



Chem 341 • Organic Chemistry I

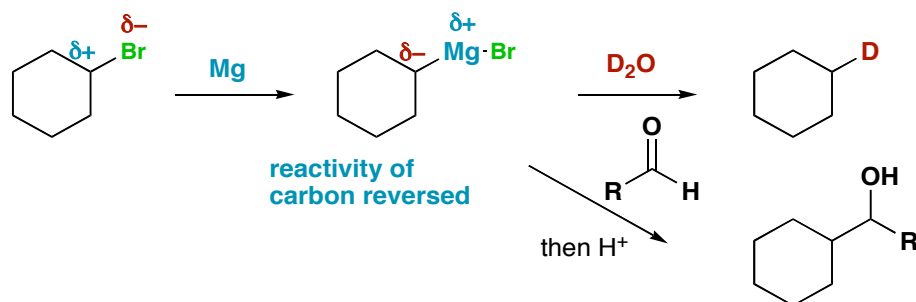
Lecture Summary 29 • November 02, 2007

Chapter 10 - Alkyl Halides

Preparation of Organometallic Compounds - Grignard reagents

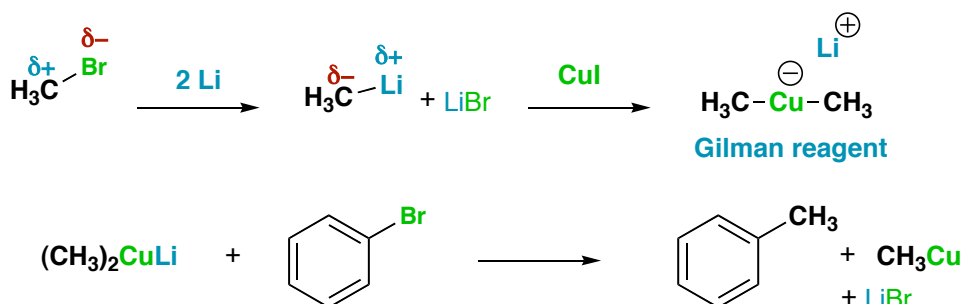
Alkyl halides are good electrophiles. We will examine their reactivity in nucleophilic substitution in detail in the next chapter. Another useful property of alkyl halides is that reducing metals can insert between the C-X bond to prepare a C-metal bond. This drastically alters the reactivity as the metal is less electronegative than carbon. Thus, the reactivity of the carbon is reversed from being an electrophile to being a nucleophile.

Grignard reagents are formed from the insertion of Mg metal into the C-X bond. These reagents are very reactive as bases and electrophiles and are extremely sensitive to any source of proton (water, ROH, RNH₂, etc). This can be useful if one wants to reduce an alkyl halide to an alkane. It is also a useful method of introducing hydrogen isotopes, such as deuterium, by reaction of the Grignard reagent with heavy water (D stands for Deuterium, the isotope of hydrogen ²H). Grignard reagents can be prepared from a variety of different kinds of organohalides (eg. Alkyl halides, vinyl halides, etc.). One important reaction of Grignard reagents is their ability to add to carbonyl compounds (C=O double bonds). You will study this in detail next semester.



Preparation of Organometallic Compounds - Gilman reagents

Lithium metal reacts with organohalides in a similar fashion as magnesium. Organolithium reagents are very basic and are often used to deprotonate compounds that are not very acidic. They will also react with copper (I) salts to form a Gilman reagent. These organocopper compounds are very useful to couple with other organohalides. Note that two organolithiums react with one copper to form a "cuprate" lithium salt. One of the two organic groups will couple with an organohalide.



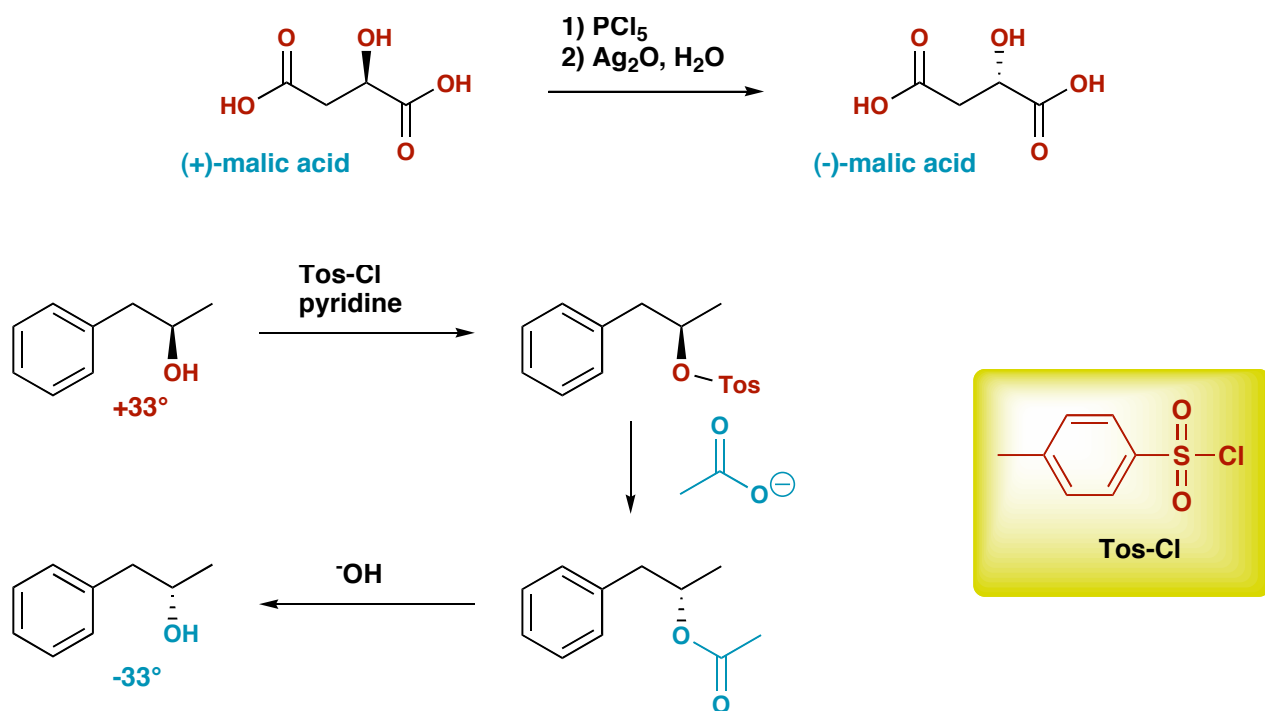
Chapter 11 - Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

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

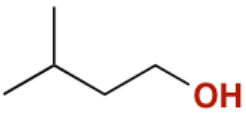
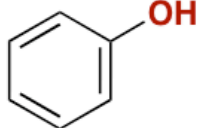
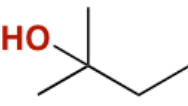
In 1896, Paul Walden found that malic acid could be converted from one enantiomer into another by a sequence of substitution reactions (OH to Cl, then Cl to OH). In the 1920's and 1930's others examined the inversion of stereochemistry during substitution reactions in detail. The reaction is complicated 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.

Quiz of the day

Q: Which of the following alcohols would be the best to prepare an alkyl bromide from using PBr_3 ?	<input checked="" type="checkbox"/> 1:	
	<input type="checkbox"/> 2:	
	<input type="checkbox"/> 3:	
	<input type="checkbox"/> 4:	