This reagent is related to thionyl chloride in the sense that it converts the —OH group into a good leaving group and, at the same time, provides a source of halide ion (bromide ion in this case) to effect the substitution reaction. (As Eq. 10.25 shows, all three bromines of PBr₃ can be used; Eq. 10.26 gives the mechanism of the first substitution only.)

This reaction is considerably more general than the reaction of alcohols with HBr because it can be used with alcohols containing other functional groups that are acid-sensitive and would not survive treatment with HBr. Also, when used with secondary alcohols, the risk of rearrangement, although not totally absent, is less than with HBr.

**PROBLEMS**

10.17 Give three reactions that illustrate the preparation of 1-bromobutane from 1-butanol.

10.18 (a) According to the mechanism of the reaction shown in Eq. 10.24, what would be the absolute configuration of the alkyl chloride obtained from the reaction of thionyl chloride with (S)-CH₃CH₂CH₂CH₂OH? Explain.

(b) According to the mechanism shown in Eq. 10.26, what would be the absolute configuration of 2-bromopentane obtained from the reaction of PBr₃ with the R enantiomer of 2-pentanol? Explain.

**CONVERSION OF ALCOHOLS INTO ALKYL HALIDES: SUMMARY**

You have now studied a variety of reactions that can be used to convert alcohols into alkyl halides. These are

1. reaction with hydrogen halides
2. formation of sulfonate esters followed by Sₘ₂ reaction with halide ions
3. reaction with SOCl₂ or PBr₃.

Which method should be used in a given situation? The method of choice depends on the structure of the alcohol and on the type of alkyl halide (chloride, bromide, iodide) to be prepared.

**Primary Alcohols:** Alkyl bromides are prepared from primary alcohols by the reaction of the alcohol with concentrated HBr or with PBr₃. HBr is often chosen for convenience and because the reagent is relatively inexpensive. The reaction with PBr₃ is quite general, but it is particularly useful when the alcohol contains another functional group that would be adversely affected by the strongly acidic conditions of the HBr reaction. (You’ll learn about such functional groups in later chapters.) Primary alkyl iodides can be prepared with HI, which is usually supplied by mixing an iodide salt such as KI with a strong acid such as phosphoric acid. Thionyl chloride is the method of choice for the preparation of primary alkyl chlorides.
because the reactions of primary alcohols with HCl are slow. The sulfonate ester method works well with primary alcohols, but it requires two separate reactions (formation of the sulfonate ester, then reaction of the ester with halide ion). Because all of these methods have an S_N2 mechanism as their basis, alcohols with several β-alkyl substituents, such as neopentyl alcohol, do not react under the usual conditions.

**Tertiary Alcohols:** Tertiary alcohols react rapidly with HCl or HBr under mild conditions to give the corresponding alkyl halides. The sulfonate ester method shown in Study Problem 10.1 is not used with tertiary alcohols because tertiary sulfonates, like tertiary alkyl halides, do not undergo S_N2 reactions.

**Secondary Alcohols:** If the secondary alcohol has no β-alkyl substitution, the thionyl chloride method can be used to prepare alkyl chlorides and the PBr_3 method can be used to prepare alkyl bromides. To avoid rearrangements completely, the alcohol can be converted into a sulfonate ester which, in turn, can be treated with the appropriate halide ion (Cl^−, Br^−, or I^−) in a polar aprotic solvent. This type of solvent provides the enhanced nucleophilicity of the halide ion necessary to overcome the relatively low S_N2 reaction rate of a secondary sulfonate ester (Sec. 9.4E). Less reactive secondary alcohols can be converted into triflates, which are much more reactive than tosylates or mesylates toward halide ions in polar aprotic solvents. The HBr method can be expected to lead to rearrangements and is thus not very satisfactory (unless rearranged products are desired). Specialized methods that have not been discussed are required for primary and secondary alcohols that have significant β-alkyl substitution.

Let’s also remind ourselves what we have learned mechanistically about the substitution and elimination reactions of alcohols. The —OH group itself cannot act as a leaving group because —OH is far too basic. To break the carbon–oxygen bond, the —OH group must first be converted into a good leaving group. Two general strategies can be used for this purpose:

1. **Protonation:** Protonated alcohols are intermediates in both dehydration to alkenes and the reaction with hydrogen halides to give alkyl halides.

2. **Conversion into sulfonate esters, inorganic esters, or related leaving groups:** Sulfonate esters, to a useful approximation, react like alkyl halides. That is, the principles of alkyl halide reactivity you learned in Chapter 9 are equally applicable to sulfonate esters. Thionyl chloride and phosphorus tribromide are additional examples of this approach in which the reagent both converts the alcohol —OH into a good leaving group and provides the displacing nucleophile.

### PROBLEMS

10.19 Suggest conditions for carrying out each of the following conversions to yield a product that is as free of isomers as possible.

(a) \[ \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{BrCH}_2\text{CH}_2\text{Br} \]

(b) \[ (\text{CH}_3)_2\text{CHCH}_2\text{OH} \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{Cl} \]

(c) \[ \text{CHCH}_3\text{OH} \rightarrow \text{BrCH}_3\text{CH}_2\text{CH}_3 \]

(d) \[ \text{HO} \rightarrow \text{Br} \]

10.20 Give the structure of two secondary alcohols that could be converted by HBr/H_2SO_4 into the corresponding alkyl bromide without rearrangement.