

**Today**

How Aldehydes and Ketones React  
Section 16.3

Reactions with Carbon Nucleophiles  
Section 16.4

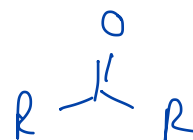
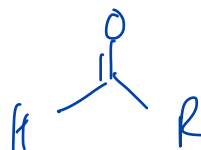
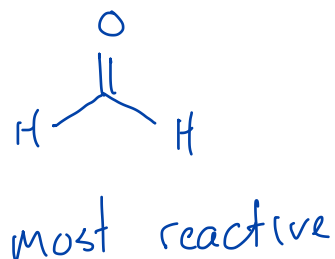
Reductions and Reactions with Hydride  
Sections 16.5 - 16.7

**Second Class from Today**

Reactions with Oxygen Nucleophiles  
Section 16.9

Protecting Groups  
16.10

and  
Other Reactions including  $\alpha,\beta$ -unsaturated  
carbonyls and the Wittig Reaction  
16.11-16.13, 16.15

**Next Class**

Reductions and Reactions with Hydride  
Sections 16.5 - 16.7

Reactions with Nitrogen Nucleophiles  
Section 16.8

Reactions with Oxygen Nucleophiles  
Section 16.8

**Third Class from Today**

Reactions with Oxygen Nucleophiles  
Section 16.9

Protecting Groups  
16.10

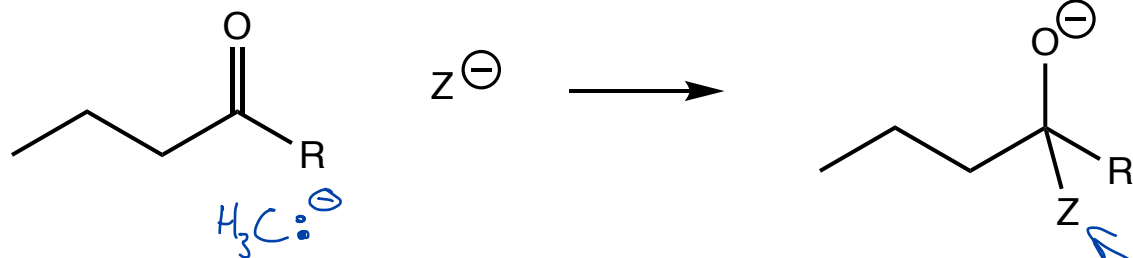
and  
Other Reactions including  $\alpha,\beta$ -unsaturated carbonyls  
and the Wittig Reaction  
16.11-16.13, 16.15

Chap 17 Reactions at the  $\alpha$ -C of a Carbonyl

Reactions with Nucleophiles

not a nucleophilic acyl substitution  
 $R^-$  too basic  
 rxn Section 16.3

Nucleophilic Addition



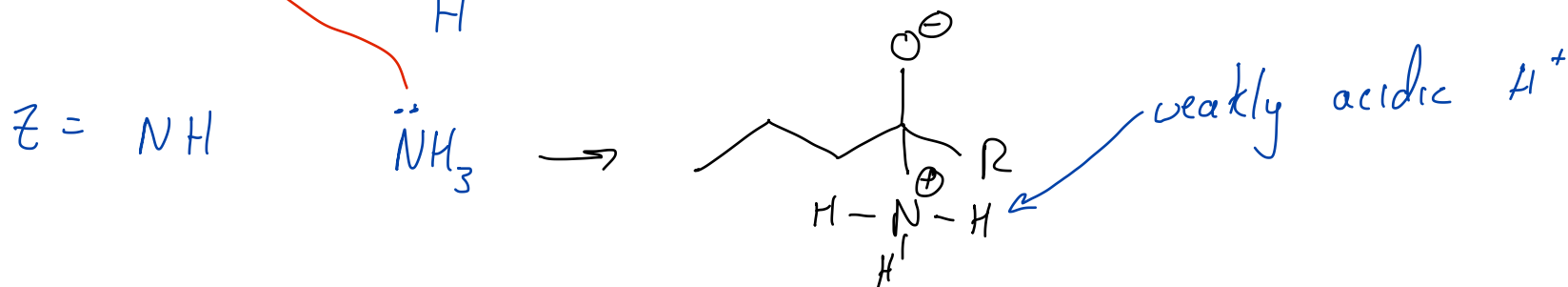
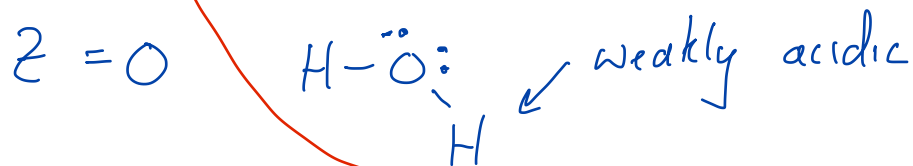
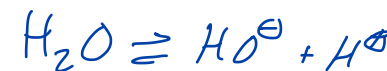
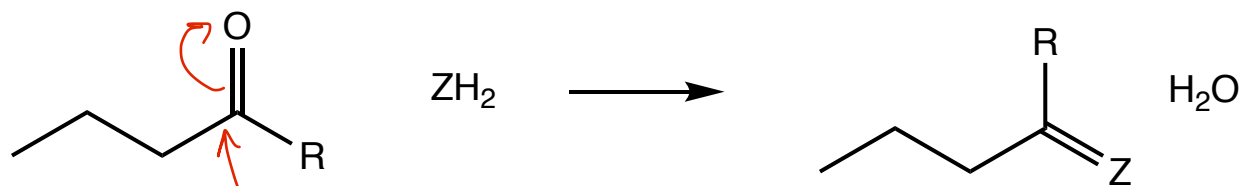
this alkoxide will not decompose back to the carbonyl because there is no LG  
 carbon or hydrogen

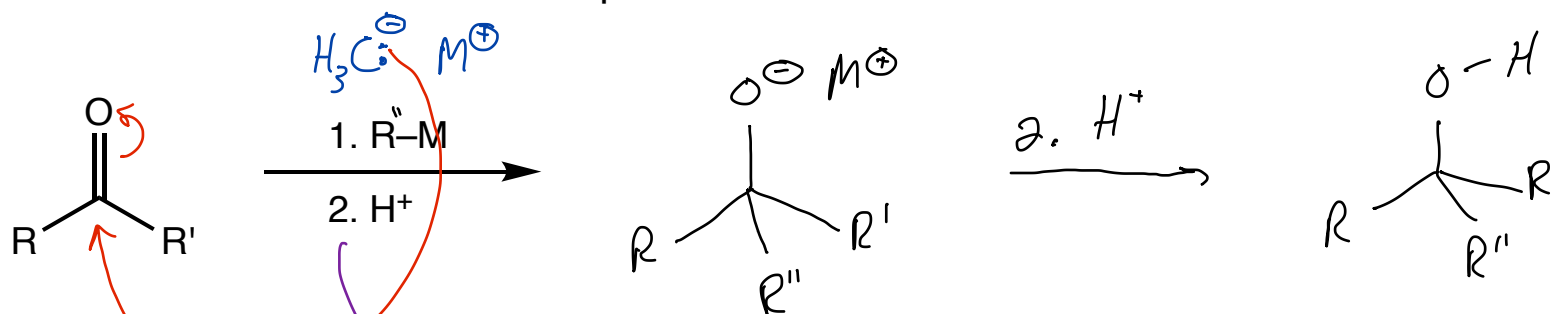
C + H nucleophiles have

1 pair of nucleophilic electrons

and none of the H's on the nucleophile are acidic

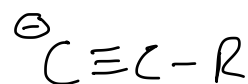
Nucleophilic Addition-Elimination





when written like this it means do two separate reactions

Grignard Reagent



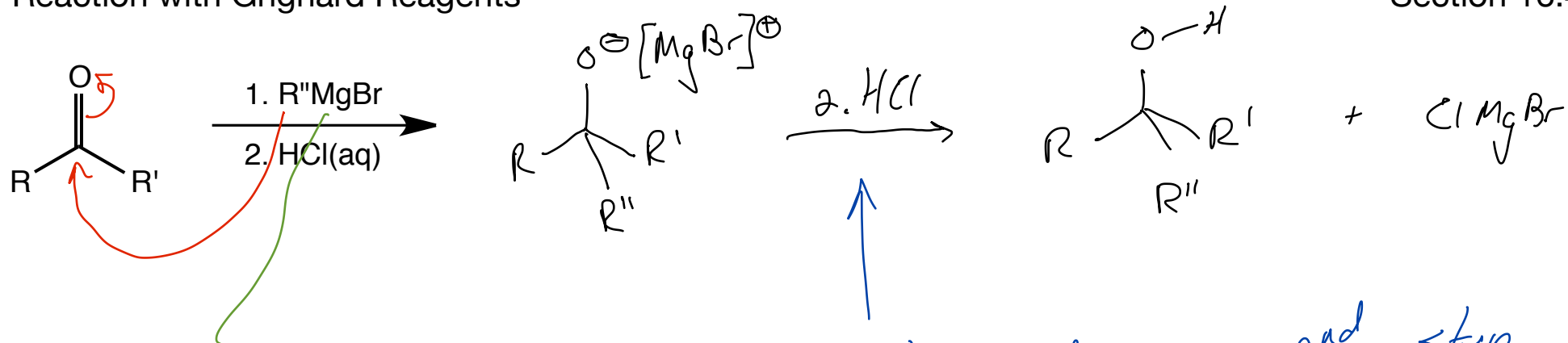
extremely basic  $\rightarrow \text{R}^\ominus [\text{Mg}^{+2} \text{Br}^\ominus]^\oplus$

any alcohol or water molecules...



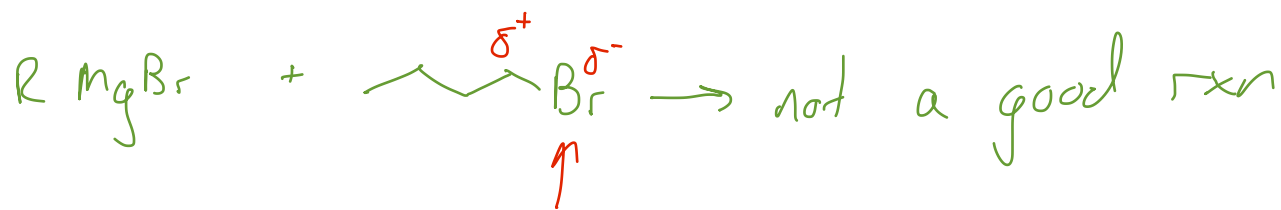
we want to examine secondary issues that arise with chemical reactions

# Reaction with Grignard Reagents



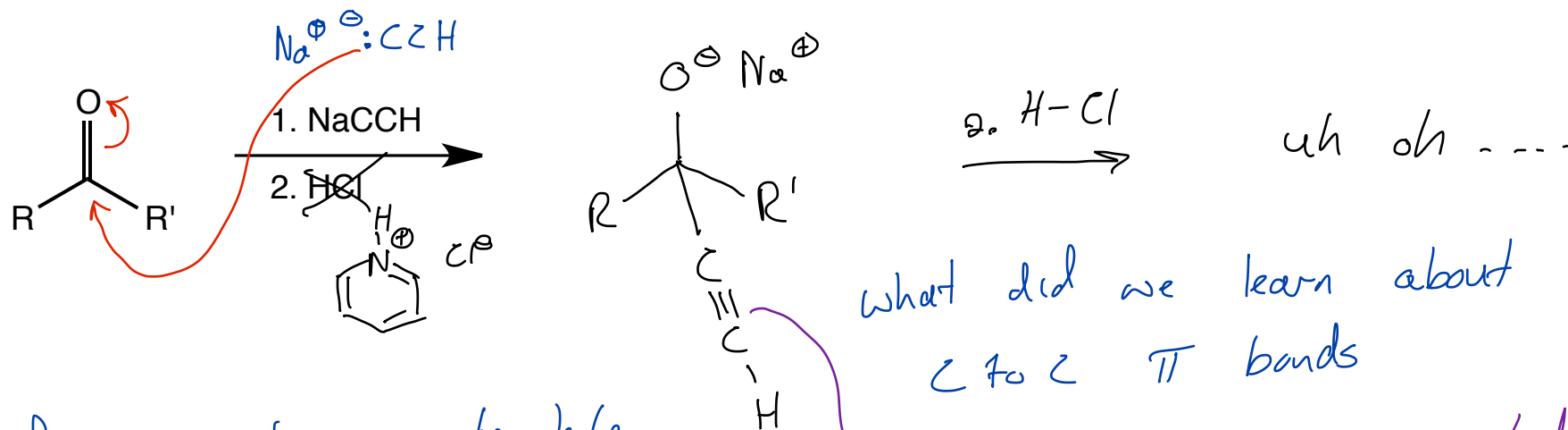
Grignard reagents react very well with C=O's...  
The Mg<sup>2+</sup> ion is strongly attracted to the O

must be done in 2nd step  
solvent cannot be a protic solvent ROH  
substrate cannot have acidic H's like an alcohol



good LG  
good S<sub>N</sub>2 substrate

# Reaction with Acetylide Ions



Because the nucleophile has a functional group that reacts with strong acids we should use a weak acid

what did we learn about C to C  $\pi$  bonds

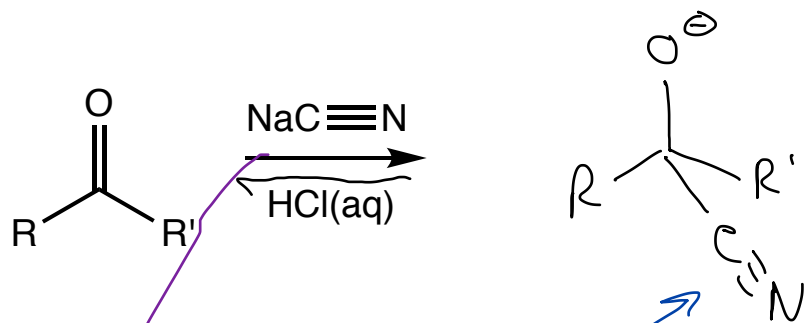
nucleophilic ... they reacted with strong electrophiles

strong acids + C to C  $\pi$  bonds do electrophilic addition reactions



similar to  $\text{NH}_4^{\oplus}$

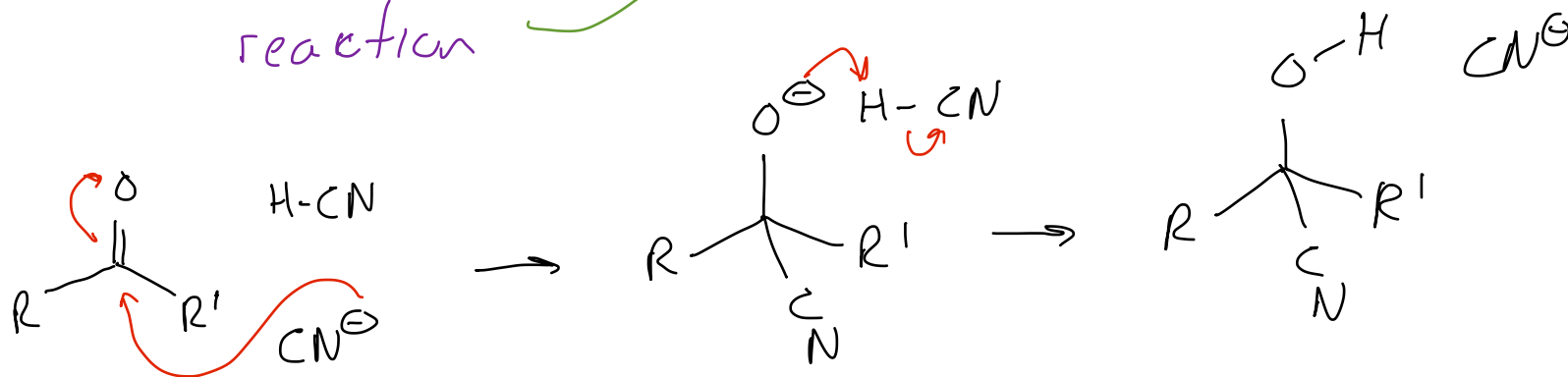
# Reaction with Cyanide

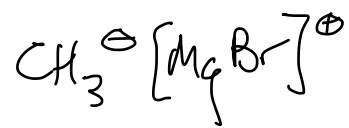
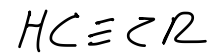


this is a weak base... so this step is reversible

use excess  $\text{CN}^\ominus$  and have HCl present in the reaction

presence of HCN (a weak acid) prevents the  $\text{O}^\ominus$  from reforming the  $\text{C}=\text{O}$





→ convert to  $\text{HCH}_3$



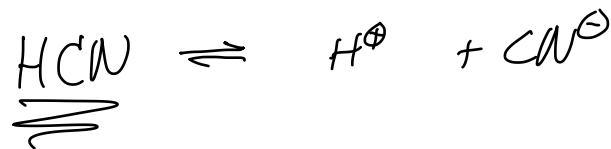
had to have acid present

converted  $^\ominus\text{CN}$  to  $\text{HCN}$

but  $\text{CN}^\ominus$  can still react

Weak acid...

can ionize



# Reactions with Hydrogen Nucleophiles

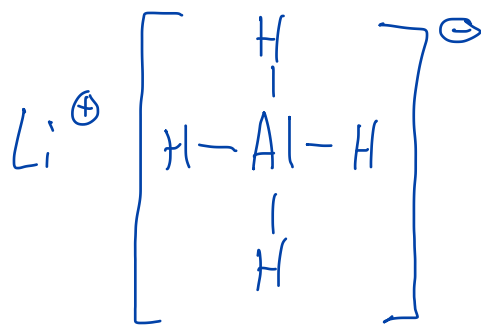
*be properly trained*

*to work in inert atmospheres*



lithium aluminum hydride

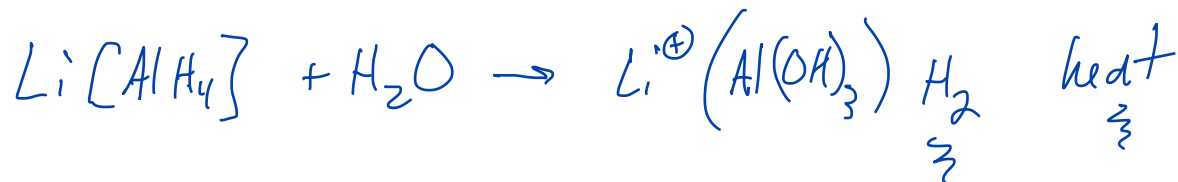
*extremely reactive!*



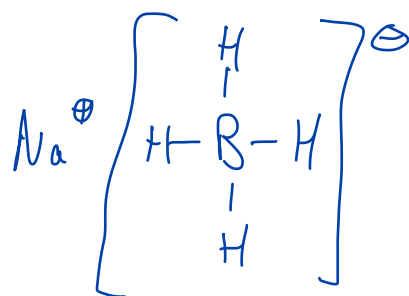
hydride  $\text{H}^{\ominus}$  like  $\text{Al}^{+3}$   $\text{H}^{\ominus}$

aluminum loves oxygen atom

$\text{H}^{\ominus}$  is extremely basic



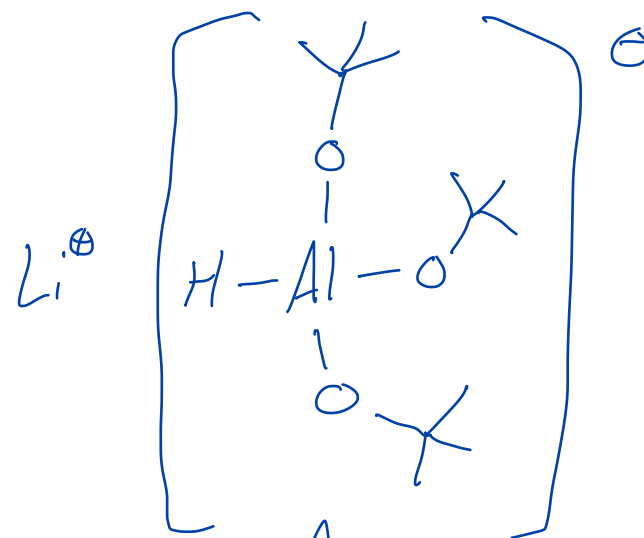
sodium borohydride



slightly less reactive  $\text{H}^{\ominus}$



lithium tri-tert-butoxyaluminum hydride



*less reactive because of the presence of the alcoxides*