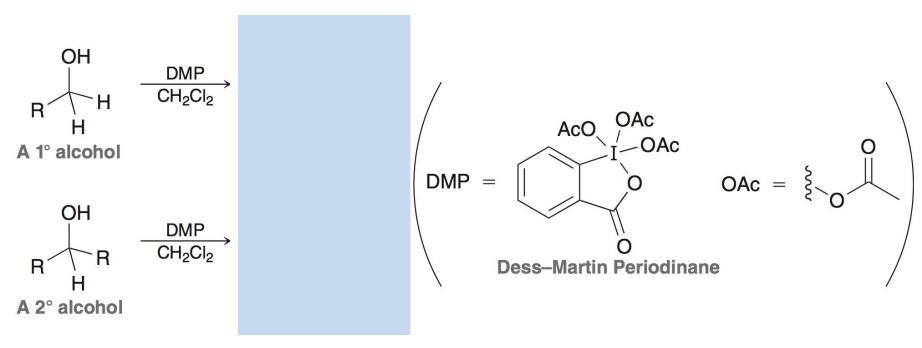
Chapter 12: Alcohols

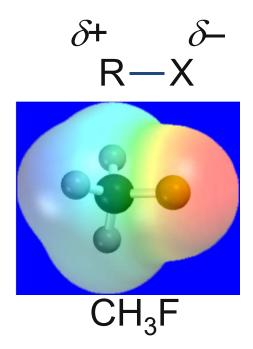
- Today –Finish up Reactions with Alcohols
 - 12.6 Preparation of Alcohols with Grignard
 - 12.7 Protection of Alcohols
 - 12.9 Alcohols Substitution and Elimination

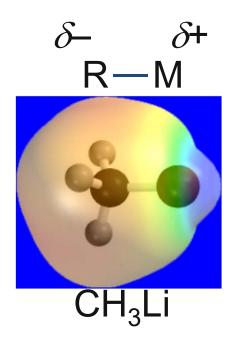
Oxidation of Alcohols

2. Dess-Martin periodane oxidation (DMP) – yields analogous results as the Swern oxidation:



Organometallic Compounds





Preparation of Organomagnesium Compounds <u>Grignard Reagents</u>

prepared by reaction of alkyl halides with magnesium

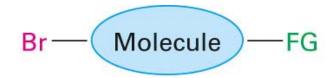
$$R - X + Mg \longrightarrow$$

$$A - Br + Mg \xrightarrow{THF}$$

$$35^{\circ}C$$

$$A - MgBr + A - Br$$

Grignard Reagents and Other Functional Groups in the Same Molecule



where
$$FG = -OH, -NH, -SH, -CO_2H$$

where FG = -OH, -NH, -SH, -CO₂H The Grignard reagent is protonated by these

FG =
$$-CH$$
, $-CR$, $-CNR_2$ The Grignard reagent adds to these groups. $-C \equiv N$, $-NO_2$, $-SO_2R$

Reactions of Grignard Reagents with Carbonyl Compounds

Formaldehyde reaction

Cyclohexylmagnesium bromide

Formaldehyde

Aldehyde reaction

Phenylmagnesium bromide

3-Methylbutanal

Ketone reaction

Ethylmagnesium bromide

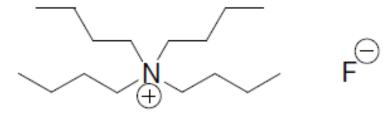
Cyclohexanone

Consider the reaction below. WHY won't it work?

 A three-step process is required to achieve the desired overall synthesis.

One such protecting group is trimethylsilyl (TMS).

- The TMS protection step requires the presence of a base.
- The TMS group can later be removed with H₃O⁺ or F⁻.
- TBAF is often used to supply fluoride ions.



tetrabutylammonium fluoride (TBAF)

 In section 7.12, we saw alcohols undergo elimination in acidic conditions:

$$OH \xrightarrow{\text{conc. H}_2SO_4}$$

• 3° follow? mechanism under these conditions:

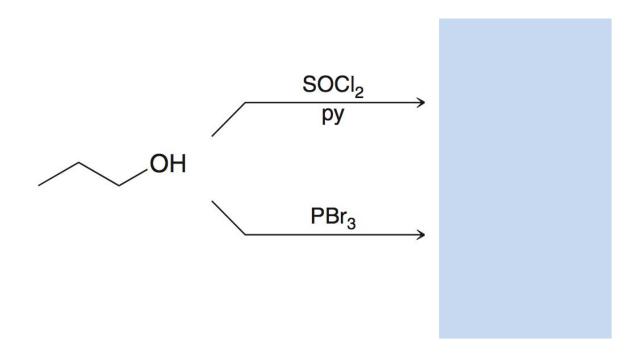
• 3° alcohols area converted to alkyl halides with HX (S_N1 rxn)

For 1° or 2° alcohols, the reaction occurs via S_N2

• To make an alkyl chloride, ZnCl₂ must be used with HCl

$$OH \xrightarrow{HCl} CI$$

• 1° and 2° alcohols can also be converted to alkyl halides using SOCl₂ or PBr₃:



For Next Time....

Suggested Homework Problems Chapter 9 # 1,7,9,13,18,20,32-37, 41,44,52,57

Suggested Homework Problems Chapter 10 # 1, 2, 12, 16, 23,24, 33, 42

Suggested Homework Problems Chapter 12! # 1, 4, 5, 7, 13, 17, 27-32, 34, 43-45