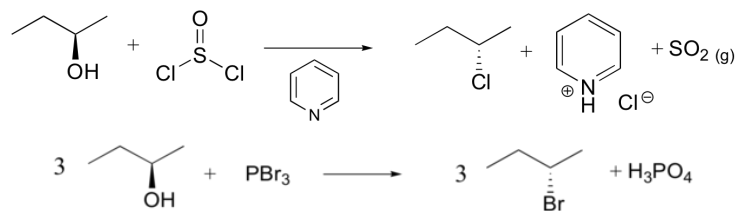


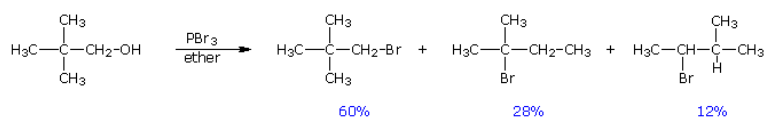
14.2: REACTIONS WITH PHOSPHORUS HALIDES AND THIONYL CHLORIDE

CARBOCATION CONTAINMENT

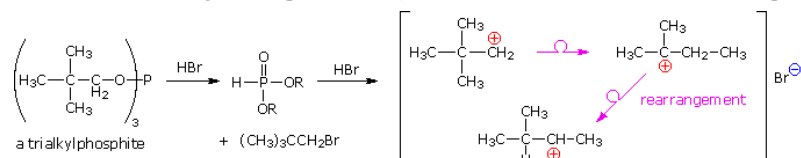
Synthetic organic chemists use phosphorus tribromide and thionyl chloride to convert an alcohol into a better leaving group without carbocation rearrangement.



Despite their general usefulness, phosphorous tribromide and thionyl chloride have shortcomings. Hindered 1°- and 2°-alcohols react sluggishly with the former, and may form rearrangement products, as noted in the following equation.



Below, an abbreviated mechanism for the reaction is displayed. The initially formed trialkylphosphite ester may be isolated if the HBr byproduct is scavenged by base. In the presence of HBr a series of acid-base and S_N2 reactions take place, along with the transient formation of carbocation intermediates. Rearrangement (pink arrows) of the carbocations leads to isomeric products.



Reaction of thionyl chloride with chiral 2°-alcohols has been observed to proceed with either inversion or retention. In the presence of a base such as pyridine, the intermediate chlorosulfite ester reacts to form an "pyridinium" salt, which undergoes a relatively clean S_N2 reaction to the inverted chloride. In ether and similar solvents the chlorosulfite reacts with retention of configuration, presumably by way of a tight or intimate ion pair. This is classified as an S_Ni reaction (nucleophilic substitution internal). The carbocation partner in the ion pair may also rearrange. These reactions are illustrated by the following equations. An alternative explanation for the retention of configuration, involving an initial solvent molecule displacement of the chlorosulfite group (as SO₂ and chloride anion), followed by chloride ion displacement of the solvent moiety, has been suggested. In this case, two inversions lead to retention.

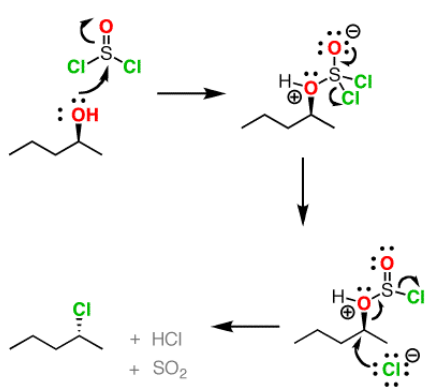
Example: Conversion of Alcohols to Alkyl Chlorides



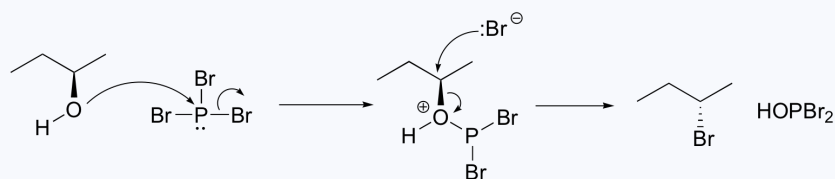
There's one important thing to note here: see the stereochemistry? It's been inverted.*(white lie alert – see below) That's an important difference between SOCl₂ and tosyl chloride, TsCl, which leaves the stereochemistry alone. The TsCl reaction is studied in section 12.3.

MECHANISMS

Since the reaction proceeds through a backside S_N2 reaction, there is inversion of configuration at the carbon



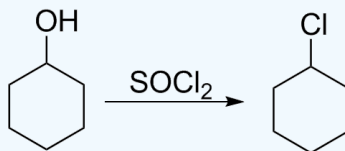
The PBr_3 reaction is thought to involve two successive $\text{S}_{\text{N}}2$ -like steps:



Notice that these reactions result in inversion of stereochemistry in the resulting alkyl halide.

Exercises

2. Draw the mechanism of the reaction of thionyl chloride with cyclohexanol, given below.

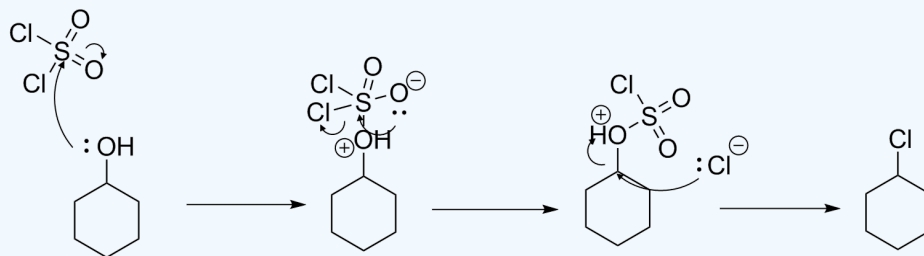


3. Draw the expected product of the reaction of cyclohexanol with the following reagents.

(a) SOCl_2 (b) PBr_3

Answer

2.



3.

