohol?

4.8 Oxymercuration–Reduction and Alkoxymercuration–Reduction

In Section 4.5, you learned that water adds to an alkene if an acid catalyst is present. This is the way alkenes are converted into alcohols industrially. However, under normal laboratory conditions, water is added to an alkene by a procedure known as oxymercuration–reduction. The addition of water by oxymercuration–reduction has two advantages over acid-catalyzed addition: It does not require acidic conditions that are harmful to many organic molecules, and because carbocation intermediates are not formed, carbocation rearrangements do not occur.

In oxymercuration, the alkene is treated with mercuric acetate in aqueous tetrahydrofuran (THF). When reaction with that reagent is complete, sodium borohydride is added to the reaction mixture. (The numbers 1 and 2 in front of the reagents above and below the arrow in the chemical equation indicate two sequential reactions; the second reagent is not added until reaction with the first reagent is completely over.)

\[
\begin{array}{c}
\text{R—CH—CH₂} & \text{1. Hg(OAc)₂, H₂O/THF} & \text{R—CH—CH₃} \\
\text{2. NaBH₄} & \text{OH} & \end{array}
\]

In the first step of the oxymercuration mechanism, the electrophilic mercury of mercuric acetate adds to the double bond. (Two of mercury’s 5d electrons are shown.) Because carbocation rearrangements do not occur, we can conclude that the product of the addition reaction is a cyclic mercurinium ion rather than a carbocation. The reaction is analogous to the addition of Br₂ to an alkene to form a cyclic bromonium ion.

mechanism for oxymercuration

\[
\begin{array}{c}
\text{CH₃CH═CH₂} & \text{CH₃CH—CH₂} & \text{CH₃CHCH₂—Hg—OAc} \\
\text{AcO⁻ = CH₃CO⁻} & \text{CH₃CHCH₂—Hg—OAc} & \text{OH + AcOH}
\end{array}
\]
In the second step of the reaction, water attacks the more substituted carbon of the mercurinium ion—the one bonded to the lesser number of hydrogens—for the same reason that it attacks the more substituted carbon of the bromonium ion in the halohydrin reaction (Section 4.7). That is, attacking at the more substituted carbon leads to the more stable transition state.

\[
\begin{align*}
\text{OAc} & \\
\delta^+ & \text{Hg} & \text{OAc} & \\
\delta^- & \text{Hg} & \delta^- & \text{Hg} & \\
\text{CH}_3\text{CHCH}_2 & \rightarrow & \text{CH}_3\text{CHCH}_2 & \rightarrow & \text{CH}_3\text{CHCH}_2 & + & \text{Hg} & + & \text{AcO}^- \\
\text{O} & \text{H} & \text{O} & \text{H} & \\
\delta^+ & \text{H} & \delta^+ & \text{H} & \\
\end{align*}
\]

More stable transition state \quad \text{less stable transition state}

Sodium borohydride \((\text{NaBH}_4)\) converts the \(\text{C—Hg}\) bond into a \(\text{C—H}\) bond. A reaction that increases the number of \(\text{C—H}\) bonds or decreases the number of \(\text{C—O}, \text{C—N}, \text{or C—X}\) bonds in a compound (where \(\text{X}\) denotes a halogen), is called a \textit{reduction reaction}. Consequently, the reaction with sodium borohydride is a reduction reaction. The mechanism of the reduction reaction is not fully understood, although it is known that the intermediate is a radical.

\[
\text{CH}_3\text{CHCH}_2\text{Hg—OAc} \xrightarrow{\text{NaBH}_4} \text{CH}_3\text{CHCH}_2 + \text{Hg} + \text{AcO}^- 
\]

The overall reaction (oxymercuration–reduction) forms the same product that would be formed from the acid-catalyzed addition of water: The hydrogen adds to the \(sp^2\) carbon bonded to the greater number of hydrogens, and \(\text{OH}\) adds to the other \(sp^2\) carbon.

We have seen that alkenes react with alcohols in the presence of an acid catalyst to form ethers (Section 4.5). Just as the addition of water works better in the presence of mercuric acetate than in the presence of a strong acid, the addition of an alcohol works better in the presence of mercuric acetate. \([\text{Mercuric trifluoroacetate, Hg(O}_2\text{CCF}_3)_2, \text{works even better}].\) This reaction is called \textit{alkoxymercuration–reduction}.

\[
\begin{align*}
\text{CH}_3 & \\
\text{1-methylcyclohexene} & \rightarrow & \text{H}_3\text{C} & \text{OCH}_3 \\
\text{1-methoxy-1-methylcyclohexane} & \text{an ether} \\
\end{align*}
\]

The mechanisms for oxymercuration and alkoxymercuration are essentially identical; the only difference is that water is the nucleophile in oxymercuration and an alcohol is the nucleophile in alkoxymercuration. Therefore, the product of oxymercuration–reduction is an alcohol, whereas the product of alkoxymercuration–reduction is an ether.

**PROBLEM 21**

How could the following compounds be synthesized from an alkene?

- a. \(\text{CH}_3\text{OCH}_2\text{CH}_3\)
- b. \(\text{CH}_3\text{OH}\)
- c. \(\text{CH}_3\text{CHCH}_2\text{CH}_3\)
- d. \(\text{OCH}_2\text{CH}_3\)
- e. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)
- f. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)
- g. \(\text{OCH}_3\text{CH}_2\text{CH}_3\)

- a. \(\text{CH}_3\text{OCH}_2\text{CH}_3\)
- b. \(\text{CH}_3\text{OH}\)
- c. \(\text{CH}_3\text{CHCH}_2\text{CH}_3\)
- d. \(\text{OCH}_2\text{CH}_3\)
- e. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)
- f. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)
- g. \(\text{OCH}_3\text{CH}_2\text{CH}_3\)
PROBLEM 22

How could the following compounds be synthesized from 3-methyl-1-butene?

\[
\begin{align*}
\text{a. } & \text{CH}_3\text{C} \text{H}_2\text{CH}_2\text{OH} \\
\text{b. } & \text{CH}_3\text{C} \text{H}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

4.9 Addition of Borane: Hydroboration–Oxidation

An atom or a molecule does not have to be positively charged to be an electrophile. Borane (BH\(_3\)), a neutral molecule, is an electrophile because boron has only six shared electrons in its valence shell. Boron, therefore, readily accepts a pair of electrons in order to complete its octet. Thus, alkenes undergo electrophilic addition reactions with borane serving as the electrophile. When the addition reaction is over, an aqueous solution of sodium hydroxide and hydrogen peroxide is added to the reaction mixture, and the resulting product is an alcohol. The addition of borane to an alkene, followed by reaction with hydroxide ion and hydrogen peroxide, is called hydroboration–oxidation. The overall reaction was first reported by H. C. Brown in 1959.

The alcohol that is formed from the hydroboration–oxidation of an alkene has the H and OH groups on opposite carbons, compared with the alcohol that is formed from the acid-catalyzed addition of water (Section 4.5). In other words, the reaction violates Markovnikov’s rule. Thus, hydroboration–oxidation is an anti-Markovnikov addition reaction. However, you will see that the general rule for electrophilic addition reactions is not violated: *The electrophile adds to the sp\(^2\) carbon that is bonded to the greater number of hydrogens.* The reaction violates Markovnikov’s rule because his rule states where the hydrogen adds, so the rule applies only if the electrophile is a hydrogen. The reaction does not violate the general rule because, as you will see, H\(^+\) is not the electrophile in hydroboration–oxidation; BH\(_3\) is the electrophile and H\(^-\) is the nucleophile. This shows why it is better to understand the mechanism of a reaction than to memorize rules. *The first step in the mechanism of all alkene reactions is the same:* the addition of an electrophile to the sp\(^2\) carbon that is bonded to the greater number of hydrogens.

Herbert Charles Brown was born in London in 1921 and was brought to the United States by his parents at age two. He received a Ph.D. from the University of Chicago and has been a professor of chemistry at Purdue University since 1947. For his studies on boron-containing organic compounds, he shared the 1979 Nobel Prize in chemistry with G. Wittig.

Because diborane (B\(_2\)H\(_6\)), the source of borane, is a flammable, toxic, explosive gas, a solution of borane—prepared by dissolving diborane in an ether such as THF—is a more convenient and less dangerous reagent. One of the ether oxygen’s lone pairs satisfies boron’s requirement for an additional two electrons: The ether is a Lewis base.