

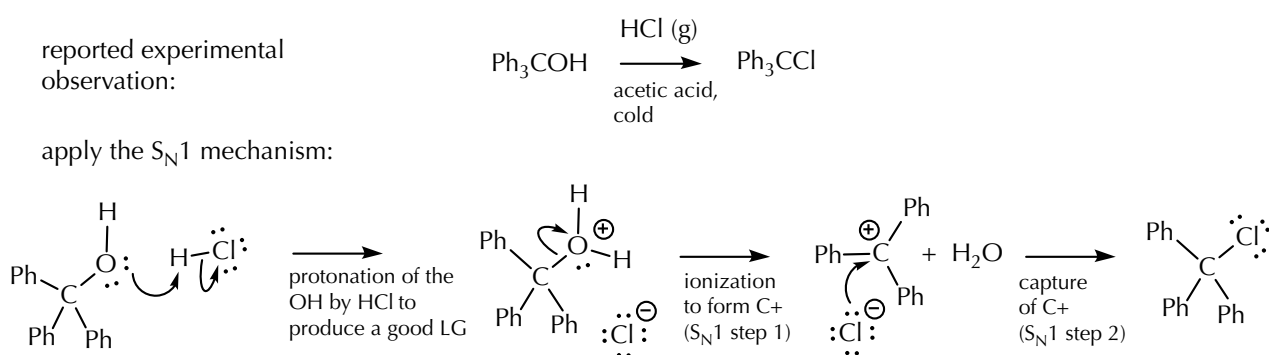
546 CHAPTER 7 Substitution and Elimination Reactions of Polar Sigma Bonds

can apply the general mechanism. These four examples are the last ones before developing the predictive model, and so one last opportunity to see that once you have the information about which mechanistic pathway is operating, you can then apply it, as a general principle, to any specific case. This identification step derives from a predictive model, and the predictive model, in turn, derives from hundreds and hundreds of experimental results.

Description for Figure 0726: Experimentally, when a solution of 1-butanol is shaken vigorously for just a few minutes with an aqueous solution of hydrobromic acid, a reaction takes place and a layer of nearly pure 1-bromobutane is observed. If you are directed to show the transformation as an application of the S_N2 mechanism, then you need to (a) turn the hydroxyl group into a good leaving group and (b) show the 1-step mechanism. Recall too that an aqueous solution of hydrobromic acid ($pK_a -8$) is really a solution of hydronium bromide, and so hydronium ($pK_a -2$) is shown as the Brønsted acid that protonates the hydroxyl group of 1-butanol. The reason that this substitution reaction works is that bromide ion is a quite poor Brønsted base, and it does not favorably deprotonate the protonated hydroxyl group ($-OH_2^+$). Instead, at some rate, the S_N2 mechanism operates (because this was part of the given information) and 1-bromobutane is formed.

Figure 0727

Transformation of R-OH to R-X using H-X (experimentally an S_N1 example).



Description for Figure 0727: Experimentally, an acetic acid solution of triphenylmethanol can be treated with HCl gas, and the resulting solid, chlorotriphenylmethane, can be isolated from the reaction. If you are directed to show the transformation as an application of the S_N1 mechanism, then you need to (a) turn the hydroxyl group into a good leaving group and (b) show the 2-step mechanism. Gaseous HCl is a pure reagent and it can be used as the Brønsted acid that protonates the hydroxyl group of triphenylmethanol. Note that, in this example, the resulting carbocation intermediate can only undergo the substitution pathway because the electrophilic carbon has no β -hydrogen atoms from which elimination might occur. These kinds of structural criteria, such as the presence or absence of β -hydrogen atoms, will become an automatic part of how to decide what might be predicted in any given set of reaction conditions.

Figure 0728

Transformation of R-OH to an alkene (experimentally an E1 example).

