An **allylic group** is a group on a carbon adjacent to a double bond. A **benzylic group** is a group on a carbon adjacent to a benzene ring or substituted benzene ring.

In many situations **allylic and benzylic groups are unusually reactive**. This chapter examines what happens when some familiar reactions occur at allylic and benzylic positions and discusses the reasons for allylic and benzylic reactivity. This chapter also presents some reactions that occur *only* at the allylic and benzylic positions. Finally, Sec. 17.6 will show that allylic reactivity is also important in some chemistry that occurs in living organisms.

### PROBLEMS

17.1 Identify the allylic carbons in each of the following structures.

(a) ![Structure](image1)

(b) ![Structure](image2)

17.2 Identify the benzylic carbons in each of the following structures.

(a) ![Structure](image3)

(b) ![Structure](image4)
17.1 REACTIONS INVOLVING ALLYLIC AND BENZYLIC CARBOCATIONS

Recall that allylic carbocations are resonance-stabilized (Sec. 15.4B). The simplest example of an allylic cation is the *allyl cation* itself:

\[
\begin{align*}
 & \text{H}_2\text{C}—\text{CH}^+—\text{CH}_2 \quad \leftrightarrow \quad \text{H}_2\text{C}—\text{CH}═\text{CH}_2 \\
\text{resonance structures of the allyl cation}
\end{align*}
\] (17.1)

These resonance structures symbolize the delocalization of electrons and electron deficiency (along with the associated positive charge) that result from the overlap of 2\(p\) orbitals to form molecular orbitals, as shown in Fig. 15.9, p. 703.

Benzylic carbocations are also resonance-stabilized. The *benzyl cation* is the simplest example of a benzylic cation:

\[
\begin{align*}
 & \text{benzyl cation} \\
\text{resonance structures of the benzyl cation}
\end{align*}
\] (17.2)

The resonance structures of the benzyl cation symbolize the overlap of 2\(p\) orbitals of the benzylic carbon and the benzene ring to form bonding MOs. As these structures show, the electron deficiency and resulting positive charge on a benzylic carbocation are shared not only by the benzylic carbon, but also by alternate carbons of the ring. As with the allyl cation (Sec. 15.4B), the resonance structures of the benzyl cation correctly account for the distribution of positive charge that is calculated from MO theory and shown by the EPM:

\[
\begin{align*}
\ast = \text{sites of partial positive charge}
\end{align*}
\]

EPM of benzyl cation

The resonance energy (p. 704) of the benzyl cation calculated from MO theory (over and above that of the benzene ring itself) is about 0.72\(\beta\), which is about 90% of the resonance energy of the allyl cation. In other words, the resonance stabilizations of the benzyl and allyl cations are about the same.

The structures and stabilities of allylic and benzylic carbocations have important consequences for reactions in which they are involved as reactive intermediates. First, *reactions in which benzylic or allylic carbocations are formed as intermediates are generally considerably faster than analogous reactions involving comparably substituted nonallylic or nonbenzylic carbocations*. This point is illustrated by the relative rates of S\(_1\) solvolysis reactions, shown in Tables 17.1 and 17.2, p. 790. For example, the tertiary allylic alkyl halide in the first entry of Table 17.1 reacts more than 100 times faster than the tertiary nonallylic alkyl halide in the
third entry. A comparison of the first and third entries of Table 17.2 shows the effect of benzylic substitution. tert-Cumyl chloride, the third entry, reacts more than 600 times faster than tert-butyl chloride, the first entry.

The greater reactivities of allylic and benzylic halides result from the stabilities of the carbocation intermediates that are formed when they react. For example, tert-cumyl chloride (the third entry of Table 17.2) ionizes to a carbocation with four important resonance structures:

\[
\begin{align*}
&\text{ tert-butyl chloride} \\
&\text{ tert-cumyl chloride}
\end{align*}
\]
Ionization of tert-butyl chloride, on the other hand, gives the tert-butyl cation, a carbocation with only one important contributing structure. The benzylic cation is more stable relative to its alkyl halide starting material than is the tert-butyl cation, and application of Hammond’s postulate predicts that the more stable carbocation should be formed more rapidly. A similar analysis explains the reactivity of allylic alkyl halides.

Because of the possibility of resonance, ortho and para substituent groups on the benzene ring that activate electrophilic aromatic substitution further accelerate $S_{N}1$ reactions at the benzylic position:

The carbocation derived from the ionization of the $p$-methoxy derivative in Eq. 17.5 not only has the same types of resonance structures as the unsubstituted compound, shown in Eq. 17.3, but also an additional structure (red) in which charge can be delocalized onto the substituent group itself:

Other reactions that involve carbocation intermediates are accelerated when the carbocations are allylic or benzylic. Thus, the dehydration of an alcohol (Sec. 10.1) and the reaction of an
alcohol with a hydrogen halide (Sec. 10.2) are also faster when the alcohol is allylic or benzylic. For example, most alcohols require forcing conditions or Lewis acid catalysts to react with HCl to give alkyl chlorides, but such conditions are unnecessary when benzylic alcohols react with HCl. The addition of hydrogen halides to conjugated dienes also reflects the stability of allylic carocations. Recall that protonation of a conjugated diene gives the allylic carbocation rather than its nonallylic isomer because the allylic carbocation is formed more rapidly (Sec. 15.4A).

A second consequence of the involvement of allylic carocations as reactive intermediates is that in many cases more than one product can be formed. More than one product is possible because the positive charge (and electron deficiency) is shared between two carbons. Nucleophiles can react at either of the electron-deficient carbon atoms and, if the two carbons are not equivalent, two different products result.

\[
(CH_3)_2C\equiv CH-C\equiv CH+Cl^- \quad \xrightarrow{H_2O} \quad [(CH_3)_2C\equiv CH-C\equiv CH]^+ + Cl^- + H_2O
\]

\[
[(CH_3)_2C\equiv CH-C\equiv CH]^+ + H_2O \quad \xrightarrow{\text{HCl}} \quad [(CH_3)_2C\equiv CH-C\equiv CH]^- + Cl^-
\]

The two products are derived from one allylic carbocation that has two resonance forms. Recall that similar reasoning explains why a mixture of products (1,2- and 1,4-addition products) is obtained in the reactions of hydrogen halides with conjugated alkenes (Sec. 15.4A).

We might expect that several substitution products in the S_N1 reactions of benzylic alkyl halides might be formed for the same reason.
As Eq. 17.8 shows, the products derived from the reaction of water at the ring carbons are not formed. The reason is that these products are not aromatic and thus lack the stability associated with the aromatic ring. Aromaticity is such an important stabilizing factor that only the aromatic product (red) is formed.

### PROBLEMS

17.3 Predict the order of relative reactivities of the compounds within each series in $S_N$1 solvolysis reactions, and explain your answers carefully.

(a) ![Structures](image1)

(b) ![Structures](image2)

17.4 Give the structure of an isomer of the allylic halide reactant in Eq. 17.7 that would react with water in an $S_N$1 solvolysis reaction to give the same two products. Explain your reasoning.

17.5 Why is trityl chloride much more reactive than the other alkyl halides in Table 17.2?

### 17.2 REACTIONS INVOLVING ALLYLIC AND BENZYLIC RADICALS

An allylic radical has an unpaired electron at an allylic position. Allylic radicals are resonance-stabilized and are more stable than comparably substituted nonallylic radicals. The simplest allylic radical is the allyl radical itself:

\[
\begin{align*}
[H_2\text{CH}=\text{CH}]=\text{CH}_2 & \quad \longleftrightarrow \quad H_2\text{CH}=\text{CH}_2 \\
\text{resonance structures of the allyl radical}
\end{align*}
\] (17.9)

Similarly, a benzylic radical, which has an unpaired electron at a benzylic position, is also resonance-stabilized. The benzyl radical is the prototype:

\[
\begin{align*}
\text{CH}_2 & \quad \longleftrightarrow \quad \text{CH}=\text{CH}_2 \\
\text{resonance structures of the benzylic radical}
\end{align*}
\] (17.10)

These resonance structures symbolize the delocalization (sharing) of the unpaired electron that results from overlap of carbon $2p$ orbitals to form molecular orbitals.

The enhanced stabilities of allylic and benzylic radicals can be experimentally demonstrated with bond dissociation energies. The bond dissociation energies of allylic and nonallylic hydro-