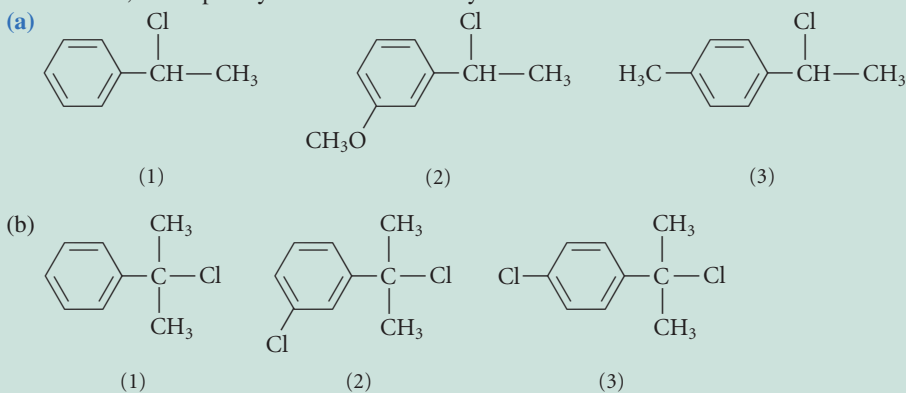


As Eq. 17.8 shows, the products derived from the reaction of water at the ring carbons are not formed. The reason is that *these products are not aromatic* and thus lack the stability associated with the aromatic ring. Aromaticity is such an important stabilizing factor that only the aromatic product (*red*) is formed.

## PROBLEMS

17.3 Predict the order of relative reactivities of the compounds within each series in  $S_N1$  solvolysis reactions, and explain your answers carefully.

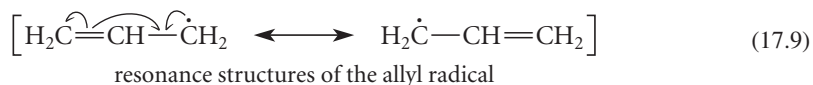


17.4 Give the structure of an isomer of the allylic halide reactant in Eq. 17.7 that would react with water in an  $S_N1$  solvolysis reaction to give the same two products. Explain your reasoning.

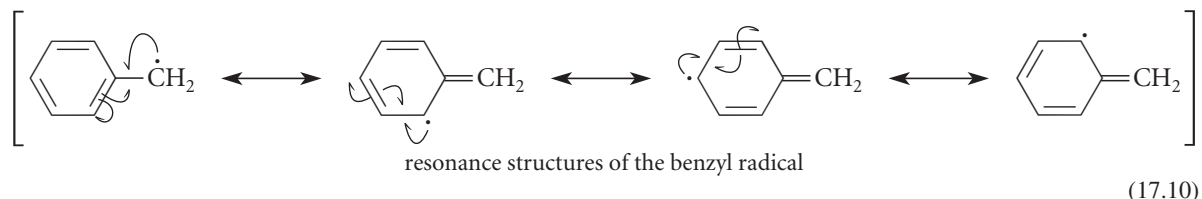
17.5 Why is trityl chloride much more reactive than the other alkyl halides in Table 17.2?

## 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:

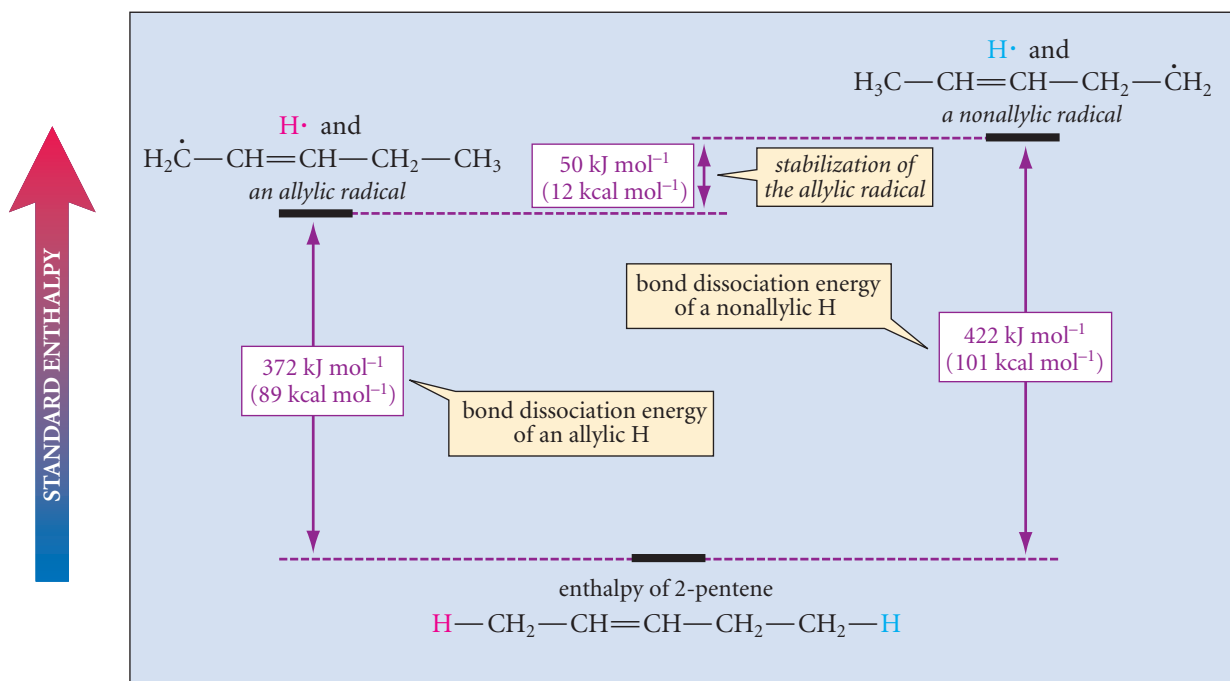


Similarly, a **benzylic radical**, which has an unpaired electron at a benzylic position, is also resonance-stabilized. The *benzyl radical* is the prototype:



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

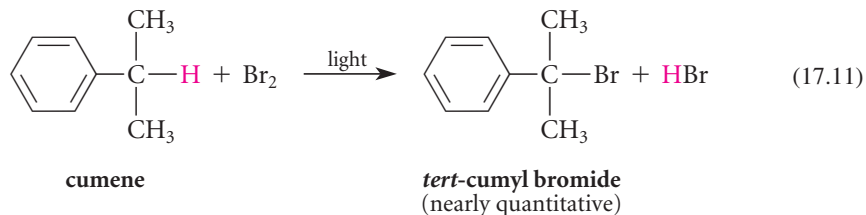
The enhanced stabilities of allylic and benzylic radicals can be experimentally demonstrated with bond dissociation energies. The bond dissociation energies of allylic and nonallylic hydro-



**Figure 17.1** Use of bond dissociation energies to determine the stabilization of an allylic radical. The stabilization of the allylic radical results from the lower energy required ( $50 \text{ kJ mol}^{-1}$ ,  $12 \text{ kcal mol}^{-1}$ ) to remove an allylic hydrogen  $\text{H}^a$  compared with a nonallylic one  $\text{H}^b$ .

gens in 2-pentene are compared in Fig. 17.1. One set of methyl hydrogens is allylic and the other is not. It takes  $50 \text{ kJ mol}^{-1}$  ( $12 \text{ kcal mol}^{-1}$ ) less energy to remove the allylic hydrogen  $\text{H}^a$  than the nonallylic one  $\text{H}^b$ . As Fig. 17.1 shows, the difference in bond dissociation energies is a direct measure of the relative energies of the two radicals. This comparison shows that the allylic radical is stabilized by  $50 \text{ kJ mol}^{-1}$  ( $12 \text{ kcal mol}^{-1}$ ) relative to the nonallylic radical. The same type of comparison shows that benzylic radicals are about  $42 \text{ kJ mol}^{-1}$  ( $10 \text{ kcal mol}^{-1}$ ) more stable than comparably substituted nonbenzylic radicals.

Because allylic and benzylic radicals are especially stable, they are more readily formed as reactive intermediates than ordinary alkyl radicals. Consider what happens, for example, in the bromination of cumene:

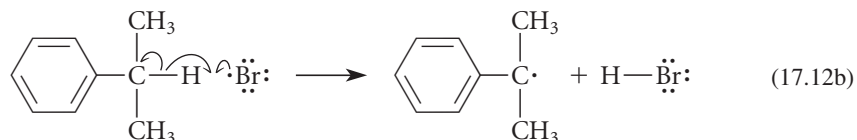


This is a free-radical chain reaction (Secs. 5.6C and 8.9A). Notice that *only the benzylic hydrogen is substituted*.

The initiation step in this reaction is the dissociation of molecular bromine into bromine atoms; this reaction is promoted by heat or light.

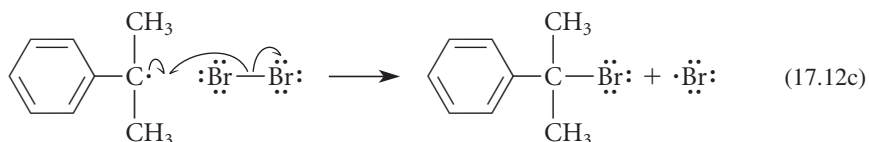


In the first propagation step, a bromine atom abstracts the one benzylic hydrogen in preference to either the six nonbenzylic hydrogens or the five hydrogens of the aromatic ring. It is in this propagation step that the selectivity for substitution of the benzylic hydrogen occurs.



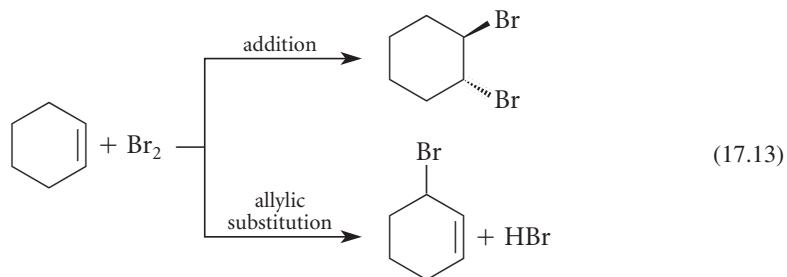
The reason for this selectivity is the weaker benzylic C—H bond (Fig. 17.1) or, equivalently, the greater stability of the benzylic radical that is formed.

In the second propagation step, the benzylic radical reacts with another molecule of bromine to generate a molecule of product as well as another bromine atom, which can react again in Eq. 17.12b.



Free-radical halogenation is used to halogenate alkanes industrially (Sec. 8.9A). Because free-radical halogenation of alkanes with different types of hydrogens gives mixtures of products, this reaction is ordinarily not very useful in the laboratory. (It can be used industrially because industry has developed efficient fractional distillation methods that can separate liquids of similar boiling points.) However, when a benzylic hydrogen is present, it undergoes substitution so much more rapidly than an ordinary hydrogen that a single product is obtained. Consequently, free-radical halogenation can be used for the laboratory preparation of benzylic halides.

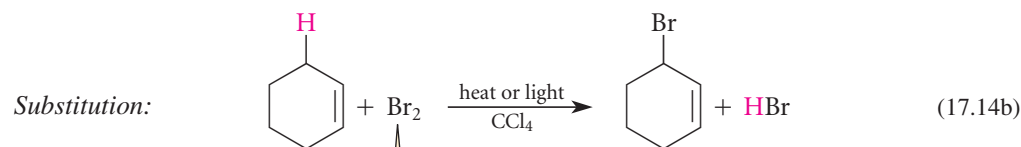
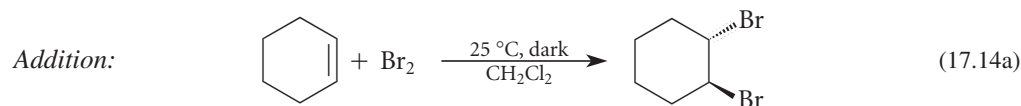
Because the allylic radical is also relatively stable, a similar substitution occurs preferentially at the allylic positions of an alkene. But a competing reaction occurs in the case of an alkene that is not observed with benzylic substitution: addition of halogen to the alkene double bond by an ionic mechanism (Sec. 5.2A).



(Such a competing addition is not a problem in benzylic bromination because bromine doesn't add to the benzene ring in Eq. 17.11. Why?)

One reaction can be promoted over the other if the reaction conditions are chosen carefully. *Addition* of bromine is the predominant reaction if (1) free-radical substitution is suppressed by avoiding conditions that promote free-radical reactions (heat, light, or free-radical initiators); and if (2) the reaction is carried out in solvents of even slight polarity that promote the ionic mechanism for bromine addition. Thus, addition is observed at 25 °C if the reaction is run in the dark in methylene chloride, CH<sub>2</sub>Cl<sub>2</sub>. On the other hand, free-radical *substitution* occurs

when the reaction is promoted by heat, light, or free-radical initiators, an apolar solvent such as  $\text{CCl}_4$  is used, and *the bromine is added slowly so that its concentration remains very low*. To summarize:



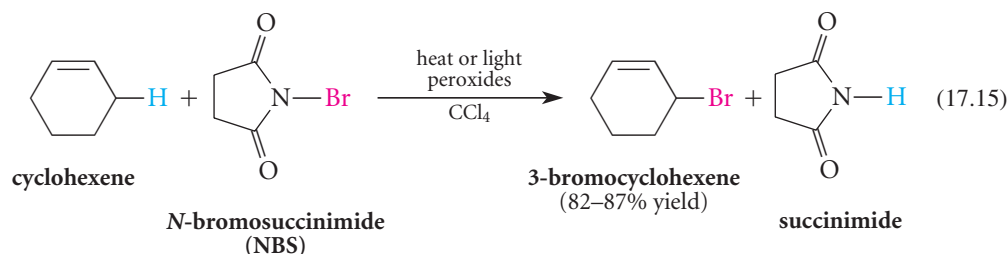
added slowly;  
concentration kept low



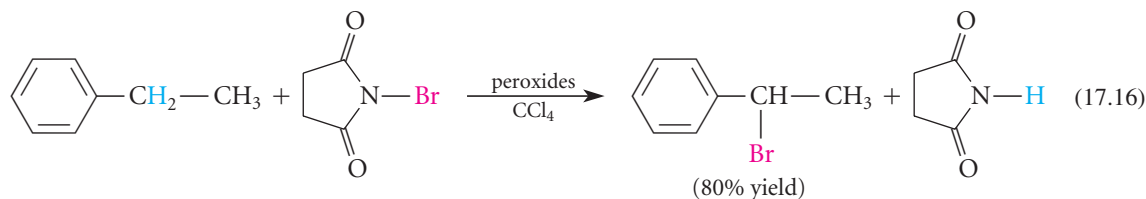
**Further Exploration 17.1**  
**Addition versus**  
**Substitution with**  
**Bromine**

The effect of bromine concentration results from the rate laws for the competing reactions. Addition has a higher kinetic order in  $[\text{Br}_2]$  than substitution. Hence, the rate of addition is decreased more than the rate of substitution by lowering the bromine concentration. This effect is discussed in Further Exploration 17.1.

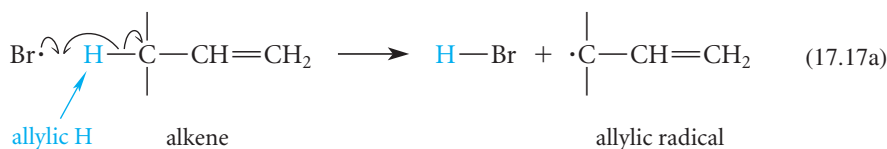
Adding bromine to a reaction so slowly that it remains at very low concentration is experimentally inconvenient, but a very useful reagent can be employed to accomplish the same objective: *N*-bromosuccinimide (abbreviated NBS). When a compound with allylic hydrogens is treated with *N*-bromosuccinimide in  $\text{CCl}_4$  under free-radical conditions (heat or light and peroxides), allylic bromination takes place, and addition to the double bond is not observed.



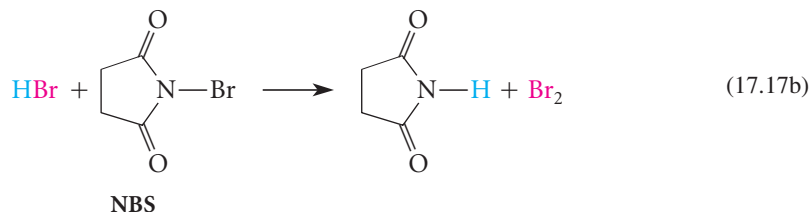
*N*-Bromosuccinimide can also be used for benzylic bromination.



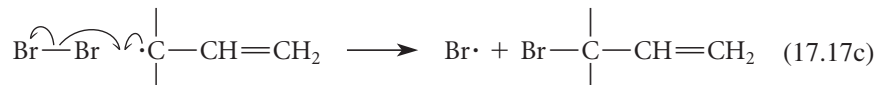
The initiation step in allylic and benzylic bromination with NBS is the formation of a bromine atom by homolytic cleavage of the  $\text{N}-\text{Br}$  bond in NBS itself. The ensuing substitution reaction has three propagation steps, which we'll illustrate for allylic bromination. First, the bromine atom abstracts an allylic hydrogen from the alkene molecule:



The HBr thus formed reacts with the NBS in the second propagation step (by an ionic mechanism) to produce a Br<sub>2</sub> molecule.



The last propagation step is the reaction of this bromine molecule with the radical formed in Eq. 17.17a. A new bromine atom is produced that can begin the cycle anew.



The first and last propagation steps are identical to those for free-radical substitution with Br<sub>2</sub> itself (Eq. 17.12b,c). The unique role of NBS is to maintain the very low concentration of bromine by reacting with HBr in Eq. 17.17b. The Br<sub>2</sub> concentration remains low because it can be generated no faster than an HBr molecule and an allylic radical are generated in Eq. 17.17a. Thus, every time a bromine molecule is formed, an allylic radical is also formed with which the bromine can react.

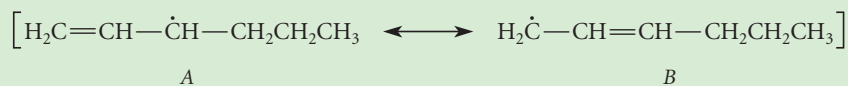
The low solubility of NBS in CCl<sub>4</sub> (≤0.005 M) is crucial to the success of allylic bromination with NBS. When solvents that dissolve NBS are used, different reactions are observed. Hence, CCl<sub>4</sub> *must* be used as the solvent in allylic or benzylic bromination with NBS. During the reaction, the insoluble NBS, which is more dense than CCl<sub>4</sub>, disappears from the bottom of the flask and the less dense by-product succinimide (Eq. 17.15) forms a layer on the surface of the CCl<sub>4</sub>. Equation 17.17b, and possibly other steps of the mechanism, occur at the surface of the insoluble NBS. (These very specific aspects of the NBS allylic bromination reaction were known many years before the reasons for them were understood.)

Mixtures of products are formed in some allylic bromination reactions because, as resonance structures indicate, the unpaired electron in the free-radical intermediate is shared by two different carbons. This point is explored in Study Problem 17.1.

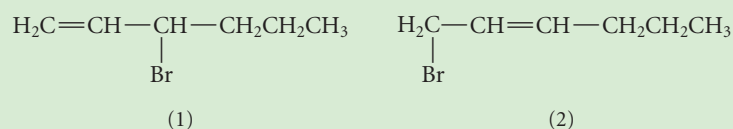
### Study Problem 17.1

What products are expected in the reaction of H<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (1-hexene) with NBS in CCl<sub>4</sub> in the presence of peroxides? Explain your answer.

**Solution** Work through the NBS mechanism with 1-hexene. In the step corresponding to Eq. 17.17a the following resonance-stabilized allylic free radical is formed as an intermediate:



Because the unpaired electron is shared by *two different carbons*, this radical can react in the final propagation step to give *two different products*. Reaction of Br<sub>2</sub> at the radical site shown in structure *A* gives product (1), and reaction at the radical site shown in structure *B* gives product (2):



Notice that product (1) is chiral, and product (2) can exist as both *cis* and *trans* stereoisomers. Hence, bromination of 1-hexene gives racemic (1) as well as *cis*- and *trans*-(2), although the *trans* isomer should predominate because of its greater stability.

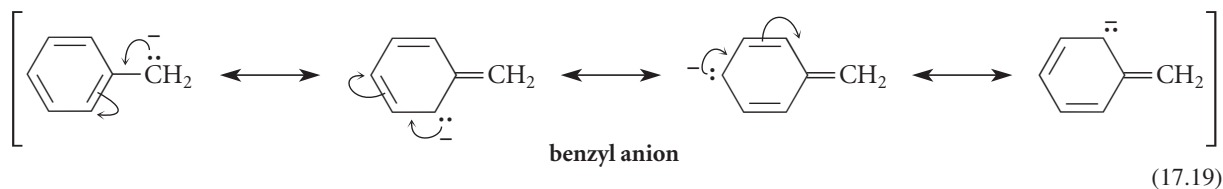
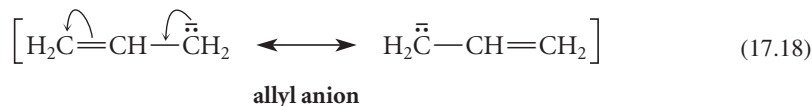
**PROBLEM**

17.6 What product(s) are expected when each of the following compounds reacts with one equivalent of NBS in CCl<sub>4</sub> in the presence of light and peroxides? Explain your answers.

- (a) cyclohexene
- (b) 3,3-dimethylcyclohexene
- (c) *trans*-2-pentene
- (d) 4-*tert*-butyltoluene
- (e) 1-isopropyl-4-nitrobenzene

**17.3 REACTIONS INVOLVING ALLYLIC AND BENZYLIC ANIONS**

The prototype for allylic anions is the *allyl anion*, and the simplest benzylic anion is the *benzyl anion*.



Allylic and benzylic anions are about 59 kJ mol<sup>-1</sup> (14 kcal mol<sup>-1</sup>) more stable than their nonallylic and nonbenzylic counterparts. There are two reasons for the stabilities of these anions. The first is resonance stabilization, as indicated by the preceding resonance structures. The second reason is the *polar effect* (Sec. 3.6C) of the double bond (in the allyl anion) or the phenyl ring (in the benzyl anion). The polar effect of both groups stabilizes anions. (Opinions differ about the relative importance of resonance and polar effects.)



Further Exploration 17.2  
Polar Effects of  
Double Bonds