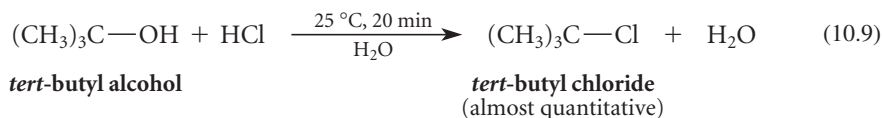
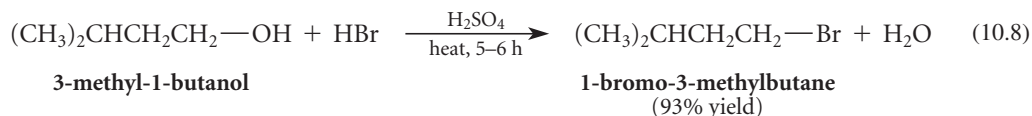


## PROBLEMS

- 10.1 What alkene(s) are formed in the acid-catalyzed dehydration of each of the following alcohols?  
 (a) 3-methyl-3-heptanol (b)  $\text{Ph}\overset{\text{OH}}{\underset{|}{\text{C}}}\text{HCH}_2\text{Ph}$
- 10.2 Give the curved-arrow mechanism for the reaction in Problem 10.1a. In each step, identify all Brønsted acids and bases, all electrophiles and nucleophiles, and all leaving groups.
- 10.3 Give the structure of the carbocation intermediate involved in the acid-catalyzed dehydration of 3-ethyl-3-pentanol.
- 10.4 Identify the *major* alkene product(s) in part (a) of Problem 10.1.
- 10.5 Give the structures of two alcohols, one secondary and one tertiary, that could give each of the following alkenes as a major acid-catalyzed dehydration product. In each case, which alcohol would dehydrate most rapidly?  
 (a) 1-methylcyclohexene (b) 3-methyl-2-pentene
- 10.6 (a) Give a curved-arrow mechanism for the reaction in Eq. 10.6.  
 (b) After reading Study Guide Link 10.2, explain why the rearrangement in Eq. 10.7 is favorable even though both of the carbocation intermediates involved are secondary.
- 10.7 A certain reaction is carried out in methanol with  $\text{H}_2\text{SO}_4$  as a catalyst.  
 (a) What Brønsted acid is present in highest concentration in such a solution? (*Hint*:  $\text{H}_2\text{SO}_4$  is completely dissociated in methanol, just as it is in water.)  
 (b) If a base is involved in the reaction mechanism, what is the basic species?

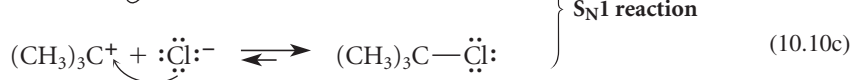
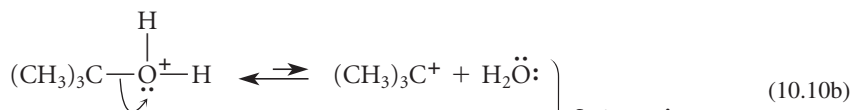
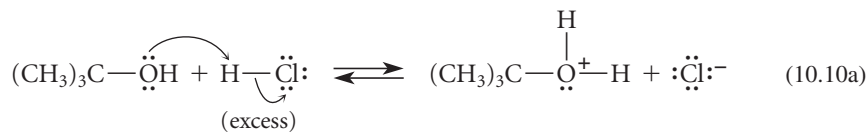
## 10.2 REACTIONS OF ALCOHOLS WITH HYDROGEN HALIDES

Alcohols react with hydrogen halides to give alkyl halides:



The equilibrium constant for the formation of alkyl halides from alcohols is not large; hence, the successful preparation of alkyl halides from alcohols, like the dehydration of alcohols to alkenes, usually depends on the application of Le Châtelier's principle (Sec. 4.9B). For example, in both Eqs. 10.8 and 10.9, the reactant alcohols are soluble in the reaction solvent, which is an aqueous acid, but the product alkyl halides are not. Separation of the alkyl halide products from the reaction mixture as water-insoluble layers drives both reactions to completion. For alcohols that are not water-soluble, a large excess of gaseous HBr can be used to drive the reaction to completion.

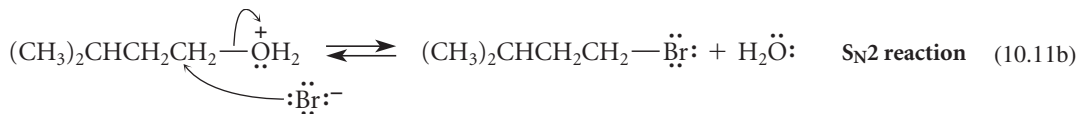
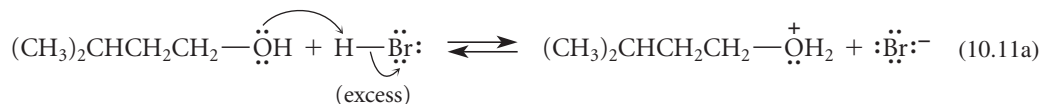
The mechanism of alkyl halide formation depends on the type of alcohol used as the starting material. In the reactions of tertiary alcohols, protonation of the alcohol oxygen is followed by carbocation formation. The carbocation reacts with the halide ion, which is formed by ionization of strong acid HCl, and which is present in great excess:



}  $S_{\text{N}}1$  reaction

Once the alcohol is protonated, the reaction is an  $S_{\text{N}}1$  reaction with  $\text{H}_2\text{O}$  as the leaving group.

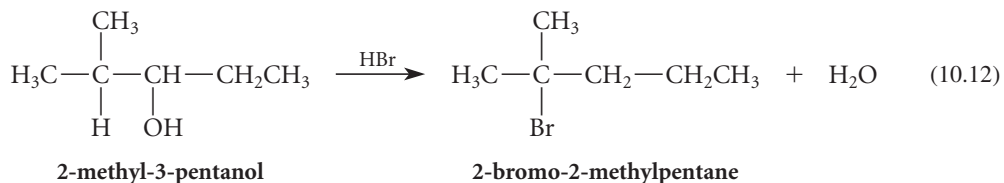
When a primary alcohol is the starting material, the reaction occurs as a concerted displacement of water from the protonated alcohol by halide ion. In other words, the reaction is an  $S_{\text{N}}2$  reaction in which water is the leaving group.



Notice that the initial step in both of these  $S_{\text{N}}1$  and  $S_{\text{N}}2$  mechanisms is protonation of the  $-\text{OH}$  group.

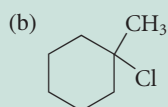
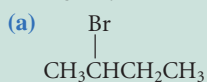
As the conditions of Eqs. 10.8 and 10.9 suggest, the reactions of tertiary alcohols with hydrogen halides are much faster than the reactions of primary alcohols. Typically, tertiary alcohols react with hydrogen halides rapidly at room temperature, whereas the reactions of primary alcohols require heating for several hours. The reactions of primary alcohols with  $\text{HBr}$  and  $\text{HI}$  are satisfactory, but their reactions with  $\text{HCl}$  are very slow. Although reactions of alcohols with  $\text{HCl}$  can be accelerated with certain catalysts, other methods for preparing primary alkyl chlorides (discussed in the following section) are better.

The reactions of secondary alcohols with hydrogen halides tend to occur by the  $S_{\text{N}}1$  mechanism. This means that carbocations are involved as reactive intermediates, and, consequently, rearrangements can occur in many cases:



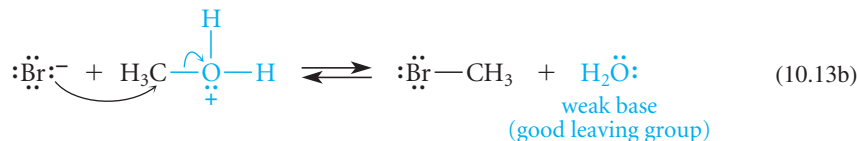
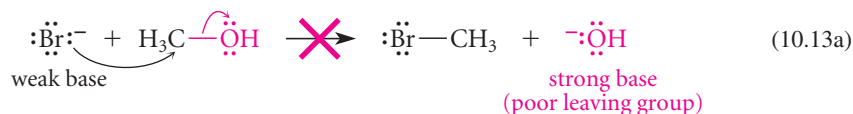
### PROBLEMS

10.8 Suggest an alcohol starting material and the conditions for the preparation of each of the following alkyl halides.



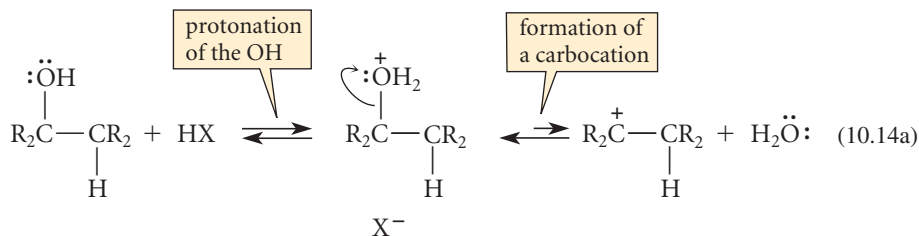
- 10.9 Give a curved-arrow mechanism for the rearrangement shown in Eq. 10.12.
- 10.10 Give the structure of the alkyl halide product expected (if any) in each of the following reactions.
- (a) 1-propanol + HBr in the presence of H<sub>2</sub>SO<sub>4</sub> catalyst
- (b) HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH + excess HI  $\xrightarrow{\text{heat}}$
- (c) 
$$\begin{array}{c} \text{OH} \\ | \\ (\text{CH}_3)_3\text{C}-\text{CH}-\text{CH}_3 \end{array} + \text{excess HBr} \xrightarrow{\text{heat}}$$
- (d) (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OH + HCl  $\xrightarrow{25^\circ\text{C}}$
- (Hint: See Fig. 9.4, p. 392.)

The dehydration of alcohols to alkenes and the reactions of alcohols with hydrogen halides have some important things in common. Both take place in very acidic solution; in both reactions, the acid converts the —OH group into a good leaving group. We've already discussed this point for dehydrations in Sec. 10.1. For substitution reactions, if acid were not present, the halide ion would have to displace <sup>-</sup>OH to form the alkyl halide. This reaction does not take place because <sup>-</sup>OH is a much stronger base than any halide ion (Table 3.1, p. 103), and strong bases are poor leaving groups (Sec. 9.4F).

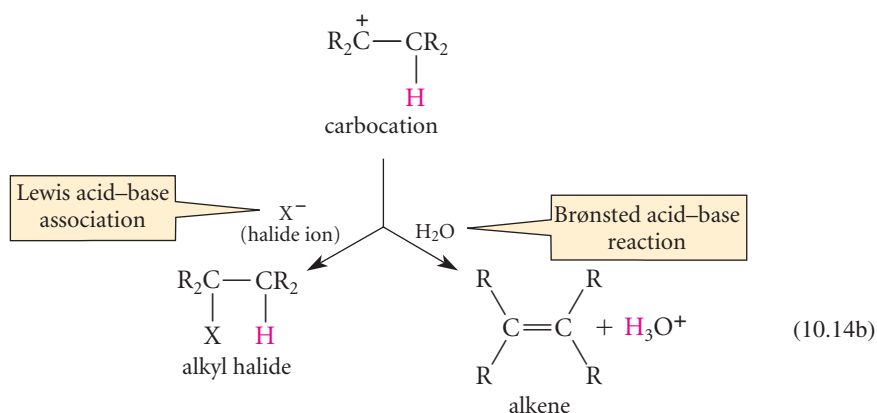


Remember: *substitution and elimination reactions of alcohols require the —OH group to be converted into a better leaving group.*

The formation of secondary and tertiary alkyl halides and the dehydration of secondary and tertiary alcohols have the same initial steps: protonation of the alcohol oxygen and formation of a carbocation.



The two reactions differ in the fate of this carbocation, which in turn is governed by the conditions of the reaction. In the presence of a hydrogen halide, the halide ion is present in excess and reacts with the carbocation. In dehydration, no halide ion is present, and when the alkene forms by loss of a β-proton from the carbocation, the conditions of the dehydration reaction force the removal of the alkene product and the water by-product from the reaction mixture. It follows, then, that *alkyl halide formation and dehydration to alkenes are alternative branches of a common mechanism:*



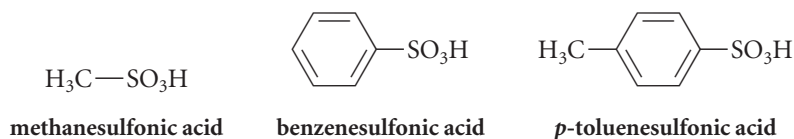
Notice that the principles you've studied in Chapter 9 for the substitutions and eliminations of alkyl halides are valid for other functional groups—in this case, alcohols.

## 10.3 SULFONATE AND INORGANIC ESTER DERIVATIVES OF ALCOHOLS

When an alkyl halide is prepared from an alcohol and a hydrogen halide, protonation converts the —OH group into a good leaving group. However, if the alcohol molecule contains a group that might be sensitive to strongly acidic conditions, or if milder or even nonacidic conditions must be used for other reasons, different ways of converting the —OH group into a good leaving group are required. Methods for accomplishing this objective are the subject of this section.

### A. Sulfonate Ester Derivatives of Alcohols

**Structures of Sulfonate Esters** An important method of activating alcohols toward nucleophilic substitution and  $\beta$ -elimination reactions is to convert them into *sulfonate esters*. Sulfonate esters are derivatives of **sulfonic acids**, which are compounds of the form  $\text{R}-\text{SO}_3\text{H}$ . Some typical sulfonic acids are the following:



(The *p* in the name of the last compound stands for *para*, which indicates the relative positions of the two groups on the benzene ring. This type of nomenclature is discussed in Chapter 16.) A **sulfonate ester** is a compound in which the acidic hydrogen of a sulfonic acid is replaced by an alkyl or aryl group. Thus, in ethyl benzenesulfonate, the acidic hydrogen of benzenesulfonic acid is replaced by an ethyl group.

