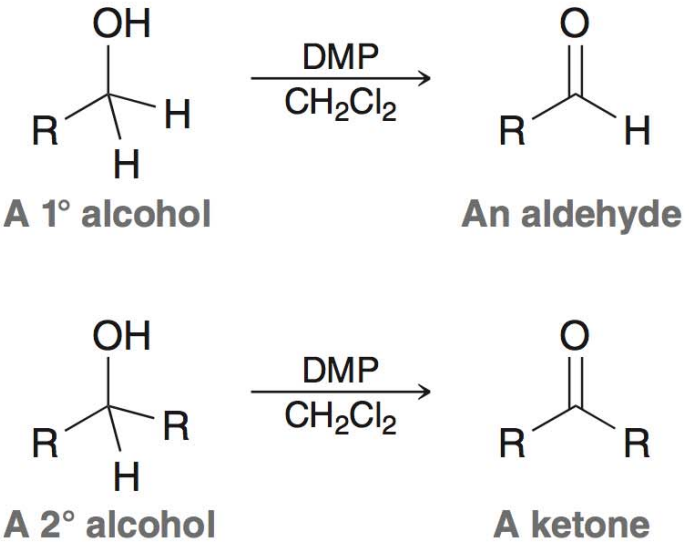
Chapter 12: Alcohols

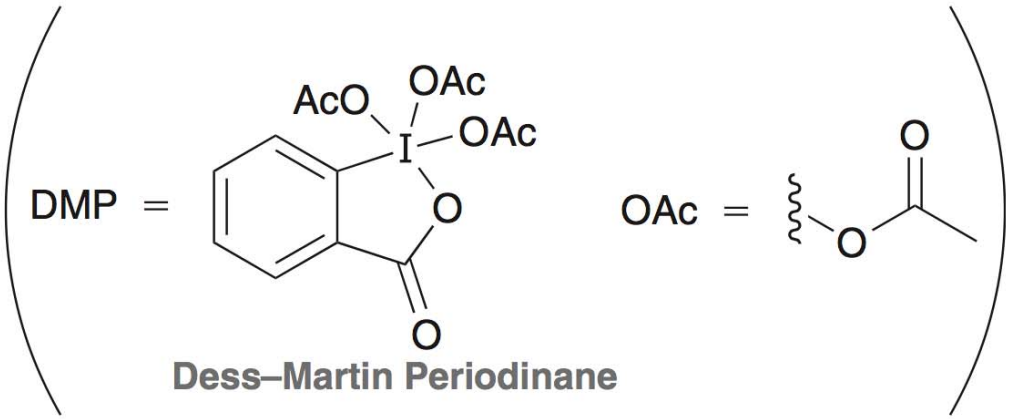
Today –Finish up Reactions with Alcohols

- 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

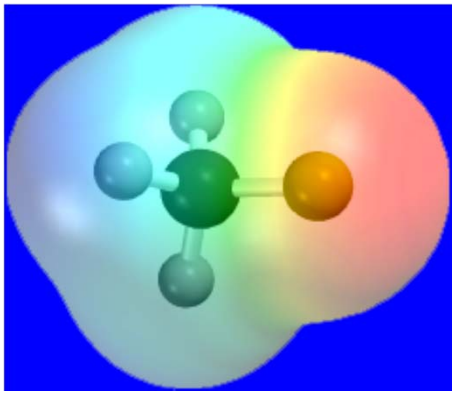
An organic compound containing a carbon–metal bond

δ– δ+ C—Mg δ– δ+ C—Li δ– δ+ C—Cu δ– δ+ C—Cd δ– δ+ C—Si

δ– δ+ C—Zn δ– δ+ C—Al δ– δ+ C—Pb δ– δ+ C—Hg δ– δ+ C—Sn

$\delta+$ $\delta-$

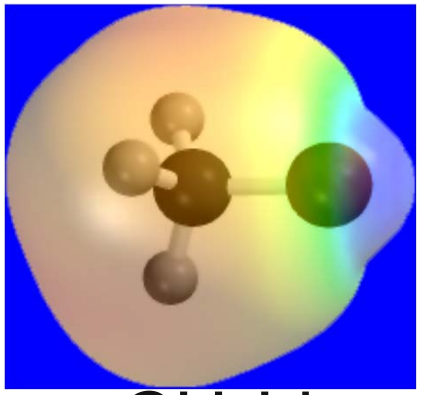
R—X



CH_3F

$\delta-$ $\delta+$

R—M

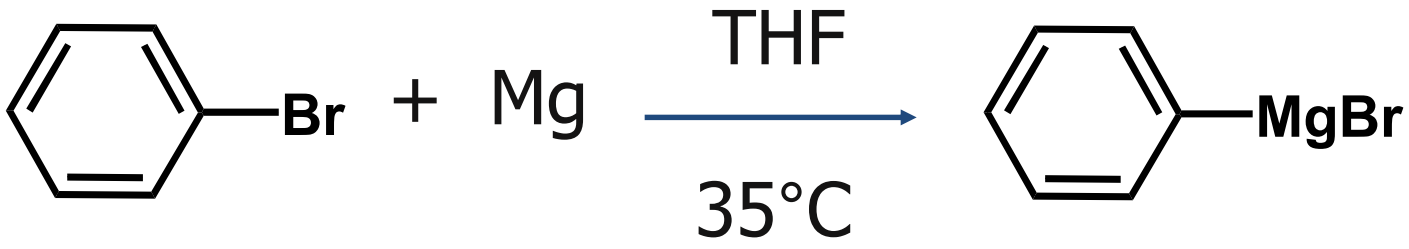


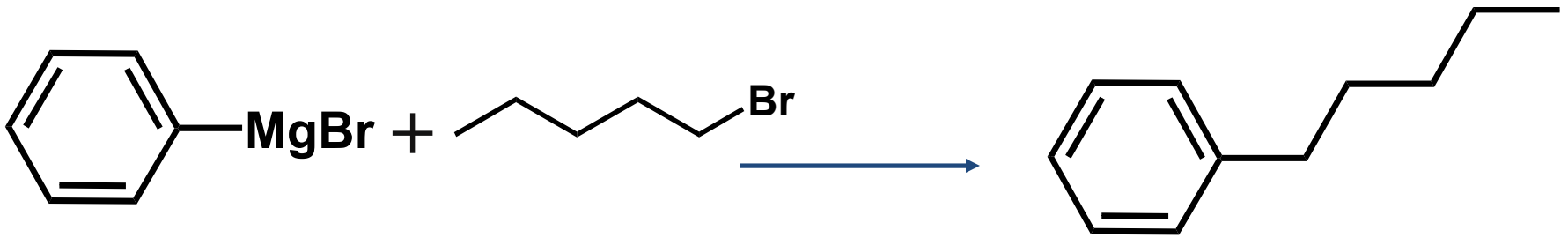
CH_3Li

organometallics are a source of *nucleophilic* carbon

Preparation of Organomagnesium Compounds
Grignard Reagents

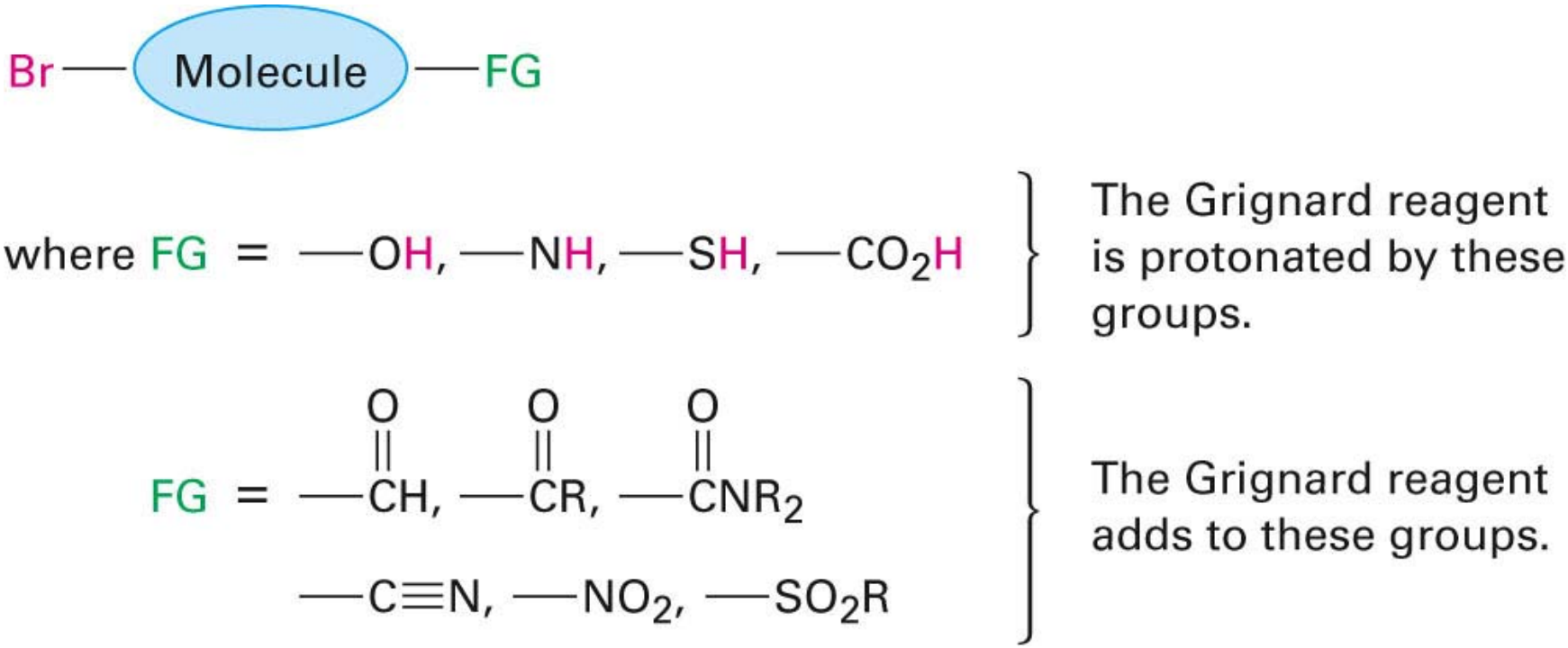
prepared by reaction of alkyl halides with magnesium





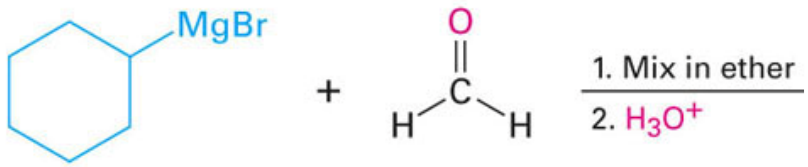
Grignard Reagents and Other Functional Groups in the Same Molecule

- Grignard reagents Can NOT be prepared if there are reactive functional groups in the same molecule, including proton donors



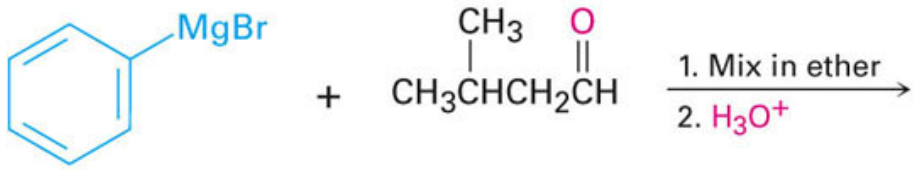
Reactions of Grignard Reagents with Carbonyl Compounds

Formaldehyde reaction



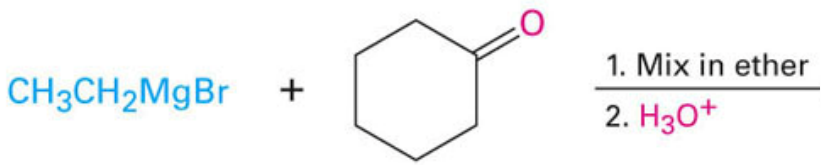
Cyclohexyl-magnesium bromide + **Formaldehyde**

Aldehyde reaction



Phenylmagnesium bromide + **3-Methylbutanal**

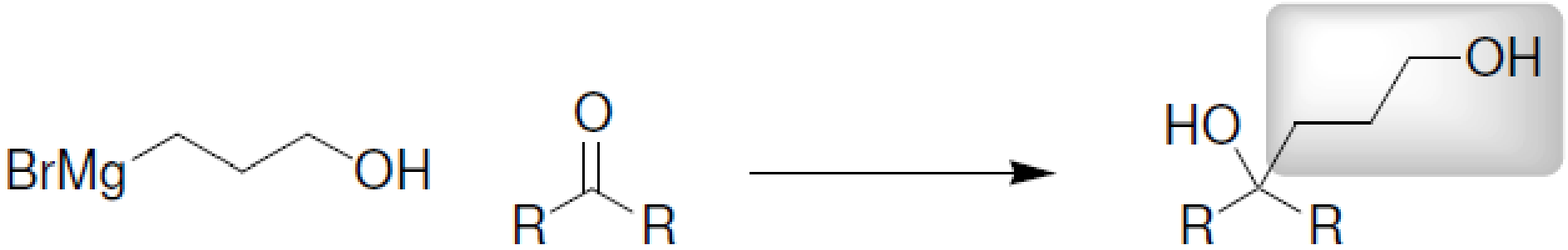
Ketone reaction



Ethylmagnesium bromide + **Cyclohexanone**

Protection of Alcohols

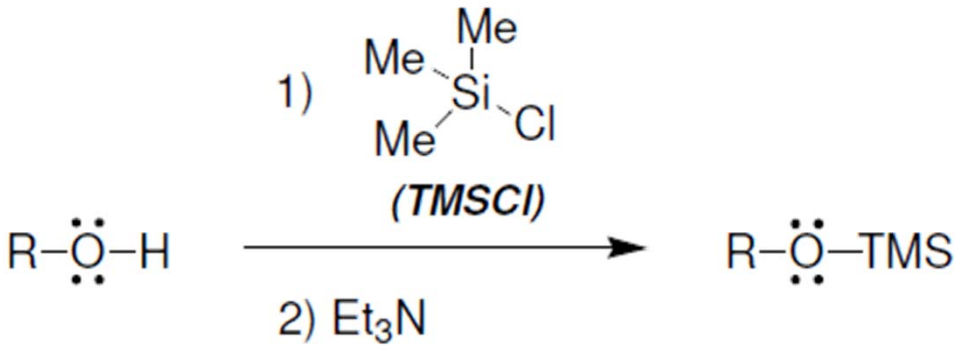
- Consider the reaction below. WHY won't it work?



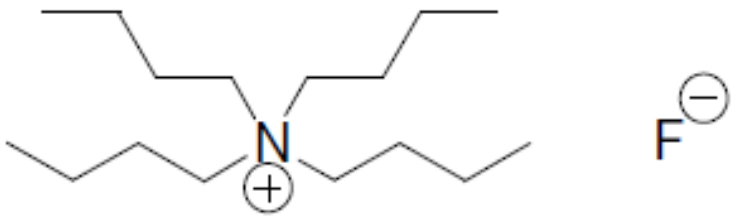
- The alcohol can act as an acid, especially in the presence of reactive reagents like the Grignard reagent.
- The alcohol can be protected to prevent it from reacting.

Protection of Alcohols

- One such protecting group is trimethylsilyl (TMS).

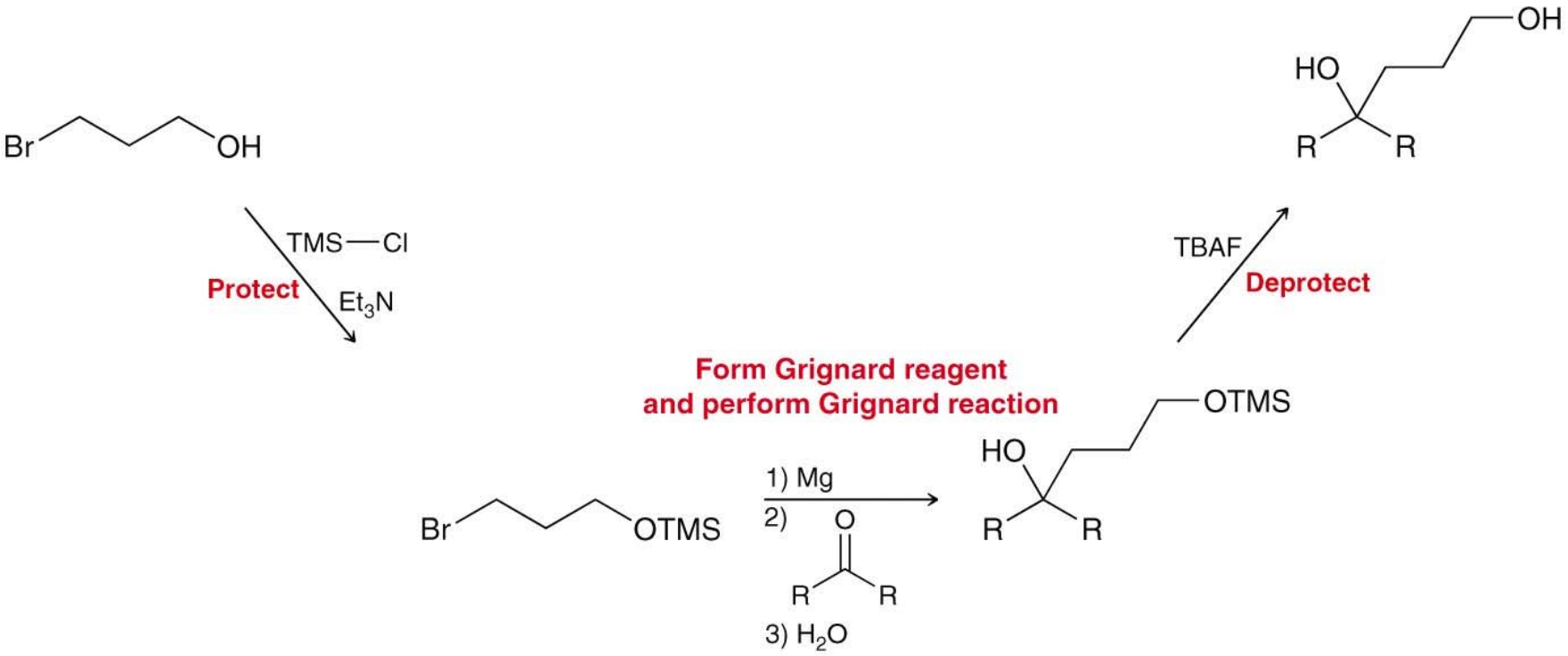


- The TMS protection step requires the presence of a base.
- The TMS group can later be removed with H_3O^+ or F^-.
- TBAF is often used to supply fluoride ions.



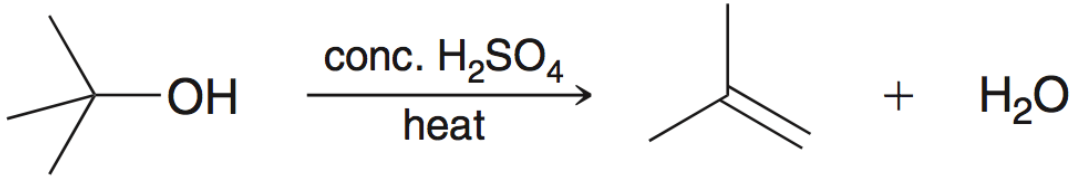
tetrabutylammonium fluoride (TBAF)

Protection of Alcohols

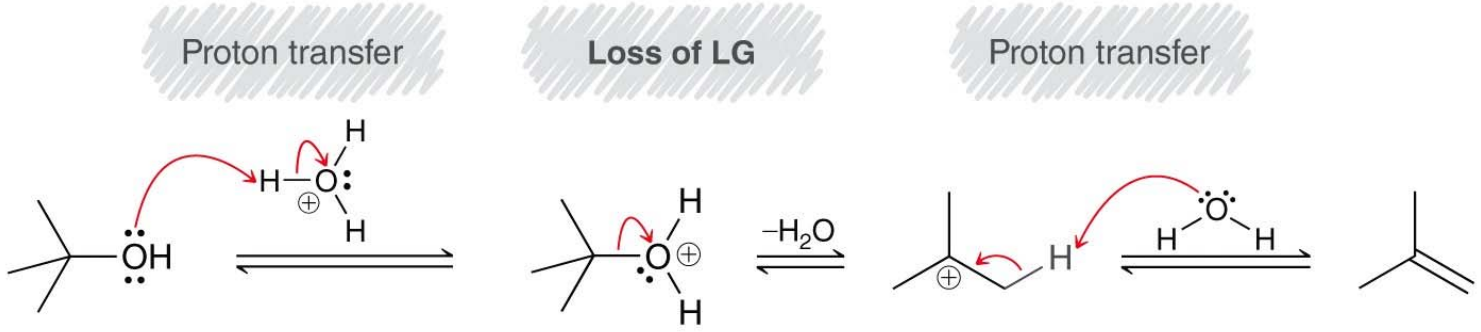


Reactions of Alcohols

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

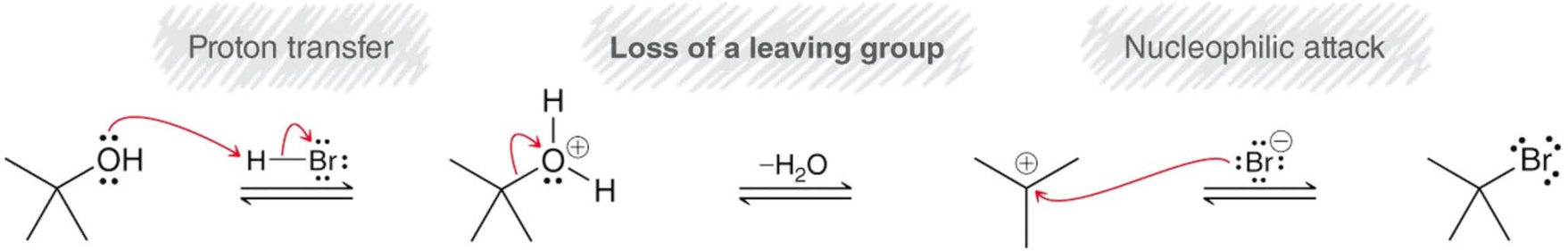


- 3˚ follow ? **mechanism** under these conditions:

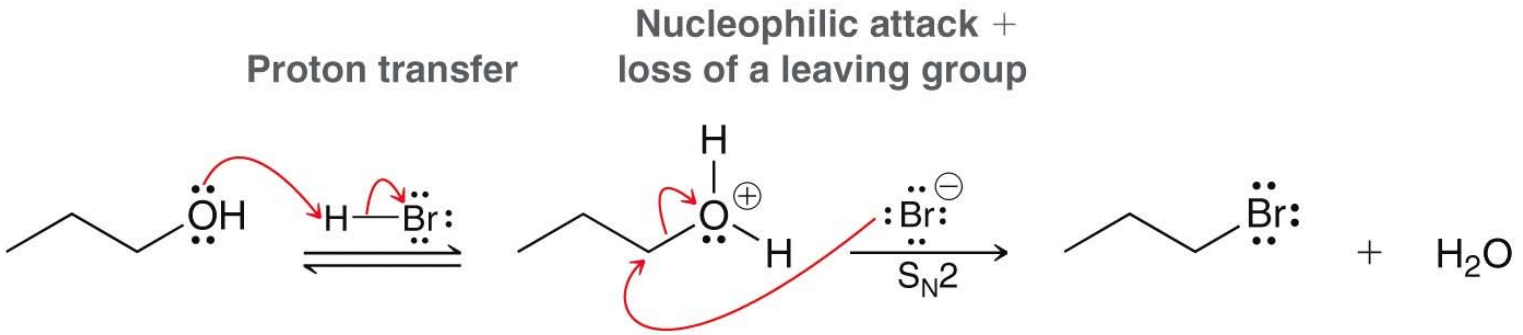


Reactions of Alcohols

- 3˚ alcohols area converted to alkyl halides with HX (S_N1 rxn)

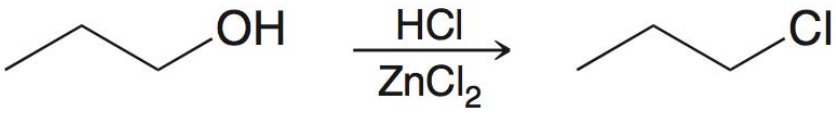


- For 1˚ or 2˚ alcohols, the reaction occurs via S_N2

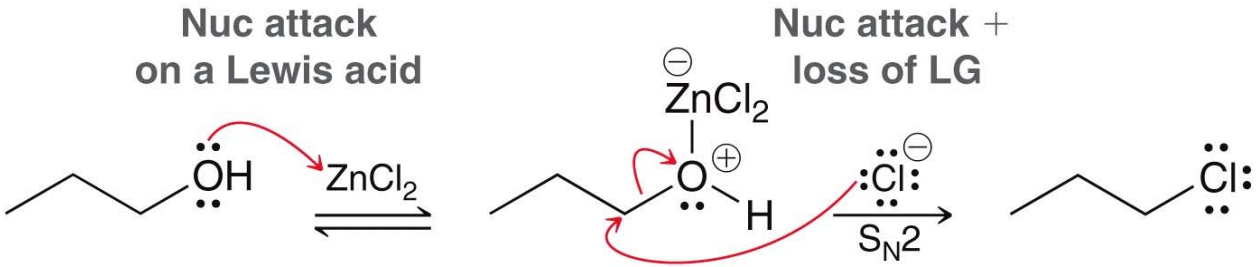


Reactions of Alcohols

- To make an alkyl chloride, $ZnCl_2$ must be used with HCl

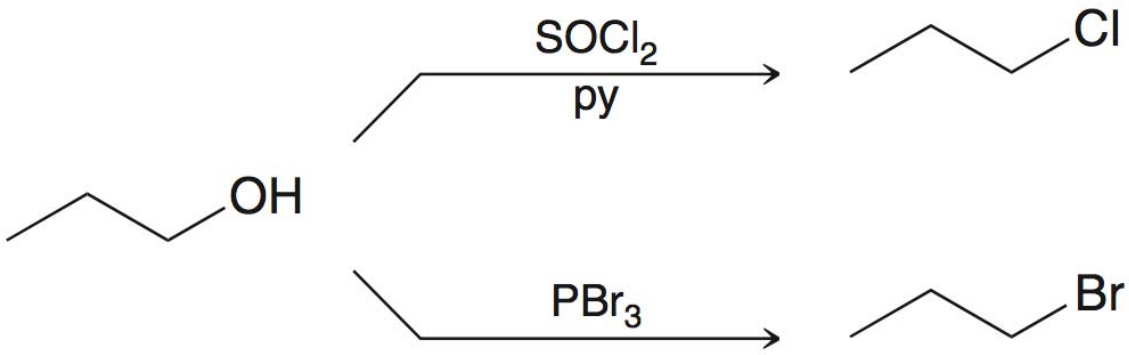


- The Zinc cation is required to make the –OH a better leaving group



Reactions of Alcohols

- 1˚ and 2˚ alcohols can also be converted to alkyl halides using $SOCl_2$ or PBr_3:



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