

10.5: PREPARING ALKYL HALIDES FROM ALCOHOLS

OBJECTIVES

After completing this section, you should be able to

1. write an equation for the conversion of an alcohol to an alkyl halide.
2. list a given series of alcohols in increasing or decreasing order of reactivity with hydrogen halides.
3. identify the alkyl halide formed when a given alcohol reacts with thionyl chloride, phosphorus tribromide, or a hydrogen halide.
4. identify the alcohol which should be used to prepare a given alkyl halide using one of the reagents specified in Objective 3.
5. select the most appropriate reagent for converting a given alcohol to a given alkyl halide.

STUDY NOTES

The use of thionyl chloride for converting alcohols to alkyl chlorides has the added benefit that both of the by-products, sulfur dioxide and hydrogen chloride, are gases. This characteristic simplifies the isolation and purification of the reaction product.

In the laboratory, one can test for the presence of alcohols with Lucas reagent (a mixture of concentrated hydrochloric acid and zinc chloride). Lucas reagent converts alcohols to alkyl chlorides: tertiary alcohols fastest followed by secondary alcohols; primary alcohols do not react to any significant extent. Thus, Lucas reagent can help distinguish among primary, secondary and tertiary alcohols due to going through a substitution reaction.

GENERAL REACTION

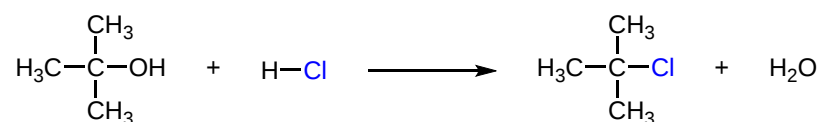
When alcohols react with an acid halide, a substitution takes place producing an alkyl halide and water:



- The order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ > \text{Methyl}$.
- The order of reactivity of the hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$ (HF is generally unreactive).

Tertiary alcohols react reasonably rapidly with HCl, HBr, or HI, but for primary or secondary alcohols the reaction rates are too slow for the reaction to be of much importance. For the reactions that do occur, bubbling HX into an alcohol solution yields a haloalkane or alkyl halide. Below the reaction shows, tert-butanol and hydrochloric acid reacting to yield t-butyl chloride and water.

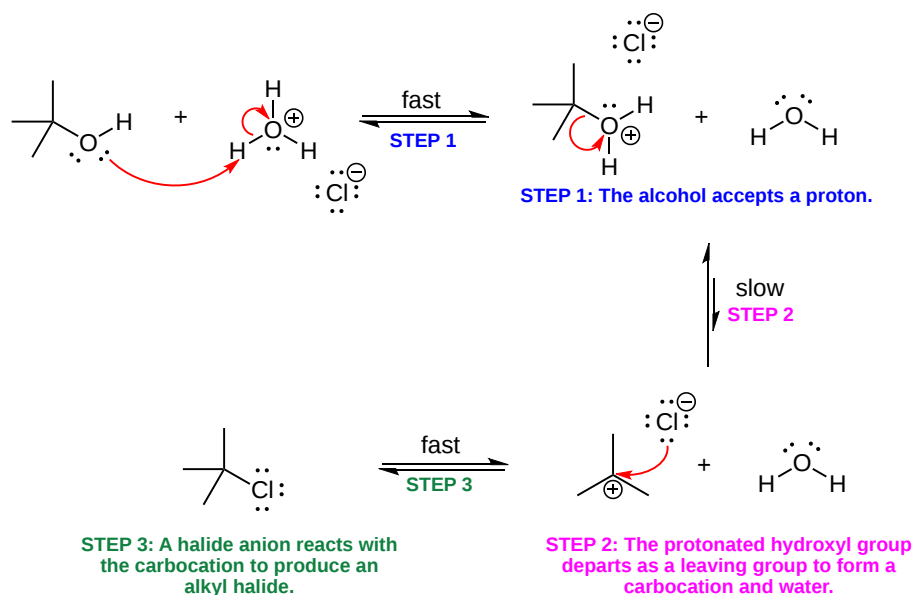
EXAMPLE



MECHANISM

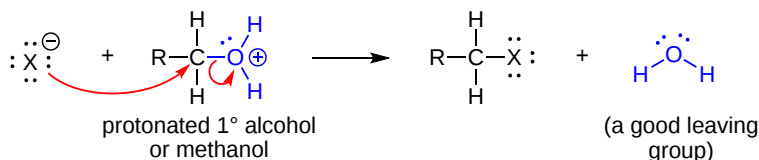
Secondary, tertiary, allylic, and benzylic alcohols appear to react by a mechanism that involves the formation of a carbocation, in an $\text{S}_{\text{N}}1$ reaction with the protonated alcohol acting as a leaving group.

The $\text{S}_{\text{N}}1$ mechanism is illustrated by the reaction of tert-butyl alcohol and aqueous hydrochloric acid (H_3O^+ , Cl^-). The first two steps in this $\text{S}_{\text{N}}1$ substitution mechanism are protonation of the alcohol to form an oxonium ion. Protonation of the alcohol converts a poor leaving group (OH^-) to a good leaving group H_2O which makes the dissociation step of the $\text{S}_{\text{N}}1$ mechanism more favorable. In step 3, the carbocation reacts with a nucleophile (a halide ion) to complete the substitution.

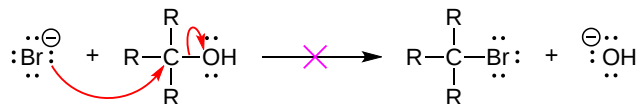


Carbocation rearrangements are extremely common in organic chemistry reactions and are defined as the movement of a carbocation from an unstable state to a more stable state through the use of various structural reorganizational "shifts" within the molecule. Once the carbocation has shifted over to a different carbon, we can say that there is a structural isomer of the initial molecule.

Not all acid-catalyzed conversions of alcohols to alkyl halides proceed through the formation of carbocations. Primary alcohols and methanol react to form alkyl halides under acidic conditions by an S_N2 mechanism. In these reactions the function of the acid is to produce a *protonated alcohol*. The halide ion then displaces a molecule of water (a good leaving group) from carbon; this produces an alkyl halide:



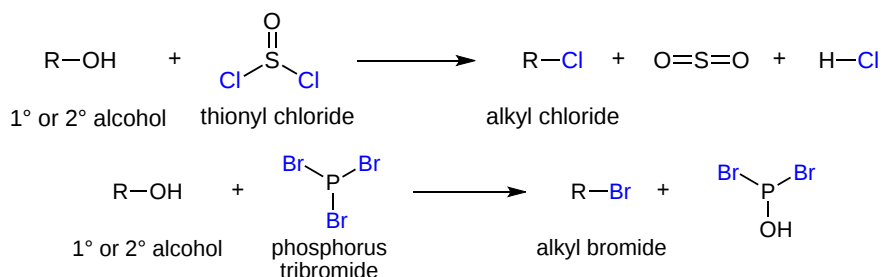
Again, acid is required. Although halide ions (particularly iodide and bromide ions) are strong nucleophiles, they are not strong enough to carry out substitution reactions with alcohols that are not activated (converted to a better leaving group). Direct displacement of the hydroxyl group does not occur because the leaving group would have to be a strongly basic hydroxide ion.



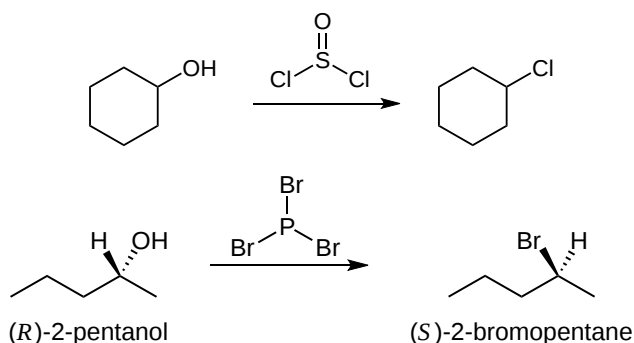
CONVERSION OF ALCOHOLS INTO ALKYL HALIDES USING SOCl_2 OR PBr_3

The most common methods for converting 1°- and 2°-alcohols to the corresponding chloro and bromo alkanes (*i.e.* replacement of the hydroxyl group) are treatments with **thionyl chloride (SOCl_2)** and **phosphorus tribromide (PBr_3)**, respectively. These reagents are generally preferred over the use of concentrated HX due to the harsh acidity of these hydrohalic acids and the carbocation rearrangements associated with their use.

GENERAL REACTION



EXAMPLE

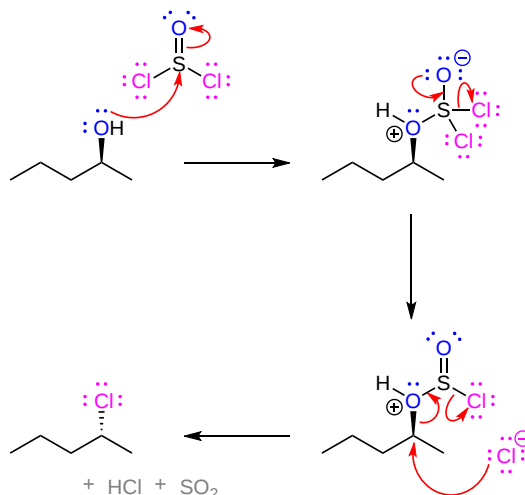


MECHANISMS

Both of these reagents form an alkyl halide through an S_N2 mechanism. The mechanism for both reactions starts by converting the hydroxide of the alcohol into a better leaving group through formation of an intermediate. Thionyl chloride creates an intermediate chlorosulfite ($-\text{OSOCl}_2$) compound and phosphorus tribromide makes an intermediate dibromophosphite ($-\text{OPBr}_2$) compound. These intermediate compounds can subsequently be eliminated as a leaving group during an S_N2 reaction with the corresponding nucleophilic halide ion. Since these reactions proceed through a backside attack, there is inversion of configuration at the carbon.

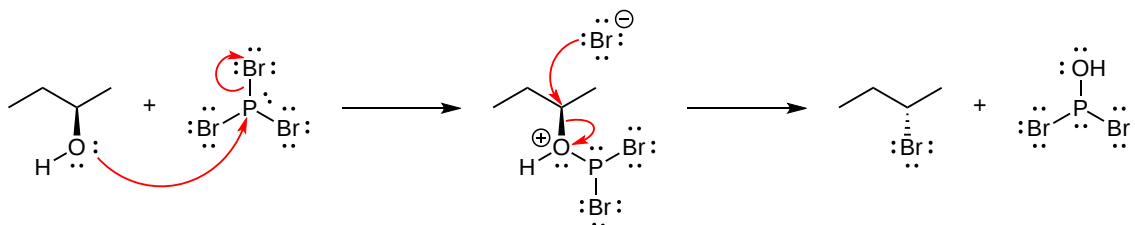
THIONYL CHLORIDE

Notice that during the reaction with thionyl chloride hydrochloric acid (HCl) and sulfur dioxide (SO_2) are produced as byproducts.



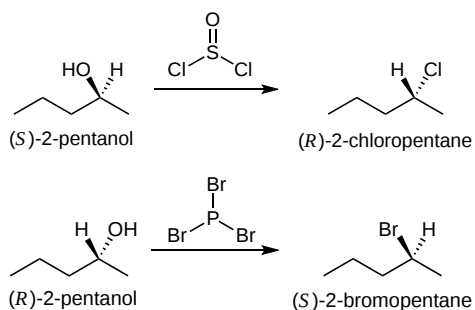
PHOSPHORUS TRIBROMIDE

During this reaction HOPBr_2 is made as a byproduct.



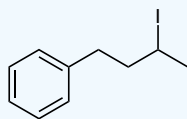
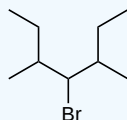
STEREOCHEMICAL CONSIDERATIONS

The S_N2 reaction with the corresponding nucleophilic halide ion contained in the mechanism of both reactions causes an inversion of configuration at the carbon atom.



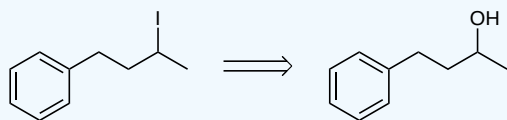
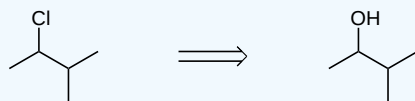
? EXERCISE 10.5.1

1) Predict the alcohol required for the synthesis of the following halides:



Answer

1)



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