

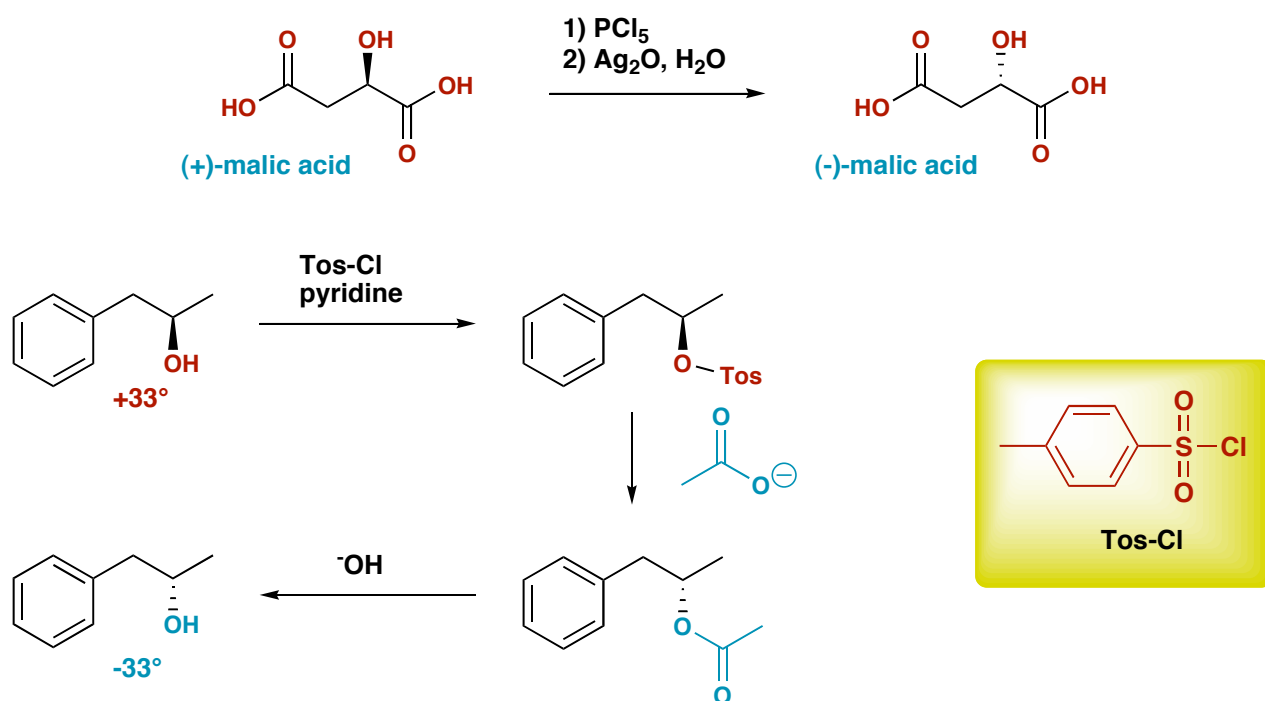
## Chapter 11 - Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

## Overview

The substitution of a halide (or other good leaving group) on a carbon with a nucleophile is a complicated reaction. There are many variables that sway a particular reactant to take one of a number of competing pathways in the mechanism. These factors include, a) the substrate, b) the nucleophile, c) the leaving group, and d) the solvent. We will discuss how each of these factors influence substitution and elimination reactions.

## History

In 1896, Paul Walden found that malic acid could be converted from one enantiomer into another by a sequence of substitution reactions (OH to Cl, then Cl to OH). In the 1920's and 1930's others examined the inversion of stereochemistry during substitution reactions in detail. The reaction is complicated by the fact that under some circumstances, racemic products are obtained. This suggests there may be more than one mechanism possible for the substitution reaction.



## Competing Mechanisms

It has been found that nucleophilic substitution reactions can occur by two different mechanisms. One involves a single step and the other proceeds by two steps via a carbocation intermediate. Additionally, substitution reactions often compete with elimination reactions. The factors outlined above have different consequences on these mechanisms as we will see in the coming class periods.



## S<sub>N</sub>2 Reaction Details - Substrate

Since the nucleophile in a S<sub>N</sub>2 reaction must attack the carbon from the back side (opposite the leaving group) and is involved in the rate determining transition state, the amount of steric bulkiness will have an influence on how well the reaction will proceed. The more substituted the alkyl halide, the harder it is for the nucleophile to approach. Thus, methyl halides are the fastest to react and tertiary halides would be nearly impossible to react.

