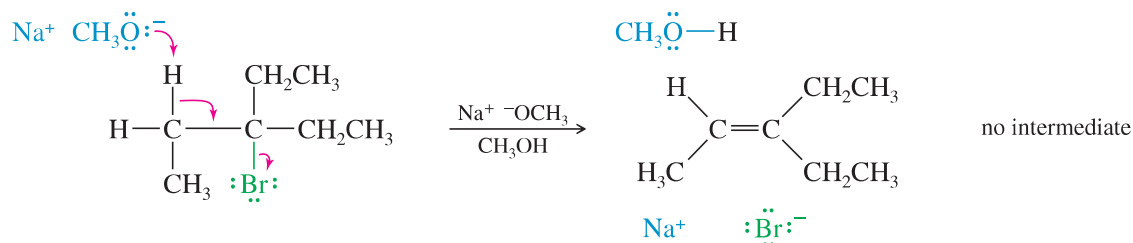


E2:



7-10 Unimolecular Elimination: The E1 Reaction

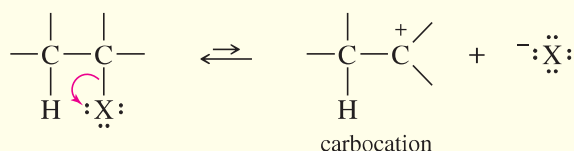
The abbreviation **E1** stands for *Elimination, unimolecular*. The mechanism is called *unimolecular* because the rate-limiting transition state involves a single molecule rather than a collision between two molecules. The slow step of an E1 reaction is the same as in the S_N1 reaction: unimolecular ionization to form a carbocation. In a fast second step, a base abstracts a proton from the carbon atom adjacent to the C^+ . The electrons that once formed the carbon–hydrogen bond now form a pi bond between two carbon atoms. The general mechanism for the E1 reaction is shown in Key Mechanism 7-1.



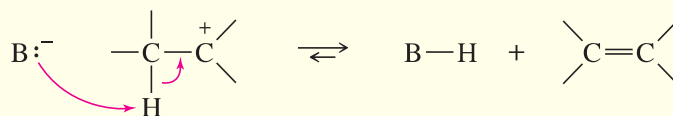
KEY MECHANISM 7-1 The E1 Reaction

The E1 reaction requires ionization to a carbocation intermediate like the S_N1 . The E1 and S_N1 reactions follow the same order of reactivity based on carbocation stability: $3^\circ \gg 2^\circ \gg 1^\circ$. Tertiary alkyl halides react readily by the E1 mechanism, secondary halides react much slower, and simple primary halides do not undergo E1 or S_N1 reactions.

Step 1: Unimolecular ionization to give a carbocation (rate-limiting).

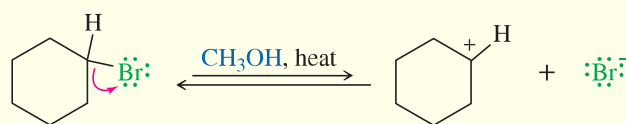


Step 2: Deprotonation by a weak base (often the solvent) gives the alkene (fast).



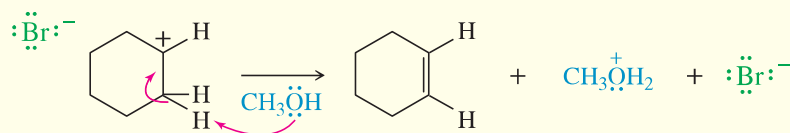
EXAMPLE: E1 elimination of bromocyclohexane in methanol.

Step 1: Ionization gives a carbocation and bromide ion in a slow step.



(CONTINUED)

Step 2: Methanol abstracts a proton to give cyclohexene in a fast step.



PROBLEM 7-16

Show what happens in step 2 of the example if the solvent acts as a *nucleophile* (forming a bond to carbon) rather than as a *base* (removing a proton).

The rate-limiting step involves ionization of the alkyl halide. Because the step is unimolecular (involves only one molecule), the rate equation is first-order. The rate depends only on the concentration of the alkyl halide, and not on the strength or concentration of the base.

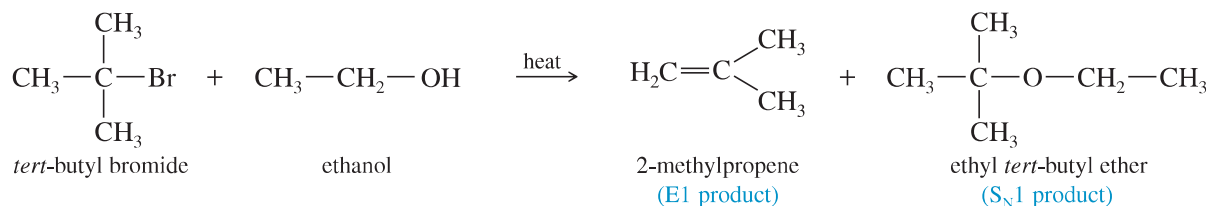
$$\text{E1 rate} = k_1[\text{RX}]$$

The weak base (often the solvent) takes part in the fast second step of the reaction.

Unimolecular (E1) dehydrohalogenations usually take place in a good ionizing solvent (such as an alcohol or water), without a strong base present to force a bimolecular (E2) reaction. The substrate for E1 dehydrohalogenation is usually a tertiary alkyl halide. If secondary halides undergo E1 reactions, they require stronger conditions and react much more slowly.

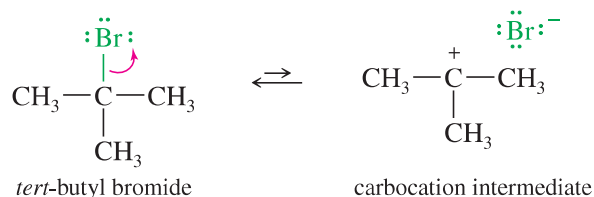
7-10A Competition between the E1 and S_N1 Reactions

The E1 elimination almost always competes with the S_N1 substitution. Whenever a carbocation is formed, it can undergo either substitution or elimination, and mixtures of products often result. The following reaction shows the formation of both elimination and substitution products in the reaction of *tert*-butyl bromide with boiling ethanol.

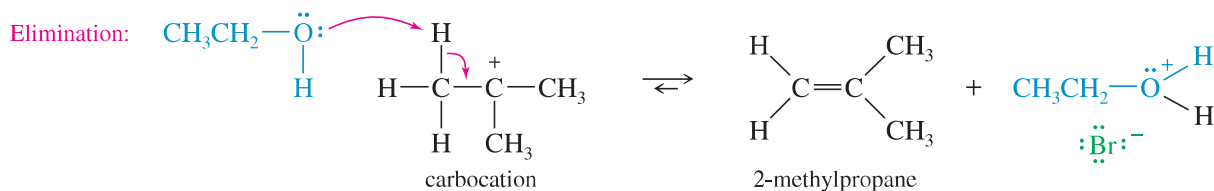


The 2-methylpropene product results from dehydrohalogenation, an elimination of hydrogen and a halogen atom. Under these first-order conditions (the absence of a strong base), dehydrohalogenation takes place by the E1 mechanism: Ionization of the alkyl halide gives a carbocation intermediate, which loses a proton to give the alkene. Substitution results from an S_N1 nucleophilic attack on the carbocation. This kind of reaction is called a **solvolysis** (*solvo* for “solvent,” *lysis* for “cleavage”) because the solvent reacts with the substrate. In this example, ethanol (the solvent) serves as a base (removing a proton) in the elimination and as a nucleophile (forming a bond to carbon) in the substitution.

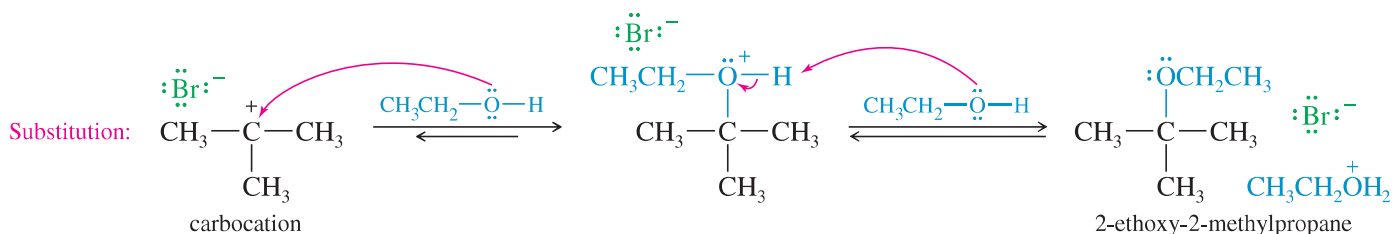
Step 1: Ionization to form a carbocation.



Step 2 (by the E1 mechanism): Basic attack by the solvent abstracts a proton to give an alkene.



or step 2 (by the S_N1 mechanism): Nucleophilic attack by the solvent on the carbocation.



Under ideal conditions, one of these first-order reactions provides a good yield of one product or the other. Often, however, carbocation intermediates react in two or more ways to give mixtures of products. For this reason, S_N1 and E1 reactions of alkyl halides are not frequently used for organic synthesis. They have been studied in great detail to learn about the properties of carbocations, however.

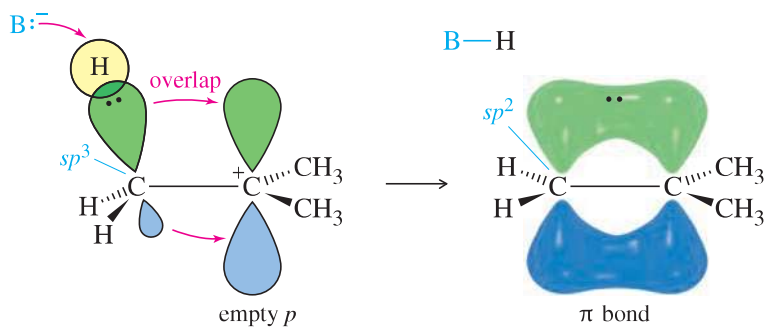
PROBLEM 7-17

S_N1 substitution and E1 elimination frequently compete in the same reaction.

- Propose a mechanism and predict the products for the solvolysis of 2-bromo-2,3,3-trimethylbutane in methanol.
- Compare the function of the solvent (methanol) in the E1 and S_N1 reactions.

7-10B Orbitals and Energetics of the E1 Reaction

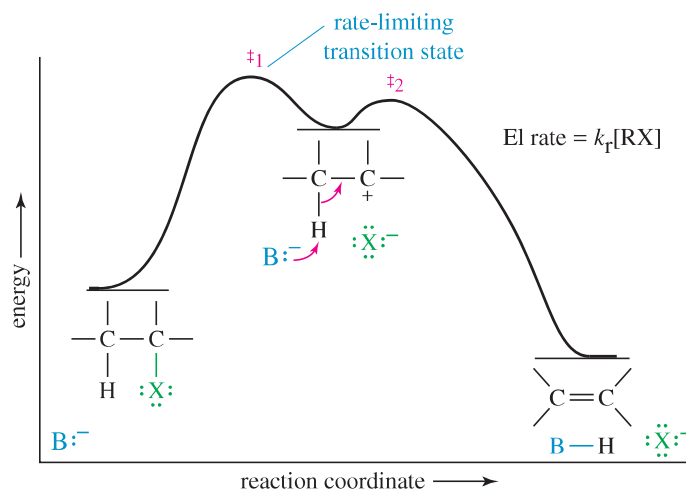
In the second step of the E1 mechanism, the carbon atom next to the C⁺ must rehybridize to sp² as the base attacks the proton and electrons flow into the new pi bond.



The potential-energy diagram for the E1 reaction (Figure 7-9) is similar to that for the S_N1 reaction. The ionization step is strongly endothermic, with a rate-limiting transition state. The second step is a fast exothermic deprotonation by a base. The base is not involved in the reaction until *after* the rate-limiting step, so the rate depends only on the concentration of the alkyl halide. Weak bases are common in E1 reactions.

FIGURE 7-9

Reaction-energy diagram of the E1 reaction. The first step is a rate-limiting ionization. Compare this energy profile with that of the S_N1 reaction in Figure 6-8.



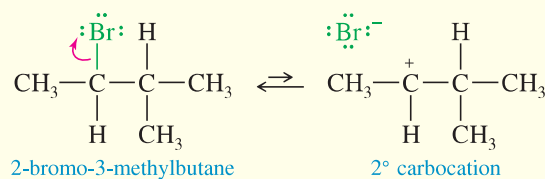
7-10C Rearrangements in E1 Reactions

Like other carbocation reactions, the E1 may be accompanied by rearrangement. Compare the following E1 reaction (with rearrangement) with the S_N1 reaction of the same substrate, shown in Mechanism 6-6. Note that the solvent acts as a *base* in the E1 reaction and a *nucleophile* in the S_N1 reaction.

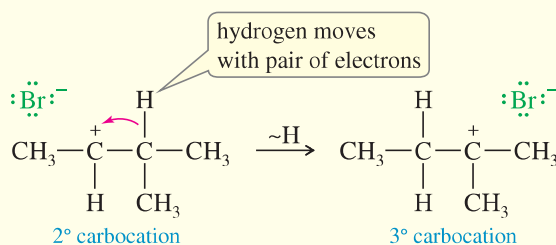
MECHANISM 7-2 Rearrangement in an E1 Reaction

Like other reactions involving carbocations, the E1 may be accompanied by rearrangements such as hydride shifts and alkyl shifts.

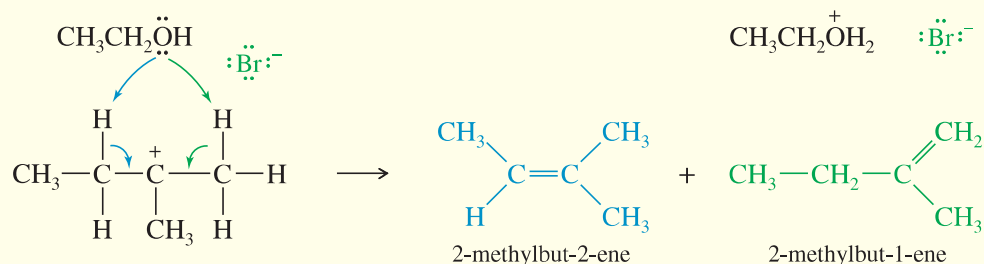
Step 1: Ionization to form a carbocation. (slow)



Step 2: A hydride shift forms a more stable carbocation. (fast)

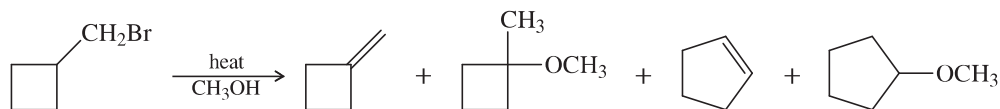


Step 3: The weakly basic solvent removes either adjacent proton. (fast)

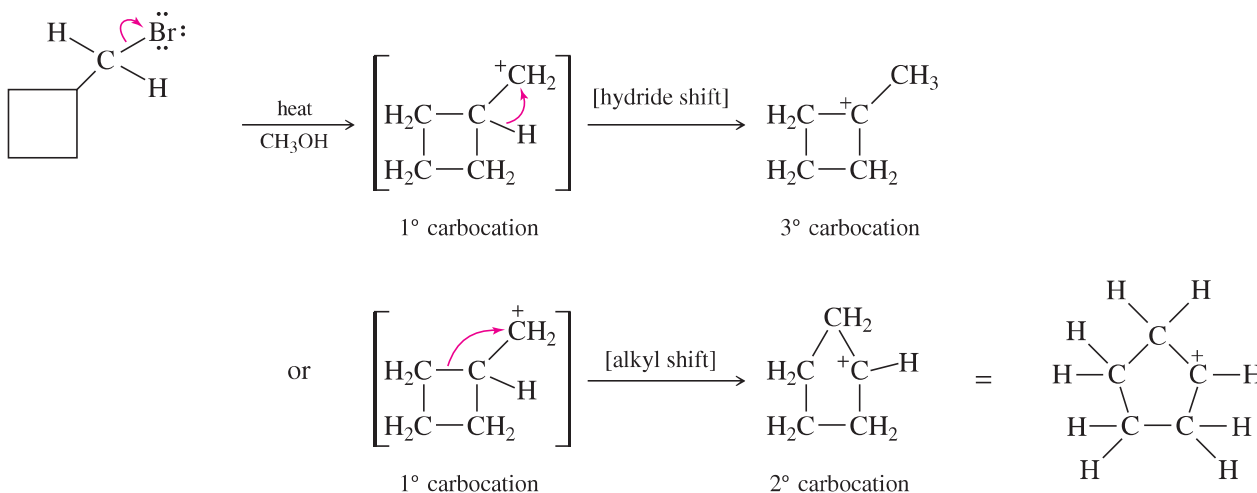


SOLVED PROBLEM 7-3

When the following compound is heated in methanol, several different products are formed. Propose mechanisms to account for the four products shown.

**PARTIAL SOLUTION**

With no strong base and a good ionizing solvent, we would expect a first-order reaction. But this is a primary alkyl halide, so ionization is difficult unless it rearranges. It might rearrange as it forms, but we'll imagine the cation forming then rearranging.



From these rearranged intermediates, either loss of a proton (E1) or attack by the solvent (S_N1) gives the observed products. Note that the actual reaction may give more than just these products, but the other products are not required for the problem.

PROBLEM 7-18

Finish Solved Problem 7-3 by showing how the rearranged carbocations give the four products shown in the problem. Be careful when using curved arrows to show deprotonation and/or nucleophilic attack by the solvent. The curved arrows always show movement of electrons, not movement of protons or other species.

PROBLEM 7-19

The solvolysis of 2-bromo-3-methylbutane potentially can give several products, including both E1 and S_N1 products from both the unrearranged carbocation and the rearranged carbocation. Mechanisms 6-6 (page 282) and 7-2 (previous page) show the products from the rearranged carbocation. Summarize all the possible products, showing which carbocation they come from and whether they are the products of E1 or S_N1 reactions.

We can now summarize four ways that a carbocation can react to become more stable.

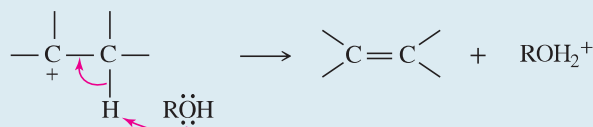
SUMMARY Carbocation Reactions

A carbocation can

1. React with its own leaving group to return to the reactant: $R^+ + :X^- \longrightarrow R-X$
2. React with a nucleophile to form a substitution product (S_N1): $R^+ + Nuc:^- \longrightarrow R-Nuc$

(continued)

3. Lose a proton to form an elimination product (an alkene) (E1):



4. Rearrange to a more stable carbocation and then react further.

The order of stability of carbocations is: resonance-stabilized, $3^\circ > 2^\circ > 1^\circ$.

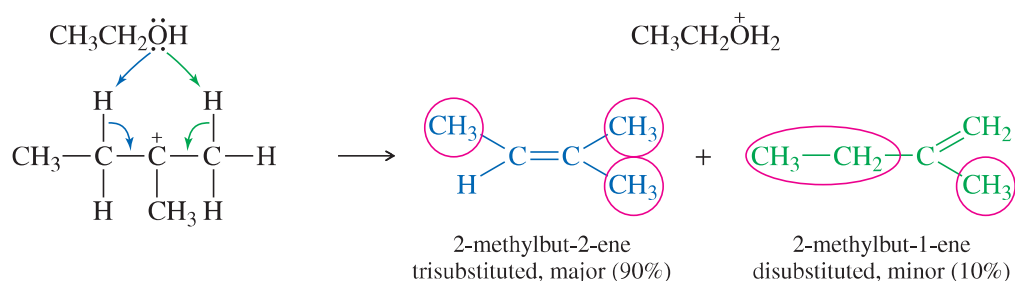
PROBLEM 7-20

Give the substitution and elimination products you would expect from the following reactions.

- 3-bromo-3-ethylpentane heated in methanol
- 1-iodo-1-phenylcyclopentane heated in ethanol
- 1-bromo-2-methylcyclohexane + silver nitrate in water (AgNO_3 forces ionization)

7-11 Positional Orientation of Elimination: Zaitsev's Rule

We have seen that many compounds can eliminate in more than one way, to give mixtures of alkenes. In many cases, we can predict which elimination product will predominate. In the example shown in Mechanism 7-2, the carbocation can lose a proton on either of two adjacent carbon atoms.

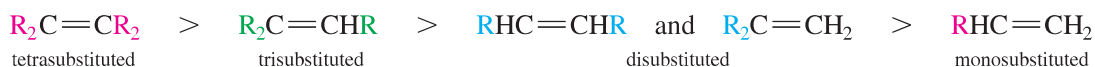


The first product has a *trisubstituted* double bond, with three substituents (circled) on the doubly bonded carbons. It has the general formula $\text{R}_2\text{C}=\text{CHR}$. The second product has a *disubstituted* double bond, with general formula $\text{R}_2\text{C}=\text{CH}_2$ (or $\text{R}-\text{CH}=\text{CH}-\text{R}$). In most E1 and E2 eliminations where there are two or more possible elimination products, *the product with the most substituted double bond will predominate*. This general principle is the applied form of **Zaitsev's rule**, which we first encountered in Section 7-8B. Reactions that give the most substituted alkene are said to follow **Zaitsev orientation**.

PROBLEM-SOLVING HINT

Zaitsev is transliterated from the Russian name, and may also be spelled **Saytzeff**.

ZAITSEV'S RULE: In elimination reactions, the most substituted alkene usually predominates.



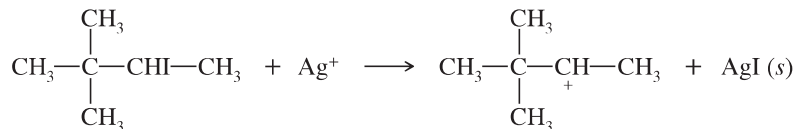
This order of preference is the same as the order of stability of alkenes.

SOLVED PROBLEM 7-4

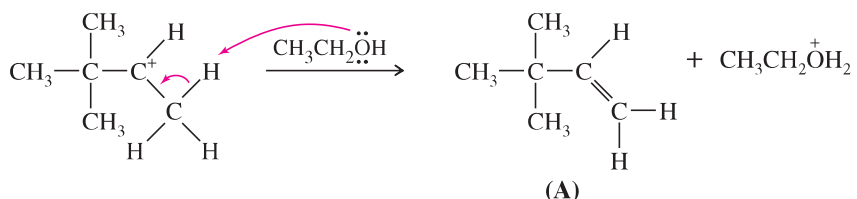
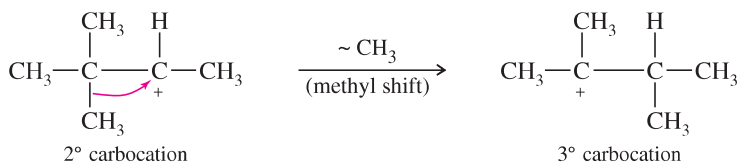
When 3-iodo-2,2-dimethylbutane is treated with silver nitrate in ethanol, three elimination products are formed. Give their structures, and predict which ones are formed in larger amounts.

SOLUTION

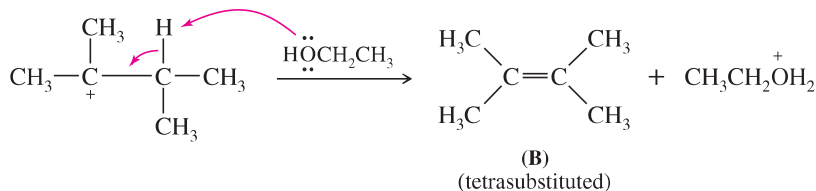
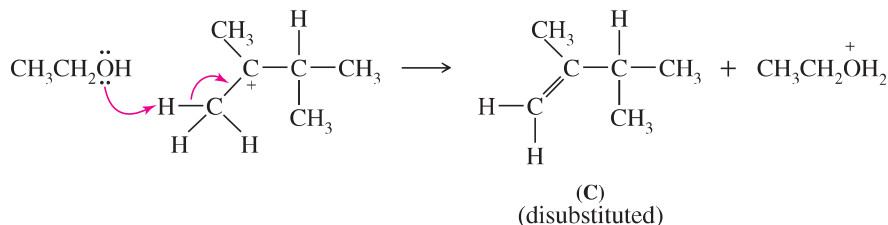
Silver nitrate forces ionization of the alkyl iodide to give solid silver iodide and a cation.



This secondary carbocation can lose a proton to give an unrearranged alkene (**A**), or it can rearrange to a more stable tertiary cation.

Loss of a proton*Rearrangement*

The tertiary cation can lose a proton in either of two positions. One of the products (**B**) is a tetrasubstituted alkene, and the other (**C**) is disubstituted.

Formation of a tetrasubstituted alkene*Formation of a disubstituted alkene*

Product **B** predominates over product **C** because the double bond in **B** is more substituted. Whether product **A** is a major product will depend on the specific reaction conditions and whether proton loss or rearrangement occurs faster.

PROBLEM-SOLVING HINT

Whenever a carbocation has the positive charge on a carbon atom next to a more highly substituted carbon, consider whether a rearrangement might occur.

PROBLEM 7-21

Each of the two carbocations in Solved Problem 7-4 can also react with ethanol to give a substitution product. Give the structures of the two substitution products formed in this reaction.