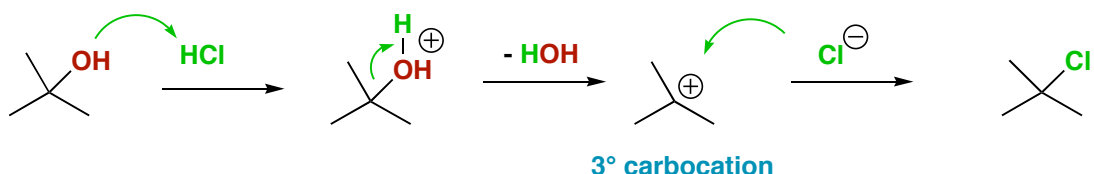


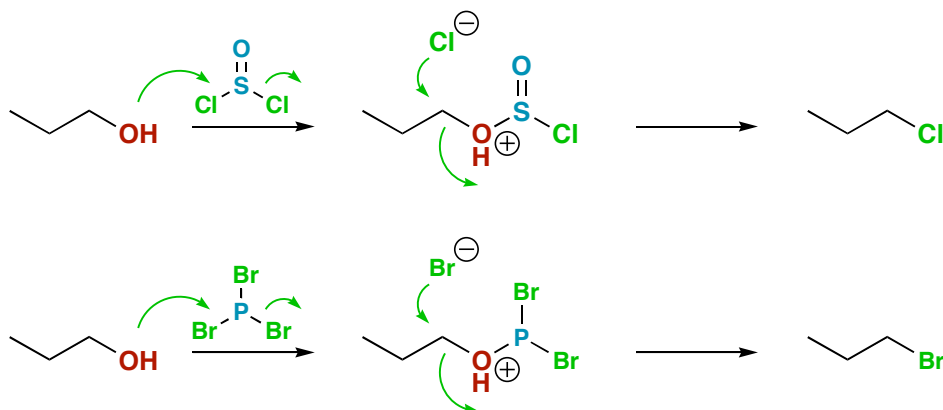
Chapter 10 - Alkyl Halides

Preparation of Alkyl Halides - substitution of alcohols

The substitution of an alcohol functional group with a halogen can be carried out on tertiary alcohols with mineral acids. This reaction only works with 3° alcohols as the mechanism involves the loss of water to form a carbocation and subsequent addition of halide.



Primary and secondary alcohols often undergo competing processes under acidic conditions such as eliminations and carbocation rearrangements. Thus, it is not practical to do the substitution reaction on these alcohols with HCl or HBr. However, bromides can be prepared by reaction with PBr₃ and chlorides with SOCl₂. These reagents provide a dual role of activating the OH group to make it a good leaving group (polarize the C-O bond more) and supplying the X⁻ for the substitution reaction.

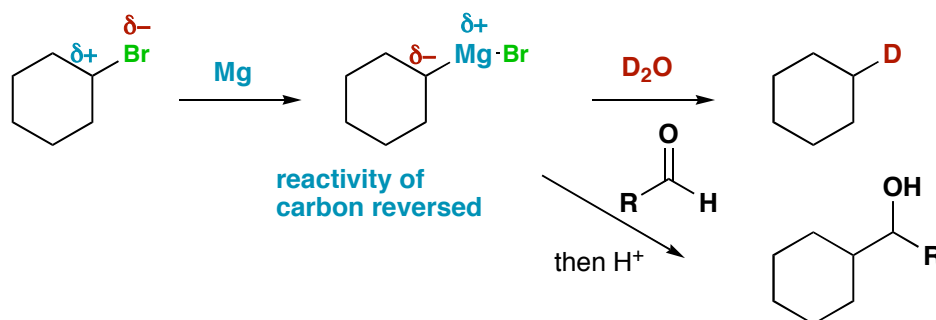


Preparation of Organometallic Compounds - Grignard reagents

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. 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 deprotonated 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.

