Today

Aldehyde and Ketone Nomenclature
Section 16.1

Relative Reactivities
Section 16.2

How Aldehydes and Ketones React
Section 16.3

Reactions with Carbon Nucleophiles
Section 16.4

Next Class

Test 2 Chap 15

Second Class from Today

Reductions and Reactions with Hydride
Sections 16.5 - 16.7

Reactions with Nitrogen Nucleophiles
Section 16.8

Third Class from Today

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls
16.11-16.13, 16.15

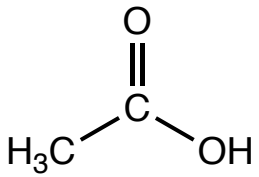
Please hand in reworked test 1

Review Session Thursday, March 23 7:30 - 9:00 in Wilson 138

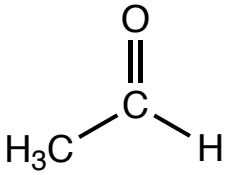
Aldehydes

Name of the acid, drop the "ic" ending and add aldehyde

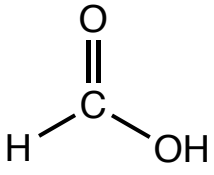
e.g.



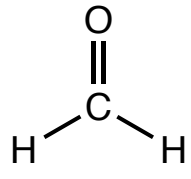
acetic acid



acetaldehyde



formic acid

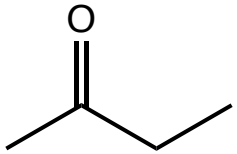


formaldehyde

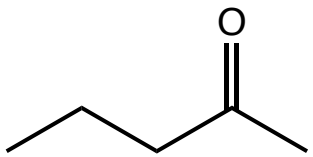
Ketones

Name of the shorter alkyl substituent, name of the longer alkyl substituent, and the word ketone

e.g.

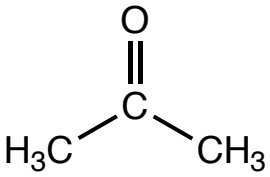


methyl ethyl ketone



methyl propyl ketone

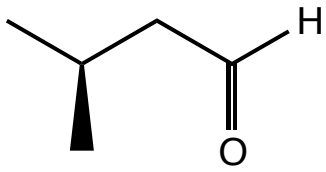
and then there's **acetone**...



it's the ketone with the acetyl group in it.

Aldehydes

#'s-(substituent names)(parent alkane)al



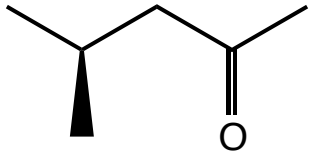
parent alkane is the longest C chain that starts with the aldehyde

remove the "e" from the parent alkane and add "al" to convert to aldehyde name

name and number substituents as in the past with aldehyde defined as C-1

Ketones

#'s-(substituent names)-#-(parent alkane)one

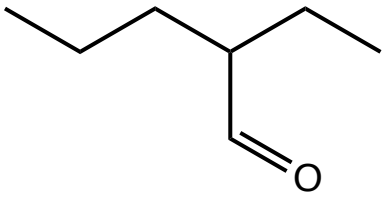


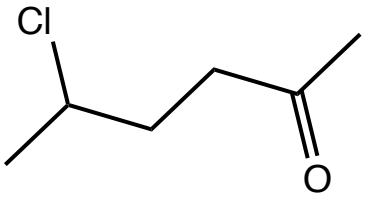
parent alkane is the longest C chain that contains the carbonyl

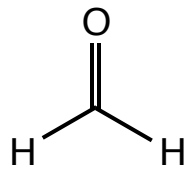
remove the "e" from the parent alkane and add "one" to convert to the ketone name

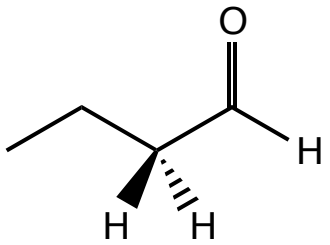
number the position of the carbonyl giving it the lowest possible number

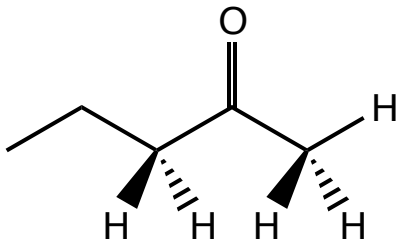
name and number substituents as in the past with the positions determined based on the numbering of the carbonyl


O

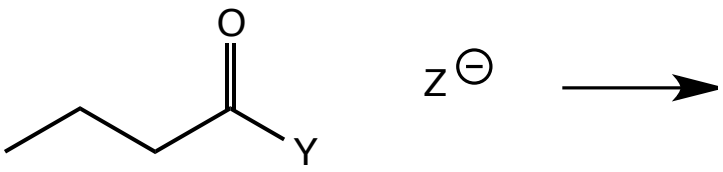

Cl
O


O
H
H

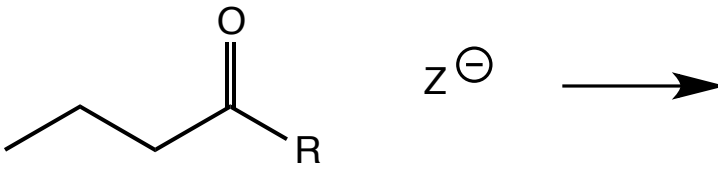

O
H
H
H


O
H
H
H
H
H

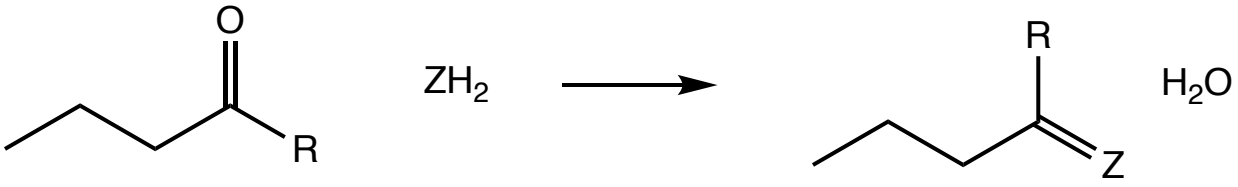
Acyl Substitution?



Nucleophilic Addition?



Nucleophilic Addition-Elimination?



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

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

Second Class from Today

Reactions with Oxygen Nucleophiles
Section 16.9

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

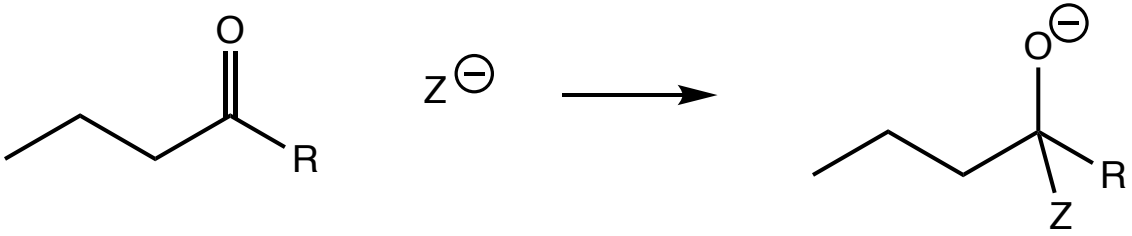
Third Class from Today

Reactions with Oxygen Nucleophiles
Section 16.9

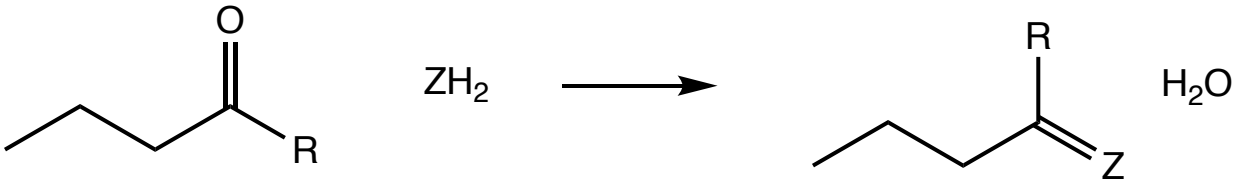
Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

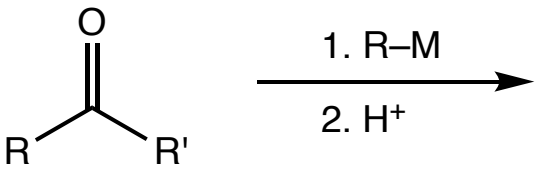
Chap 17 Reactions at the α-C of a Cabonyl

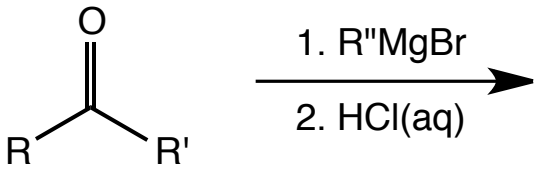
Nucleophilic Addition

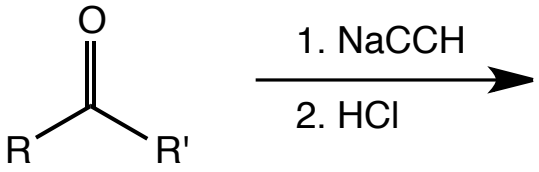


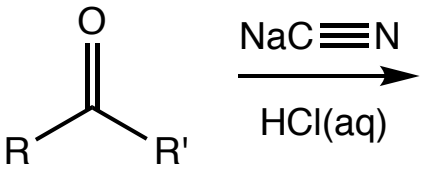
Nucleophilic Addition-Elimination




O
R
R'
1. R–M
2. H+


O
R
R'
1. R"MgBr
2. HCl(aq)


O
R
R'
1. NaCCH
2. HCl


O
R
R'
NaC≡N
HCl(aq)

$LiAlH_4$	$NaBH_4$	$LiAl[OC(CH_3)_3]_3H$
lithium aluminum hydride	sodium borohydride	lithium tri-tertbutoxyaluminum hydride

Today

Reductions and Reactions with Hydride
Sections 16.5 - 16.7

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.8

Next Class

Reactions with Oxygen Nucleophiles
Section 16.8

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Second Class from Today

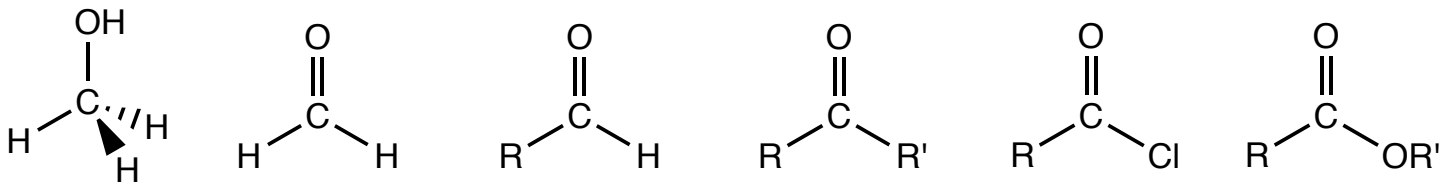
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Chap 17 Reactions at the α-C of a Carbonyl

Third Class from Today

Chap 17 Reactions at the α-C of a Cabonyl

$LiAlH_4$	$NaBH_4$	$LiAl[OC(CH_3)_3]_3H$
lithium aluminum hydride	sodium borohydride	lithium tri-tertbutoxyaluminum hydride
Fully reduces esters, carboxylic acids, and amides to alcohols and amines	Fully reduces ketones, aldehydes, and acid chlorides to alcohols. Does not reduce esters, carboxylic acids, and amides	Reduces acid chlorides to aldehydes



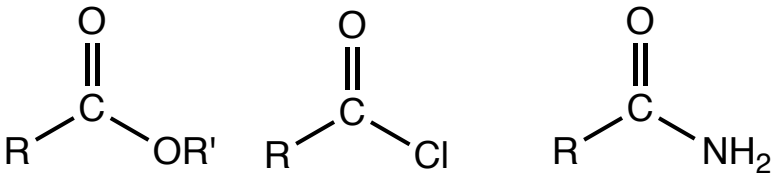
– 2 0 +1 +2 +3 +3

oxidation number for the C atoms in blue

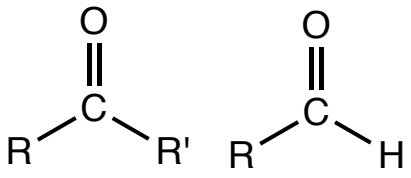
For each bond, assign
–1 to the more electonegative atom and
+1 to the less electronegative atom
0 if the electronegativities are the same

For each atom sum the assigned charges.

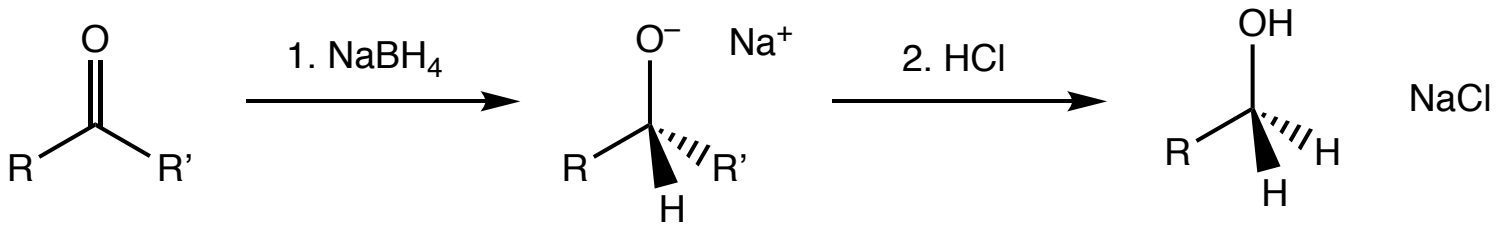
That number is the oxidation number for the atom.

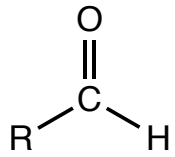


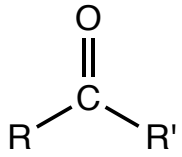
Carbonyl compounds with leaving groups

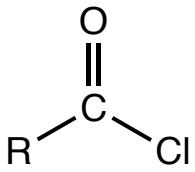


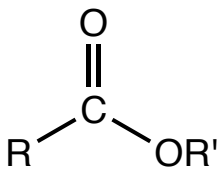
Carbonyl compounds without leaving groups


O
R
R'
1. NaBH4
O−
Na+
R
R'
H
2. HCl
OH
R
H
H
NaCl


O
C
R
H


O
C
R
R'


O
C
R
Cl

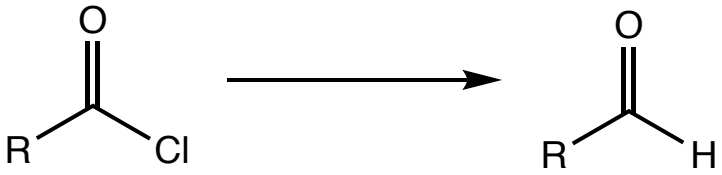

O
C
R
OR'

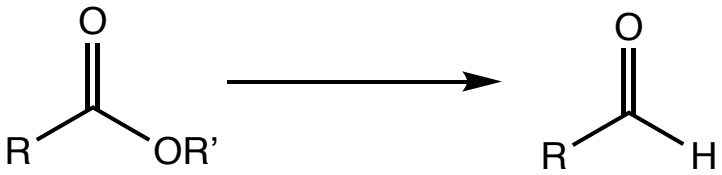
Oxidation-Reduction Reactions - Selective Reductions
Stopping at an Aldehyde

$LiAlH_4$

$NaBH_4$

$Li[Al(OC(CH_3)_3)_3H]$





lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

Today

Reductions and Reactions with Hydride
Sections 16.5 - 16.7

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.8

Next Class

Reactions with Oxygen Nucleophiles
Section 16.8

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Second Class from Today

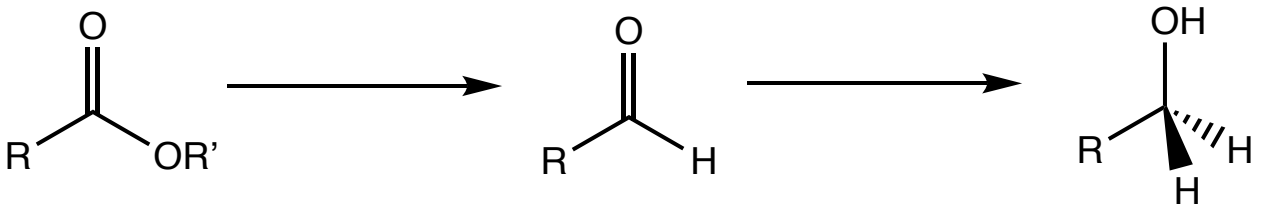
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Chap 17 Reactions at the α-C of a Carbonyl

Third Class from Today

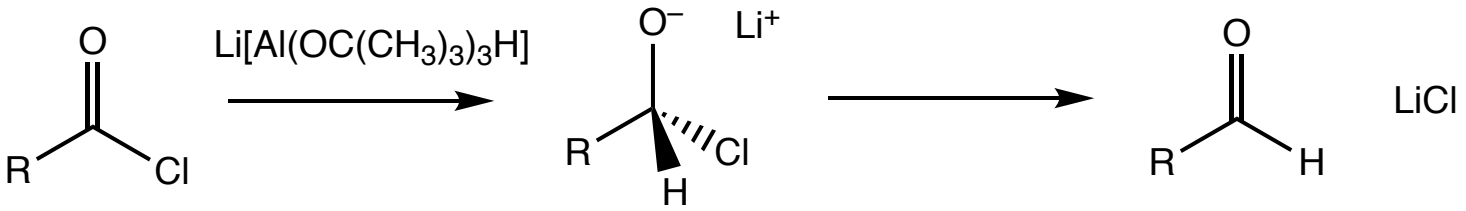
Chap 17 Reactions at the α-C of a Cabonyl

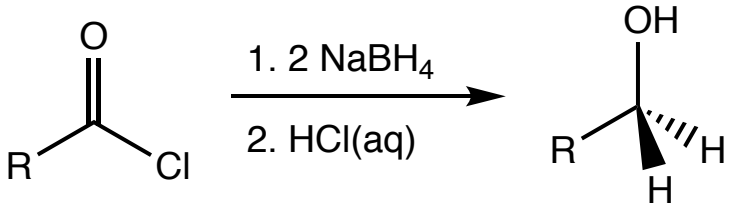
Understanding the Mechanism Allowed Chemists to Discover a Way to Stop the Reduce of Esters at the Aldehyde Functional Group

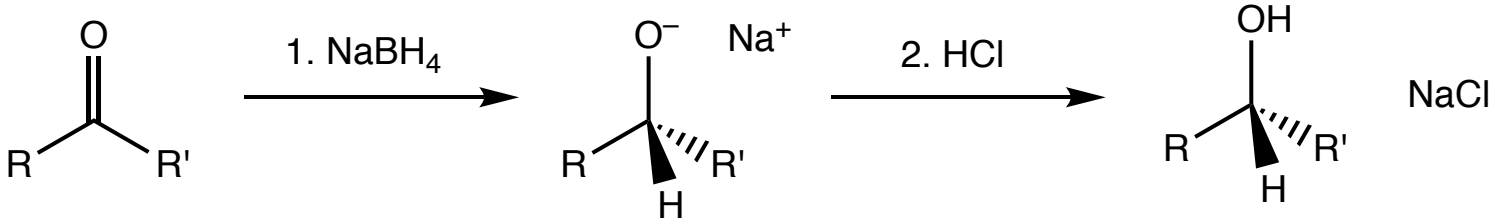


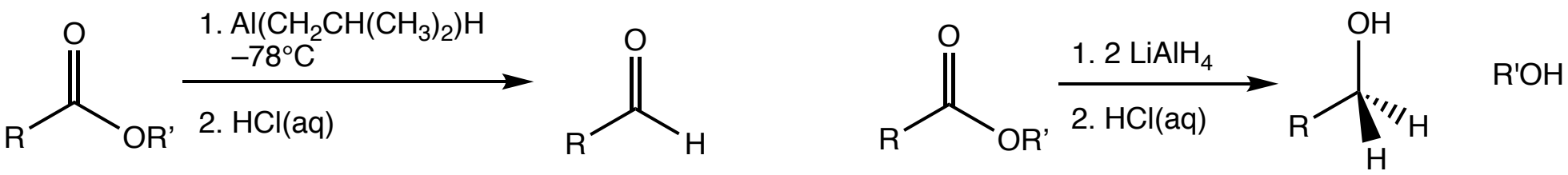
lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

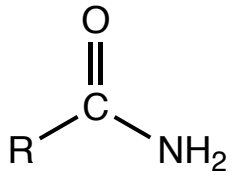
Summary: Reduction of Aldehydes, Ketones, Acid Chlorides, and Esters

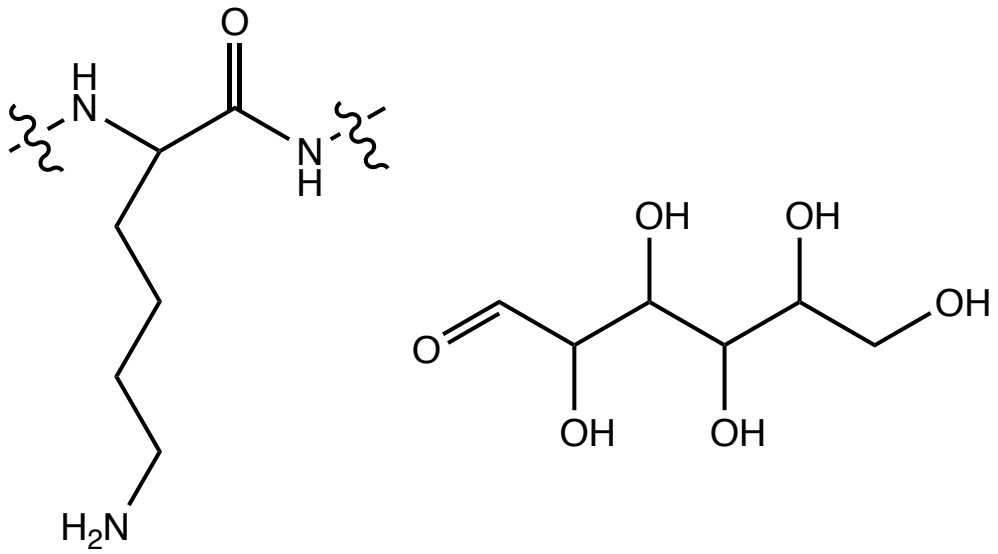


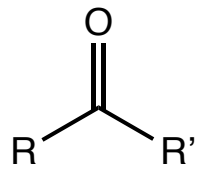


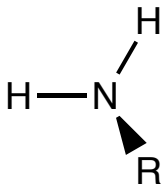


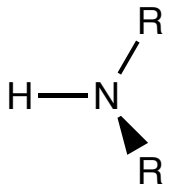


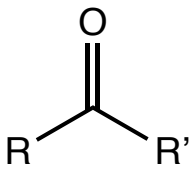

O
C
R
NH2

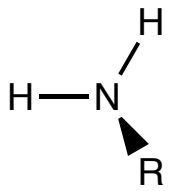

O
H
N
N
H
H2N
O
OH
OH
OH
OH
OH


O
R
R'


H
H
N
R


R
H
N
R


O
R
R'


H
H
N
R

Today

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.8

Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Next Class

Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

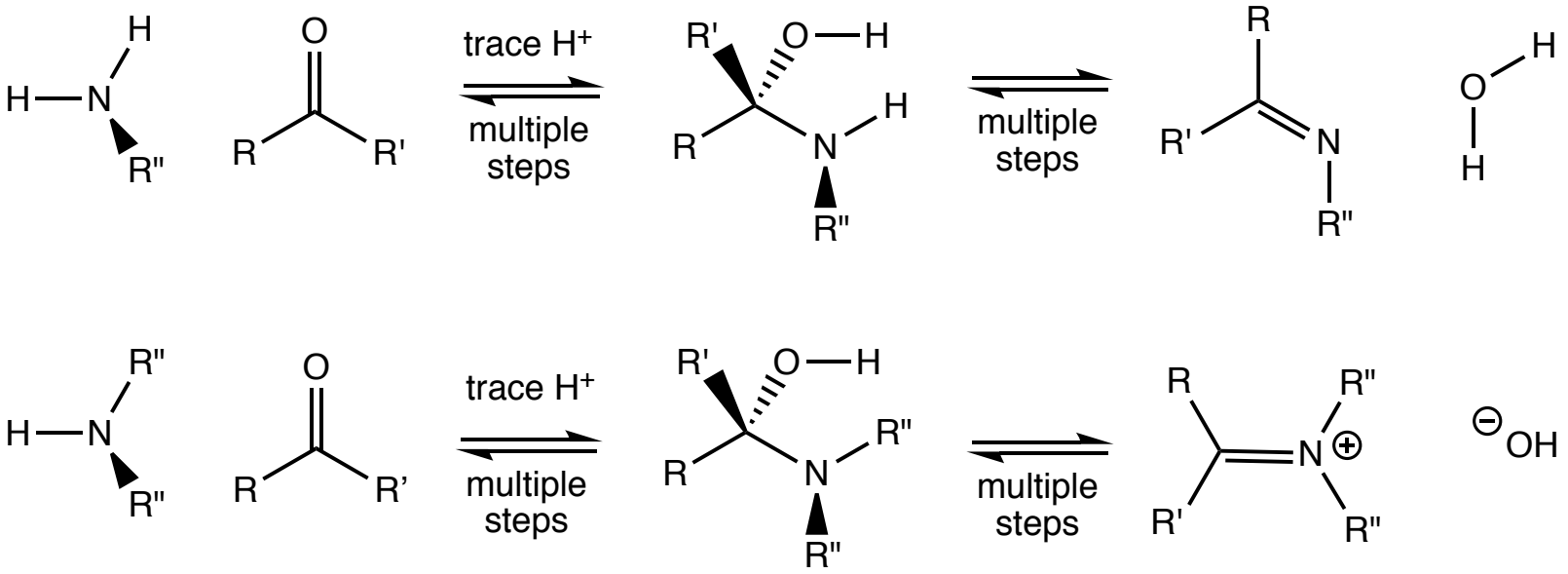
Chap 17 Reactions at the α-C of a Carbonyl

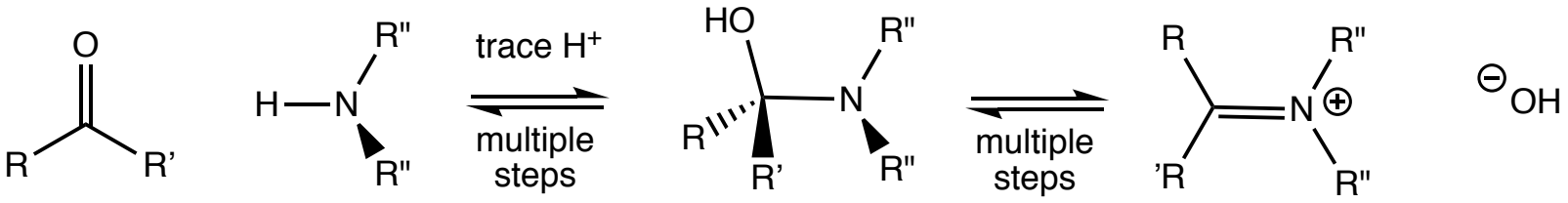
Second Class from Today

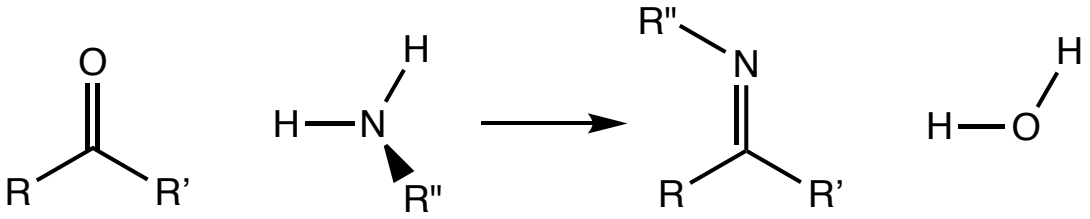
Chap 17 Reactions at the α-C of a Carbonyl

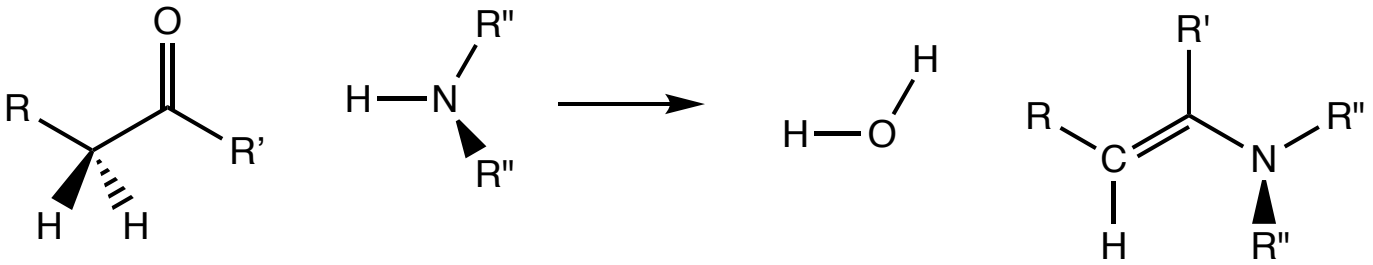
Third Class from Today

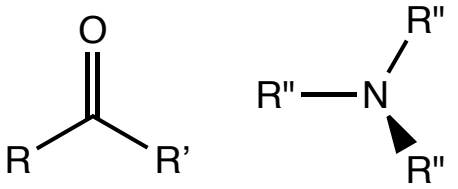
Chap 17 Reactions at the α-C of a Cabonyl


trace H+
multiple steps
multiple steps
trace H+
multiple steps
multiple steps
OH

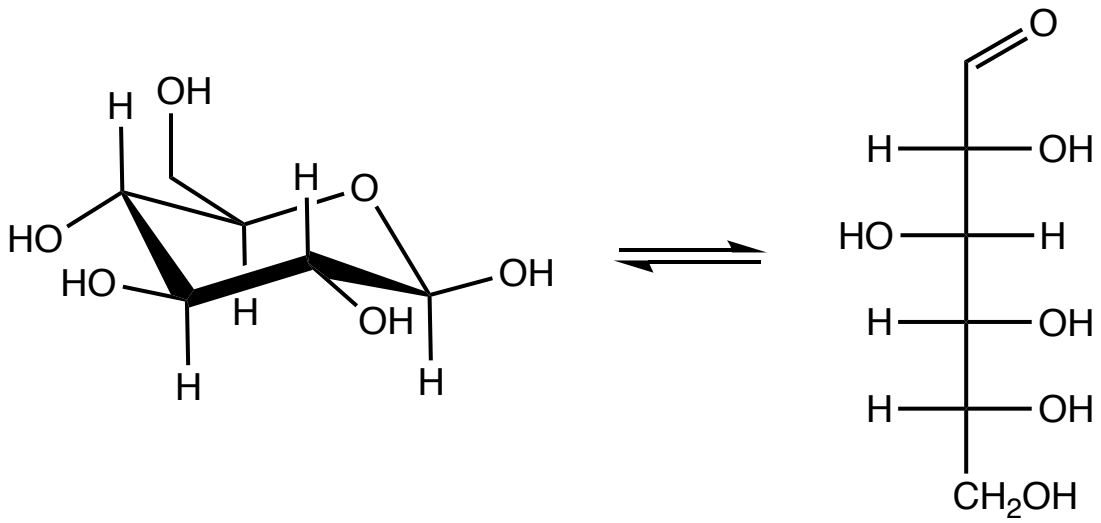

O
R
R'
H
N
R"
R"
trace H+
multiple steps
HO
R"
N
R
R'
R"
multiple steps
R
R"
N
'R
R"
OH

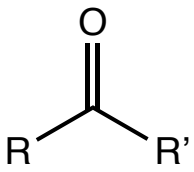


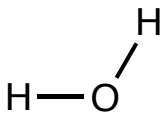


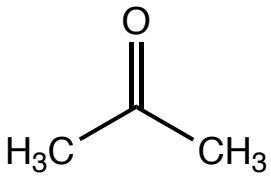


R" ≠ H

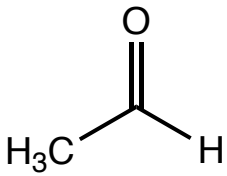

H
OH
H
O
HO
HO
OH
H
OH
H
H
O
H
OH
HO
H
H
OH
H
OH
CH2OH



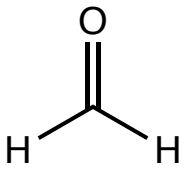




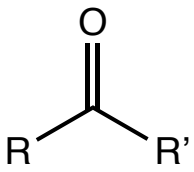
99.8 : 0.2

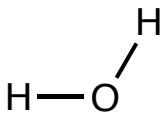


42 : 58



0.1 : 99.9


O
R
R’


H
H
O

Today

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.8

Acetals as Protecting Groups
16.10
and
Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.13, 16.15

Next Class

Other Reactions including α,β-unsaturated carbonyls and the Wittig Reaction
16.11-16.13, 16.15

Chap 17 Reactions at the α-C of a Carbonyl

Second Class from Today

Chap 17 Reactions at the α-C of a Carbonyl

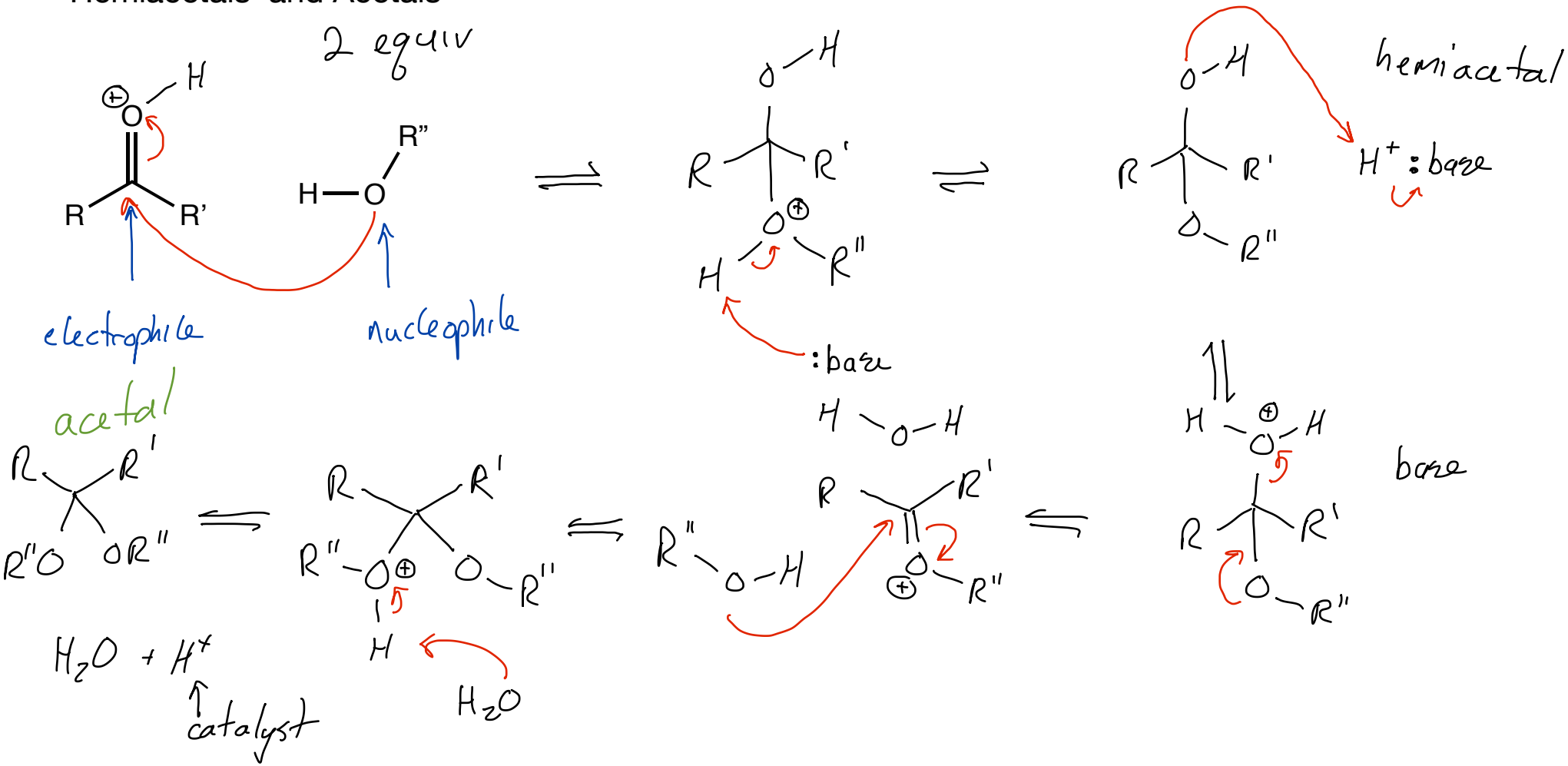
Third Class from Today

Chap 17 Reactions at the α-C of a Cabonyl

Sorry, still not graded :

Reactions of Aldehydes and Ketones* with Oxygen Nucleophiles - Hemiacetals and Acetals

Section 16.9

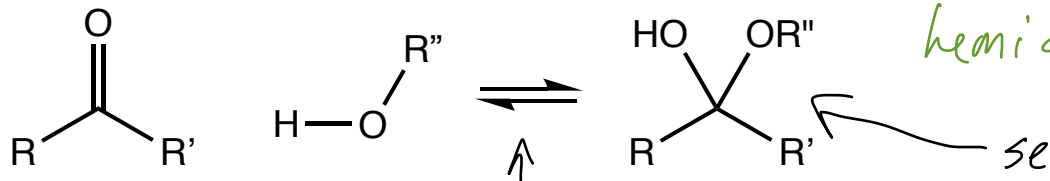


hemiacetal is when an OH and a OR (R≠H) are bonded to the same C

acetal is when two ether groups are bonded to the same C

*Even though, nomenclature-wise, ketones form hemiketals and ketals chemists typically refer to the entire class of molecules as hemiacetals and acetals.

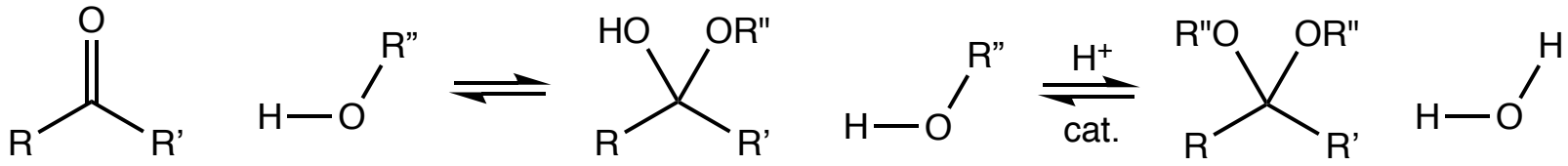
aldehyde ketone



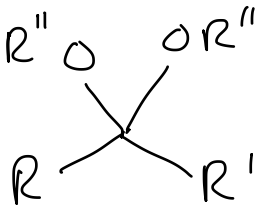
hemiacetal

self contained hemiacetals will always be able to go back and forth between the C=O & the hemiacetal

will occure slowly
add H^+ to speed up rxn



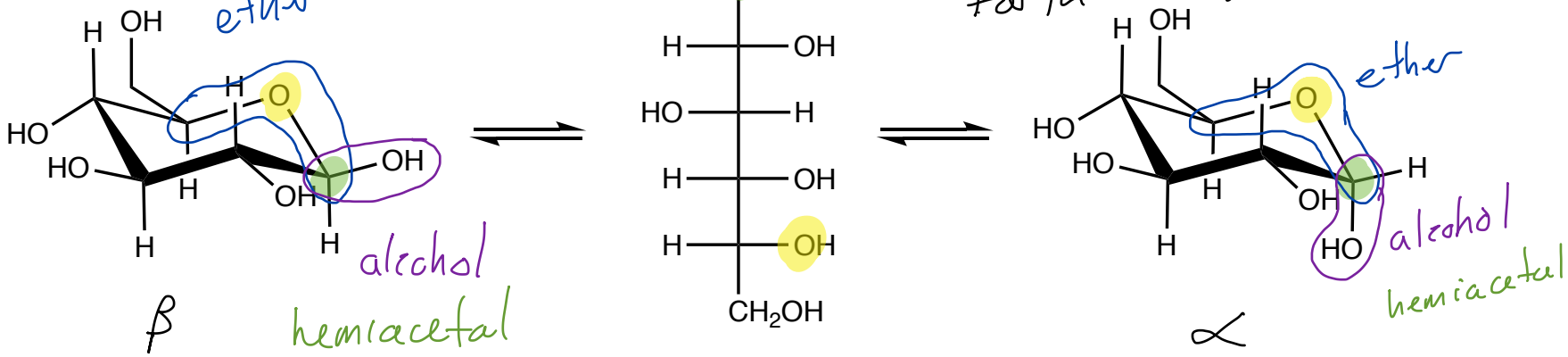
when the reaction makes it all the way to the acetal/hetal for the reaction to go backwards H_2O must be present.



is stable and can be stored
is stable and more chemistry can be done

O on C_5 can form a 6-membered ring by reacting with C_1

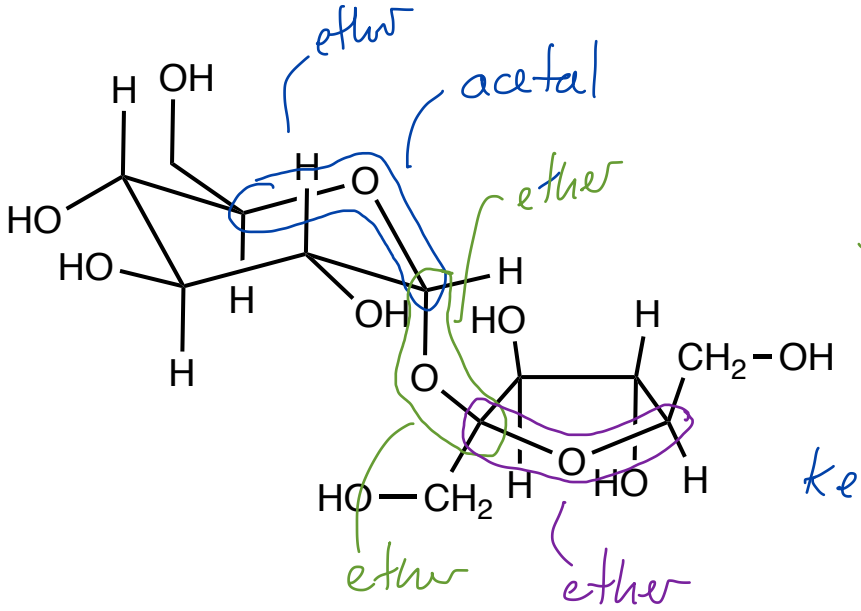
glucose



can be converted back & forth with ease

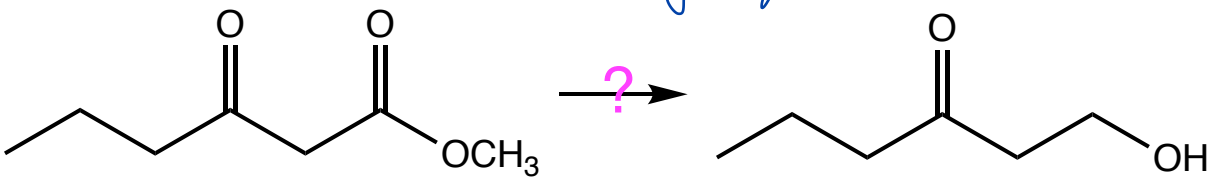
and an acetal & a ketal

sucrose



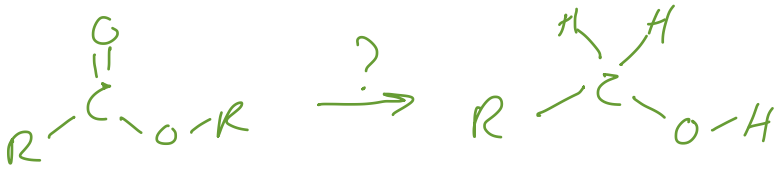
acetal & ketal are stable & can be stored... won't be able to break open without added water

Chemists want to make stuff, often the things we make have more than 1 functional group



We need to find ways to protect one part of the molecule while doing chemistry on another.

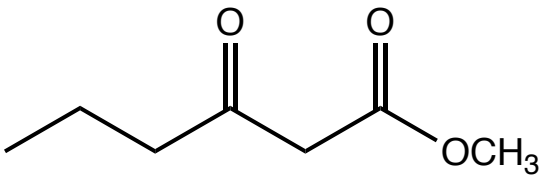
How can I convert an ester to an alcohol...



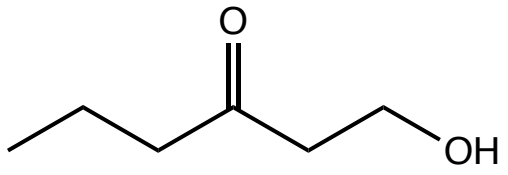
how do I reduce an ester...? use $LiAlH_4$!

$LiAlH_4$	$Al(\text{iBu})_2H$	$NaBH_4$	$Li[Al(OC(CH_3)_3)_3H]$
$H:^{\ominus}$	$H:^{\ominus}$	$H:^{\ominus}$	$H:^{\ominus}$
strongest reduces everything	strong reduces everything	medium reduces ketone + aldehyde	weakest only reacts with acid chloride

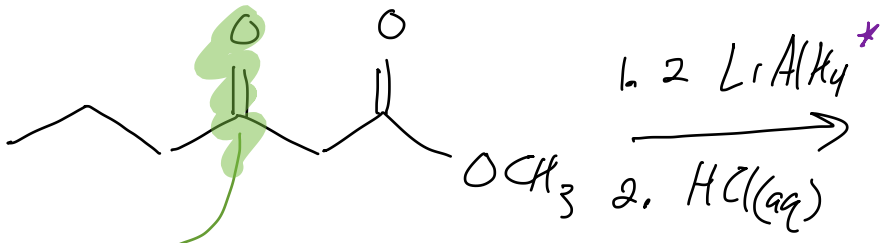
Use $LiAlH_4$?



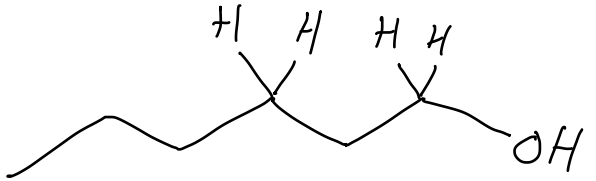
?



* complete reduction of both functional groups would require 4 eq $LiAlH_4$



1. 2 $LiAlH_4$ *
2. $HCl_{(aq)}$



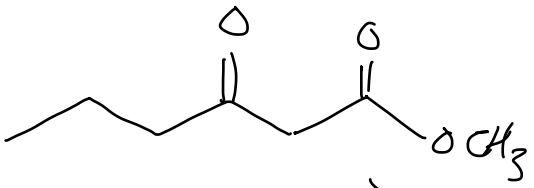
$HOCH_3$

H_2O

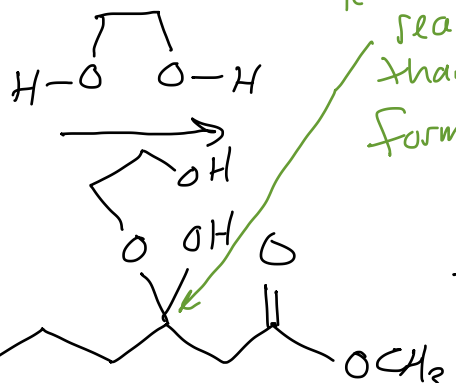
can I hide this one... protect it from the $LiAlH_4$

we reduced both of them

Yes, I can protect the C=O by (hiding it) converting it to an acetal.

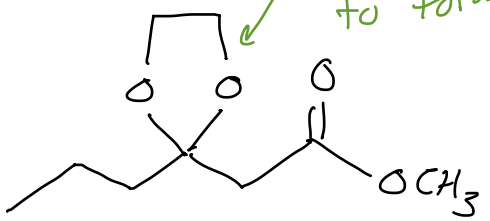


H^+

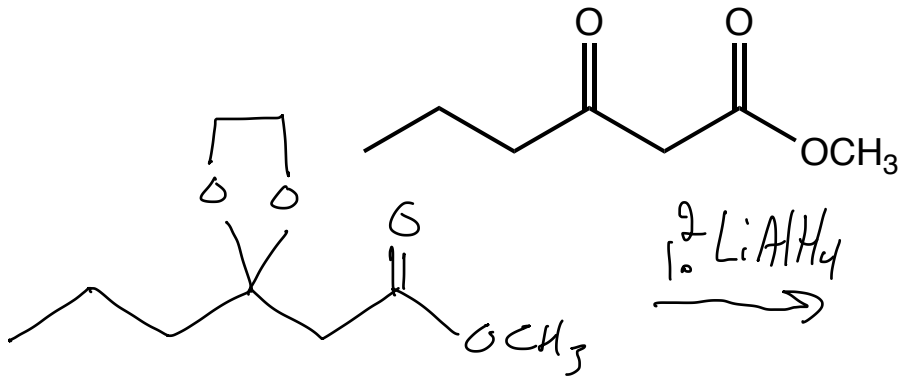


feature more reactive than ester forms hemiacetal...

intramolecular rxn to form acetal

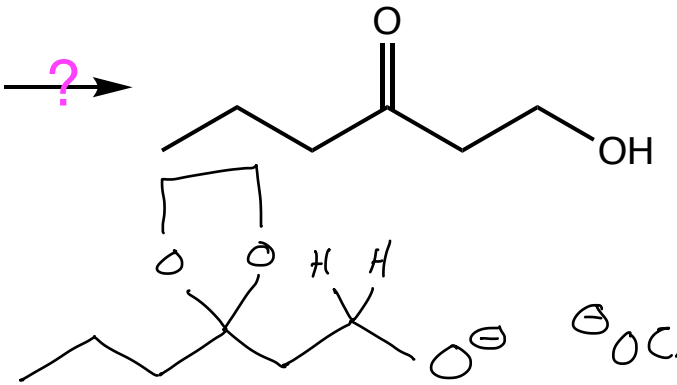


+ H_2O — remove water



1. 2 LiAlH4

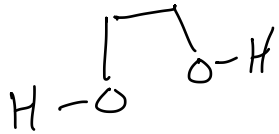
?

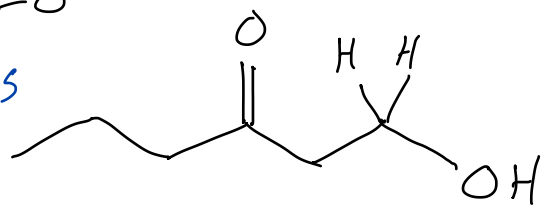


LiAlH4 reduces ester to alkoxy group

the ketone is now hidden as an acetal... LiAlH4 reacts with C=O's... not acetals

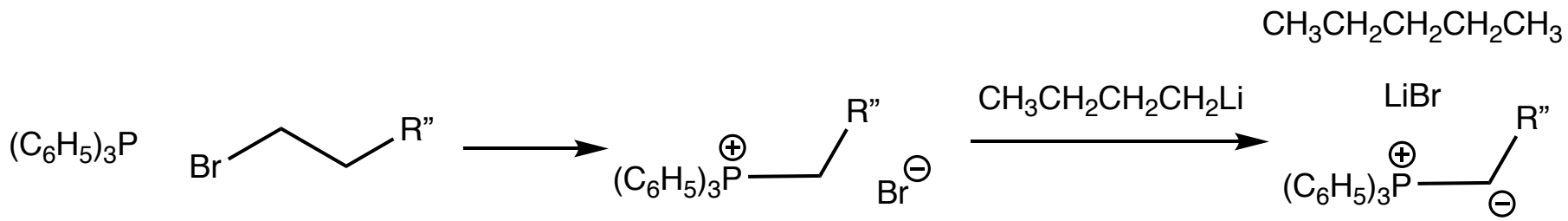
2. HCl (aq)

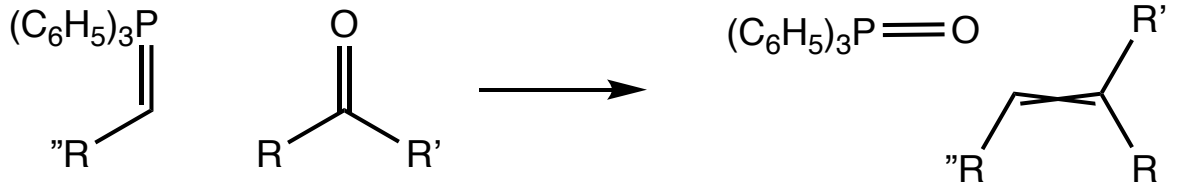


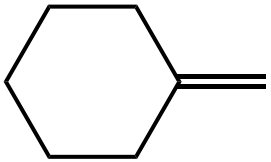


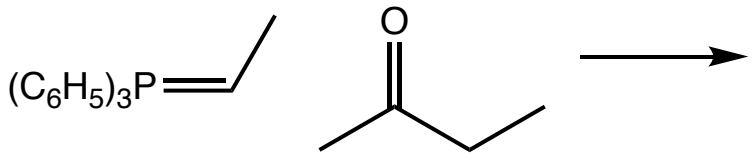
catalyzes the conversion of ketal back to alcohol + ketone

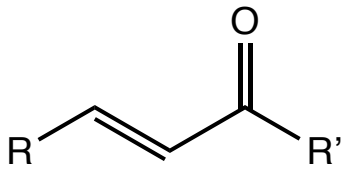
second step of reduction sequence protonates alkoxy groups and...

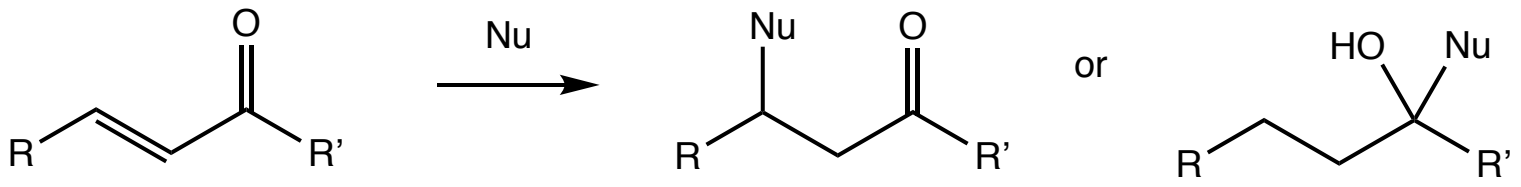

$CH_3CH_2CH_2CH_2CH_3$
$(C_6H_5)_3P$
Br
R”
$(C_6H_5)_3P$
Br
R”
$CH_3CH_2CH_2CH_2Li$
LiBr
$(C_6H_5)_3P$
R”

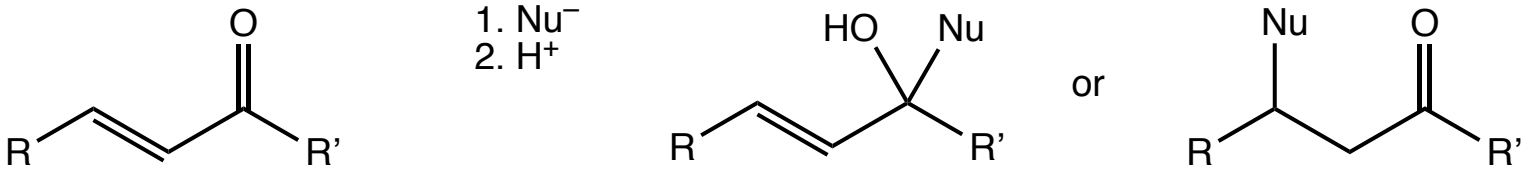

$(C_6H_5)_3P$
”R
O
R
R’
$(C_6H_5)_3P=O$
”R
R’
R




$(C_6H_5)_3P$
O


O
R
R'


O
R
R'
Nu
Nu
O
R
R'
or
HO
Nu
R
R'


O
R
R’
1. Nu⁻
2. H⁺
HO
Nu
R
R’
or
Nu
O
R
R’

Still it is difficult to predict the outcome.