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

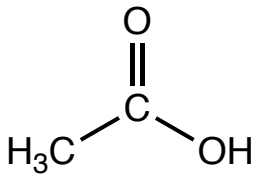
Please hand in reworked test 1

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

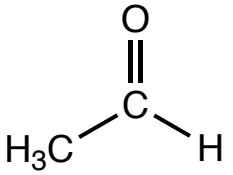
Aldehydes

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

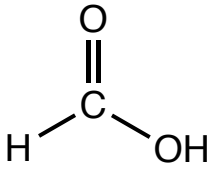
e.g.



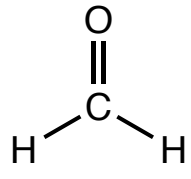
acetic acid



acetaldehyde



formic acid

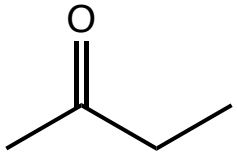


formaldehyde

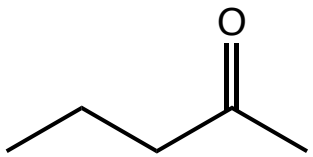
Ketones

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

e.g.

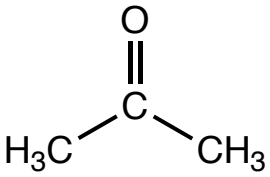


methyl ethyl ketone



methyl propyl ketone

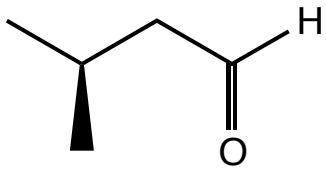
and then there's **acetone**...



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

Aldehydes

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



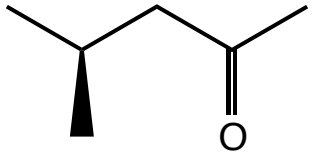
parent alkane is the longest C chain that starts with the aldehyde

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

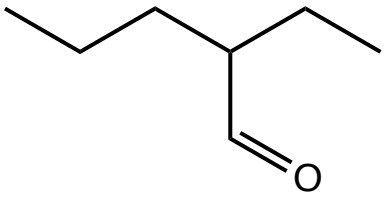


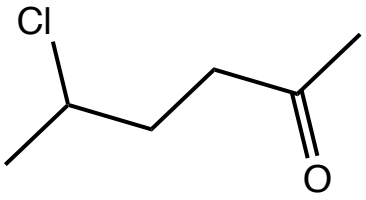
parent alkane is the longest C chain that contains the carbonyl

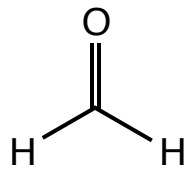
remove the "e" from the parent alkane and add "one" to convert to the ketone name

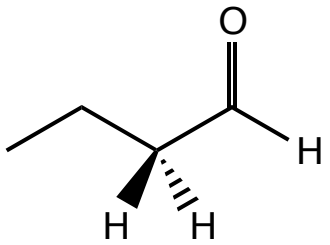
number the position of the carbonyl giving it the lowest possible number

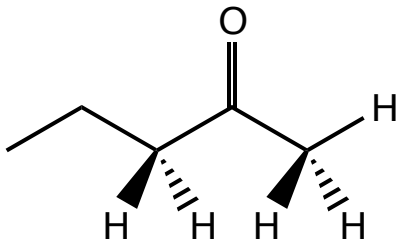
name and number substituents as in the past with the positions determined based on the numbering of the carbonyl


O

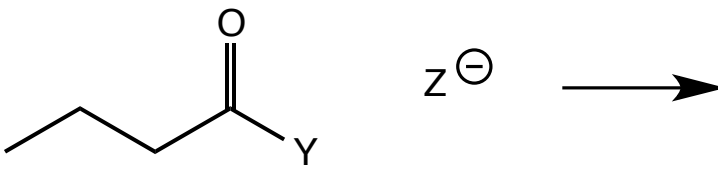

Cl
O


O
H
H

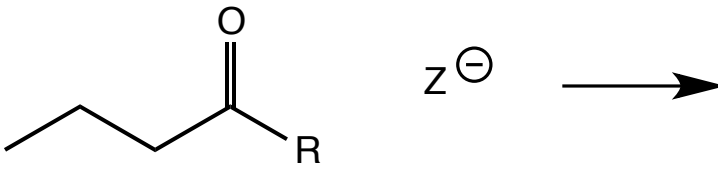

O
H
H
H


O
H
H
H
H
H

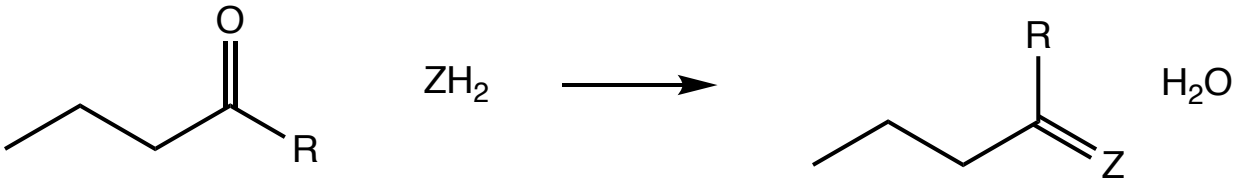
Acyl Substitution?



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

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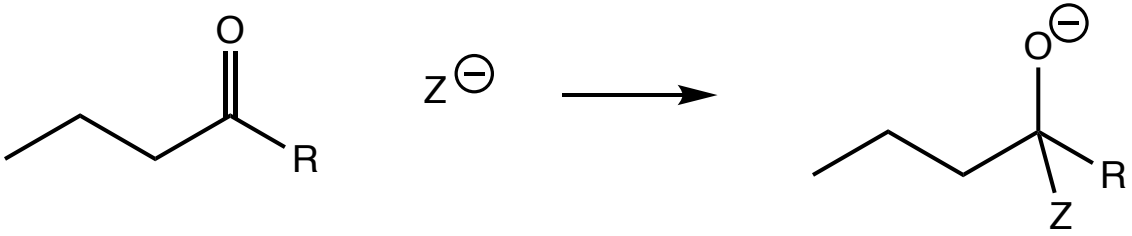
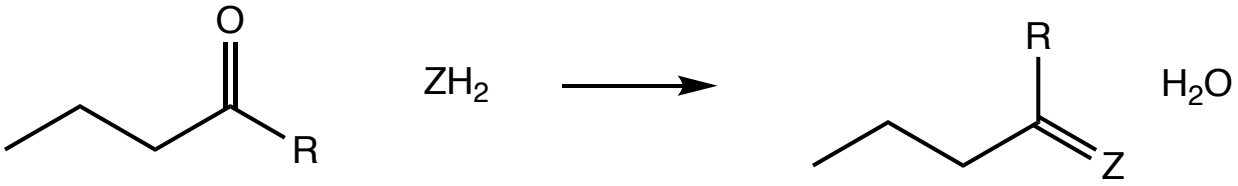
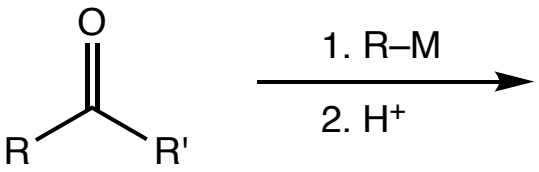
Chap 17 Reactions at the α-C of a Cabonyl

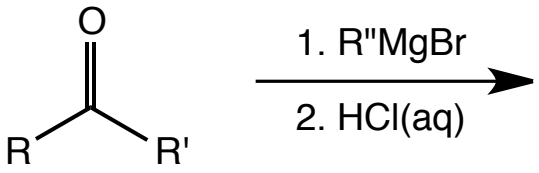
Nucleophilic Addition

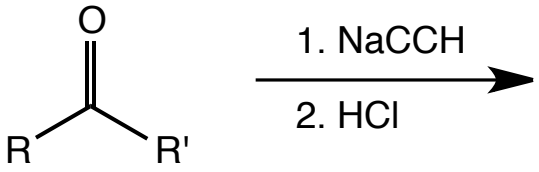


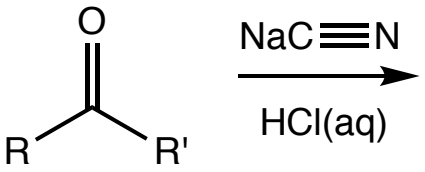
Nucleophilic Addition-Elimination




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

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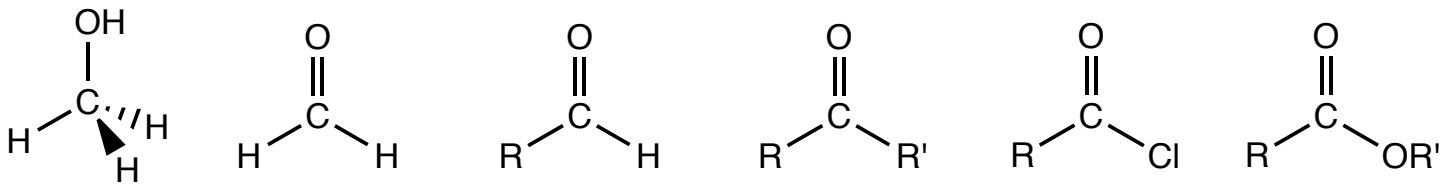
Chap 17 Reactions at the α-C of a Carbonyl

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



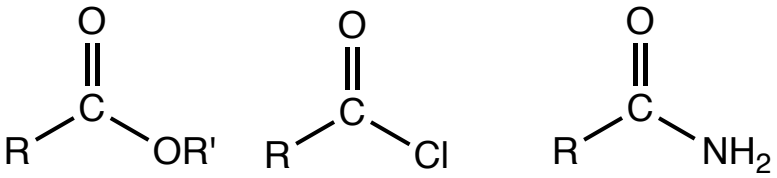
– 2 0 +1 +2 +3 +3

oxidation number for the C atoms in blue

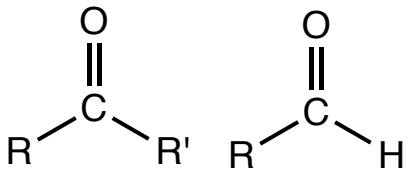
For each bond, assign
–1 to the more electonegative atom and
+1 to the less electronegative atom
0 if the electronegativities are the same

For each atom sum the assigned charges.

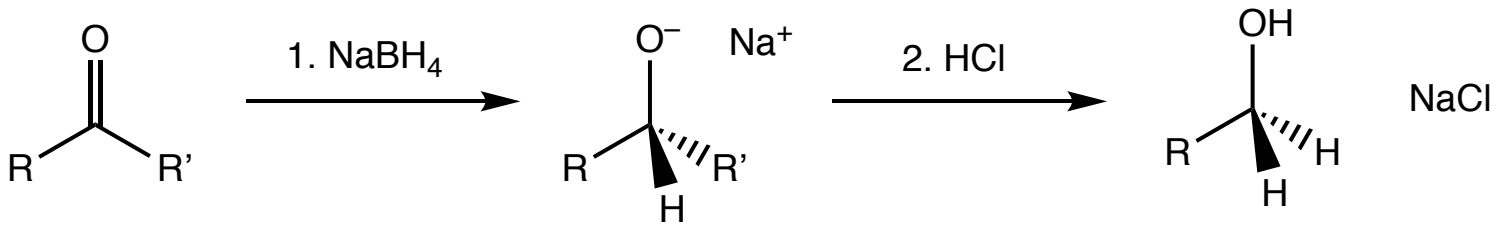
That number is the oxidation number for the atom.

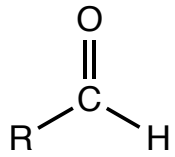


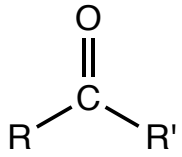
Carbonyl compounds with leaving groups

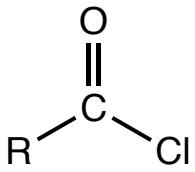


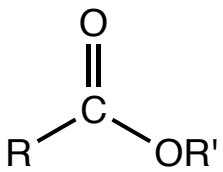
Carbonyl compounds without leaving groups


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

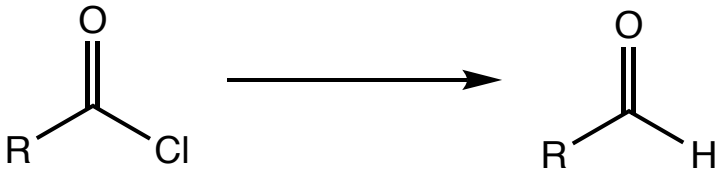

O
C
R
OR'

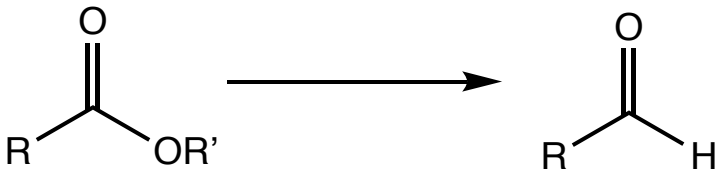
Oxidation-Reduction Reactions - Selective Reductions
Stopping at an Aldehyde

$LiAlH_4$

$NaBH_4$

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





lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

Today

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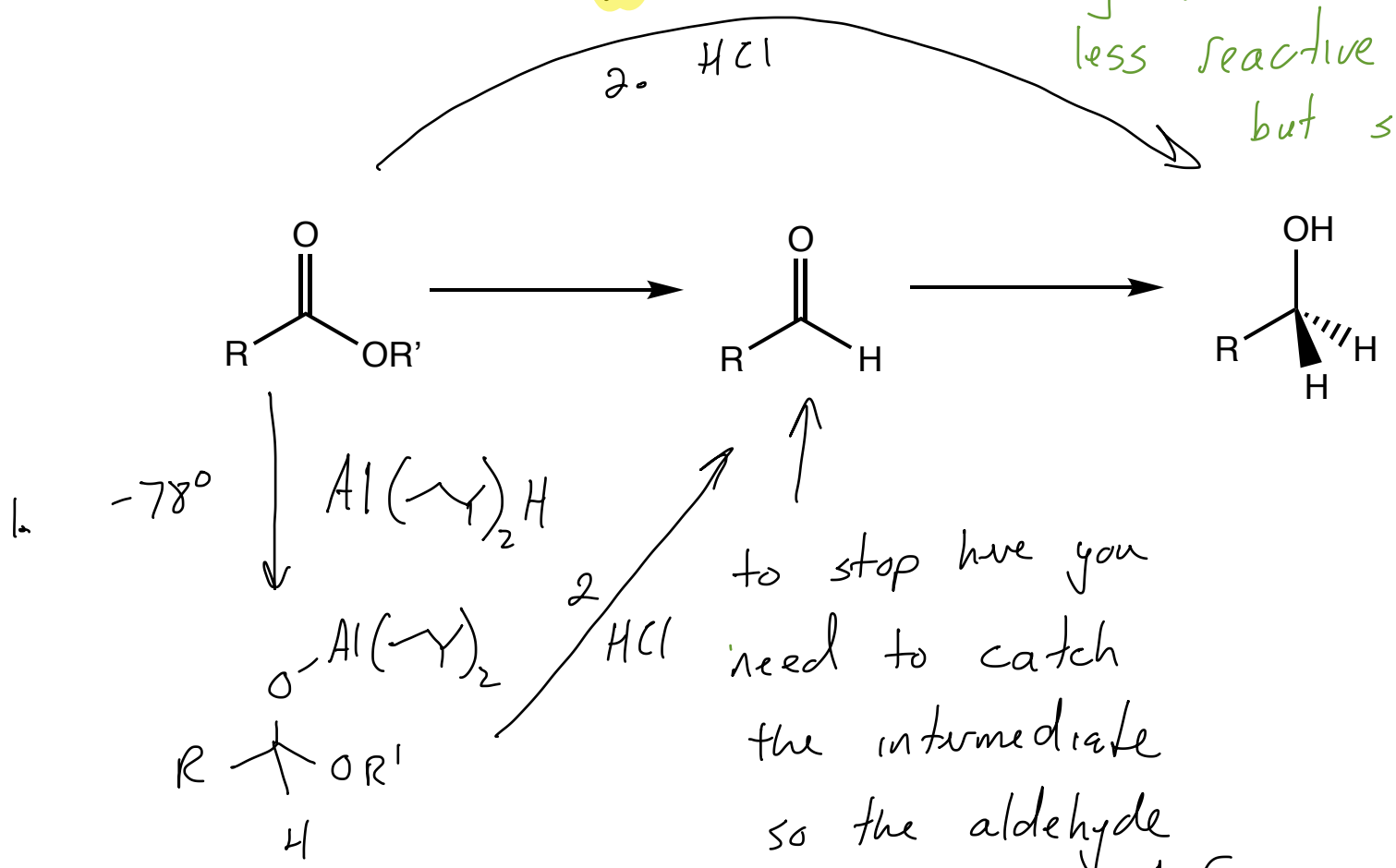
Chap 17 Reactions at the α-C of a Carbonyl

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

Section 16.5-16.7

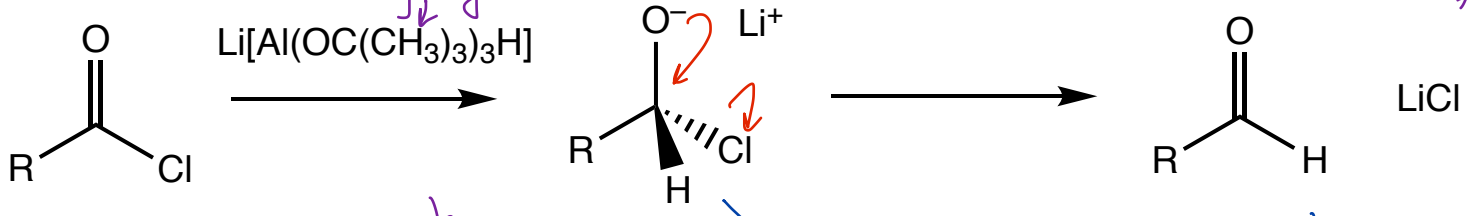


reduction requires strong reducing agent to reduce less reactive ester, but since the product of the 1st reduction (the aldehyde) is more reactive the reduction doesn't stop at the aldehyde. To avoid a mixture of ester + alcohol 2 equiv LiAlH4 are required

to stop here you need to catch the intermediate so the aldehyde doesn't form before the reducing agent is used up

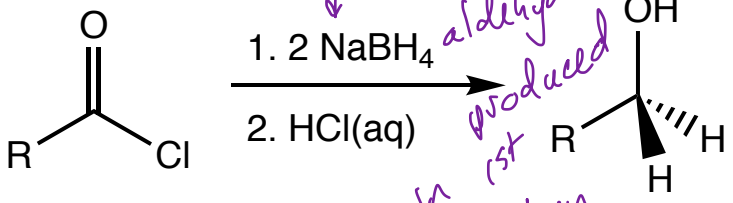
lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

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



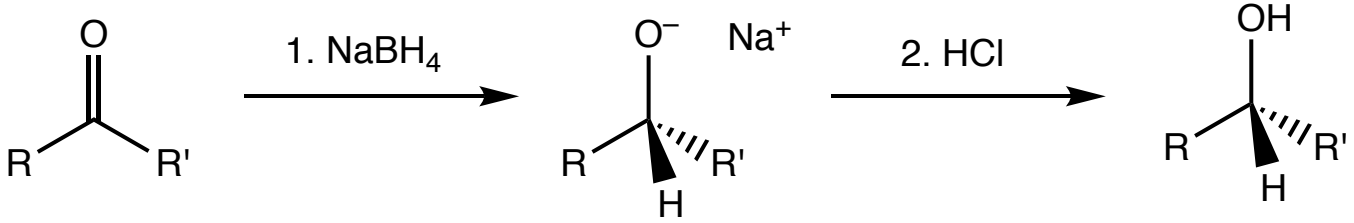
this an intermediate with a good LG, Cl^-

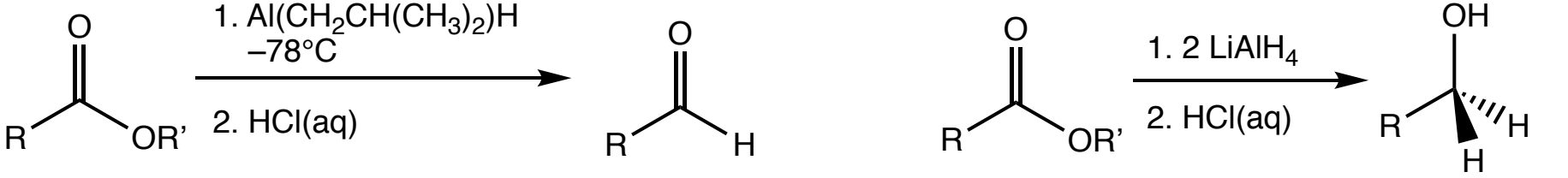
acid chlorides are the most reactive C=O compound can react with least reactive reducing agent

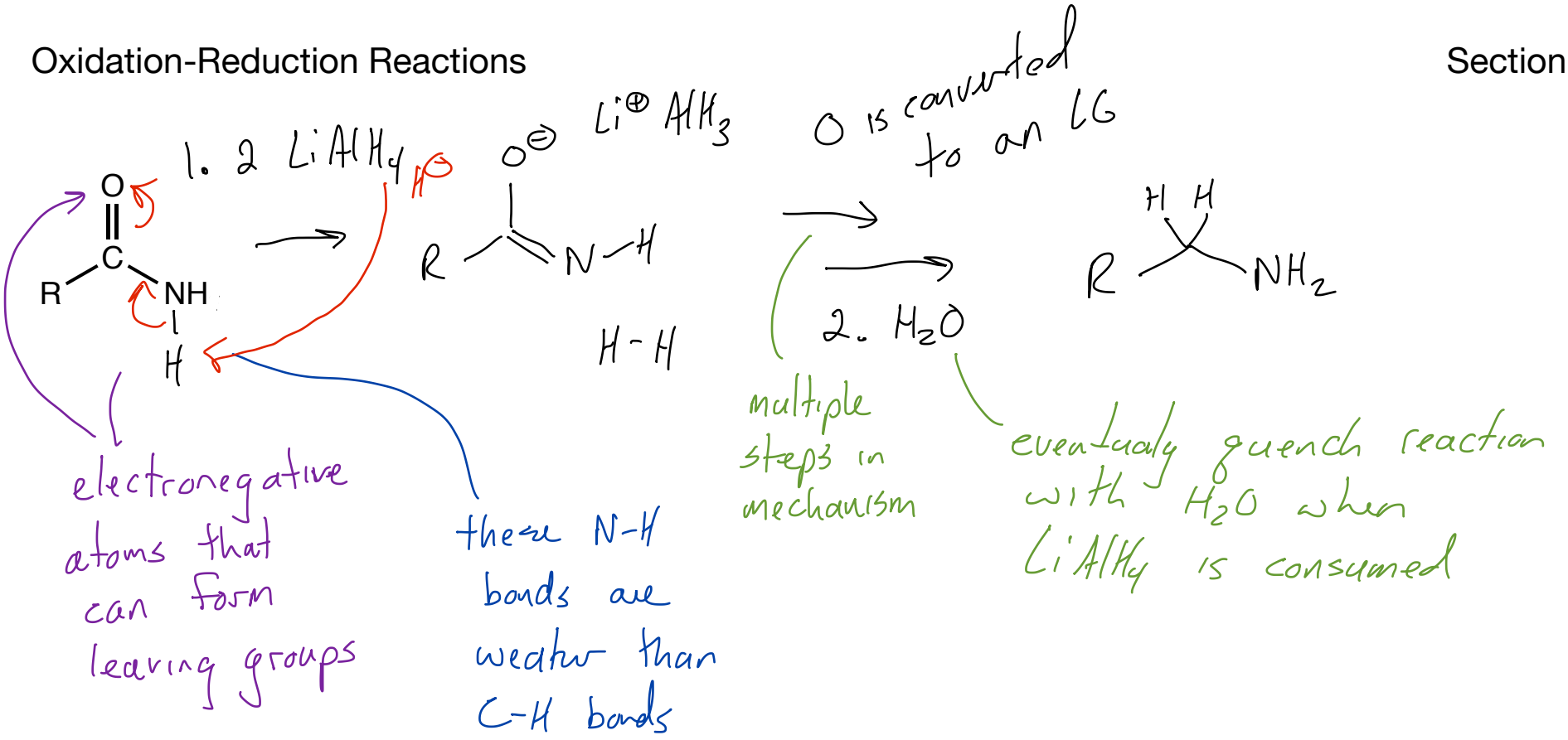


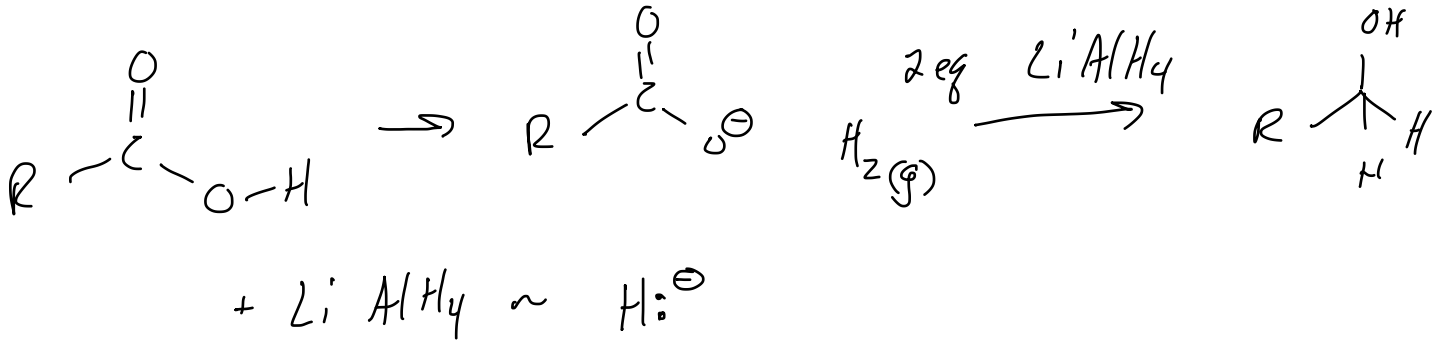
also acid chloride + $LiAlH_4$ rxn

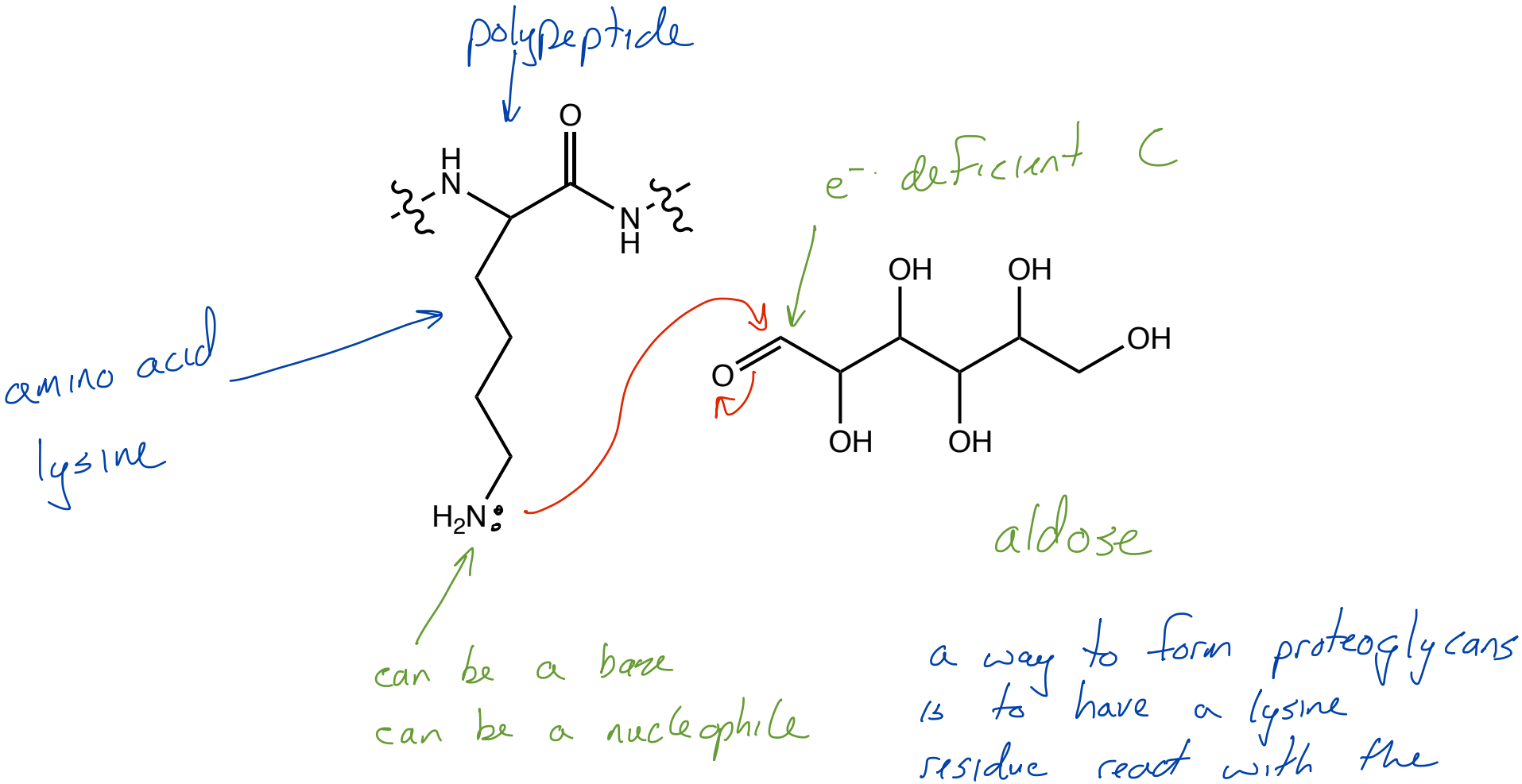
strong reducing agent after first reduction to aldehyde, aldehyde will react again



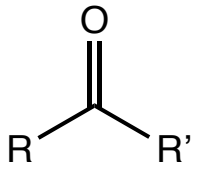



1. 2 LiAlH4
Li⊕ AlH3
O is converted to an LG
2. H2O
multiple steps in mechanism
eventualy quench reaction with H2O when LiAlH4 is consumed
electronegative atoms that can form leaving groups
these N-H bonds are weaker than C-H bonds

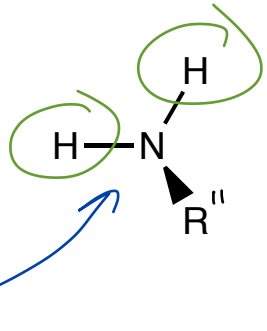

+ LiAlH4 ~ H:⊖
2 eq LiAlH4
H2(g)


polypeptide
e⁻ deficient C
amino acid
lysine
aldose
can be a base
can be a nucleophile
a way to form proteoglycans is to have a lysine residue react with the carbonyl C of a sugar

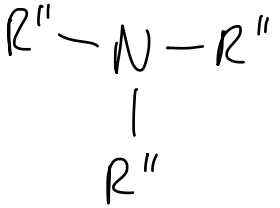
$R'' \neq H$



can't do what

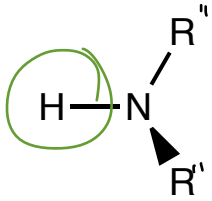


1° amine
1 C atom directly bonded to N



3° amine - 3 C atoms directly bonded to N.

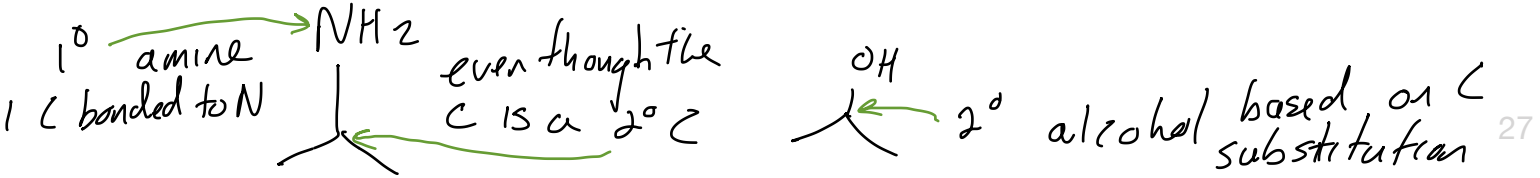
3° amines can't do what 1° & 2° amines do

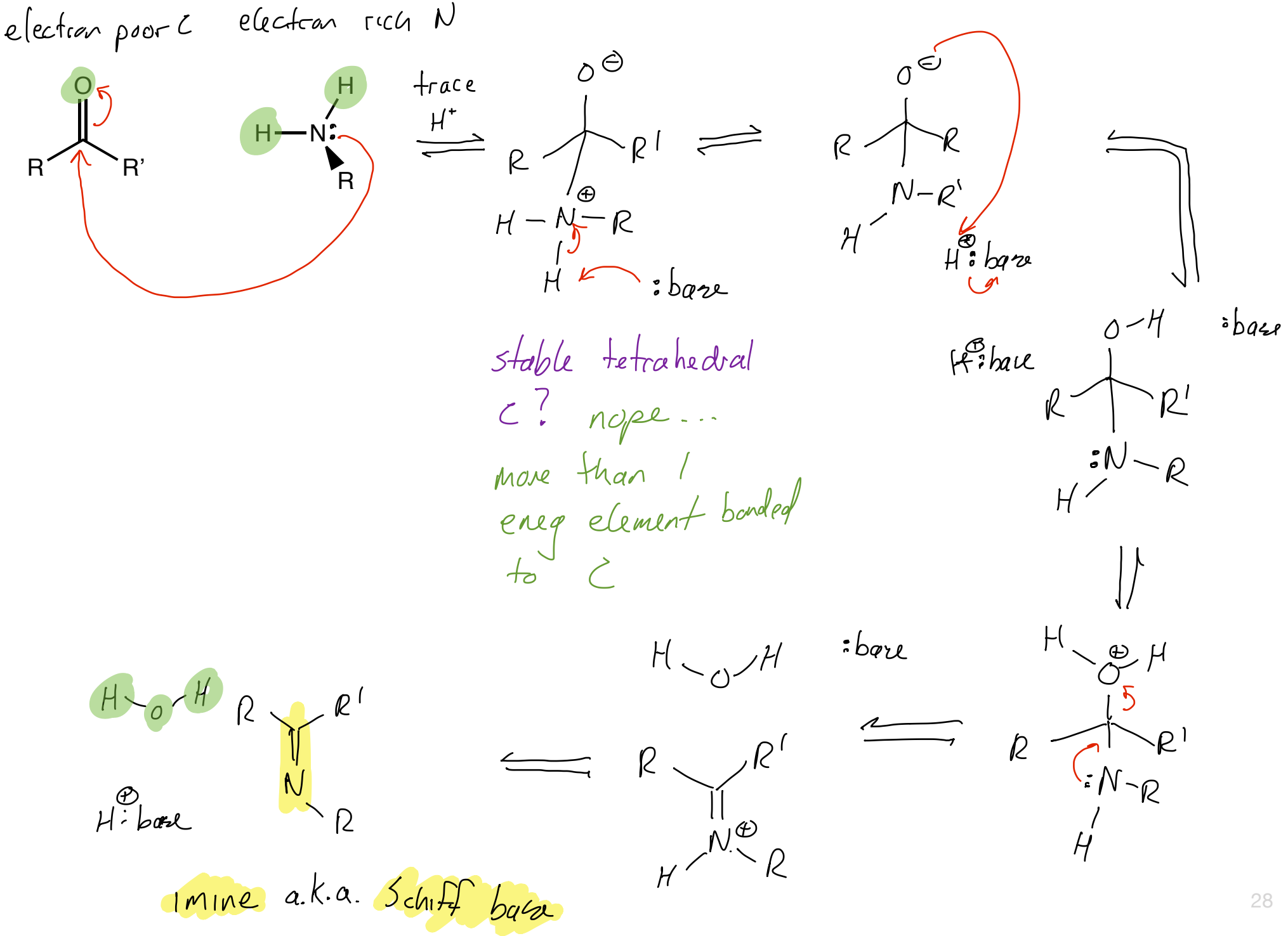


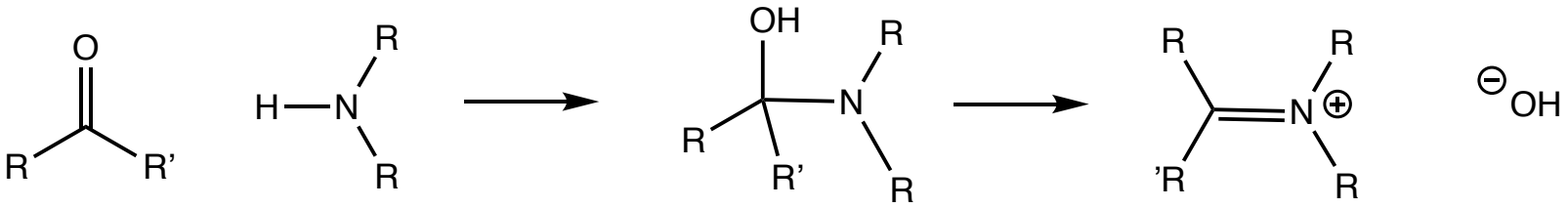
2° amine
2 C atoms directly bonded to N

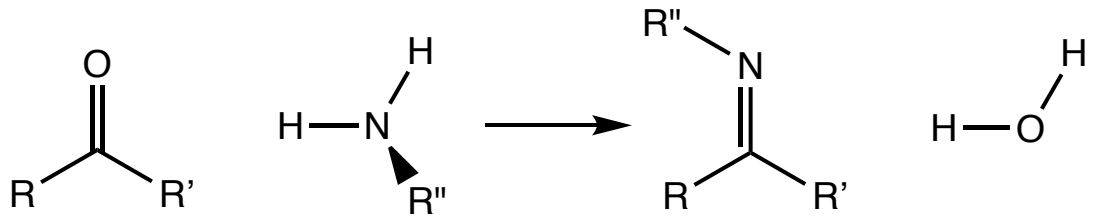
the # of H atoms bonded to the N is important in these reactions

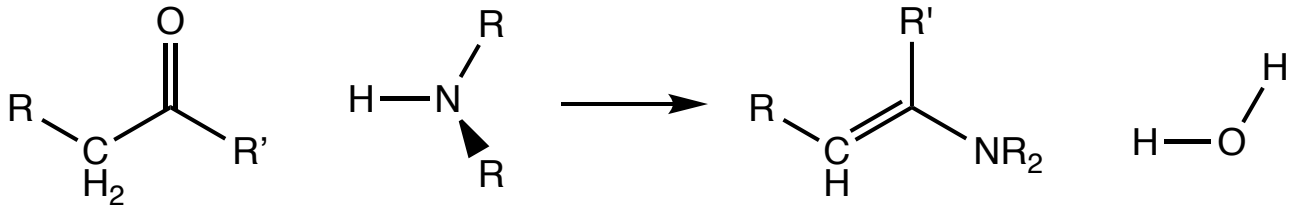
The nomenclature for the degree of substitution for an amine is different as compared to other functional groups. Other functional groups consider the substitution on the C. Amines consider substitution on the N

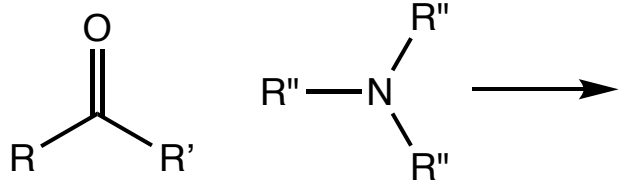


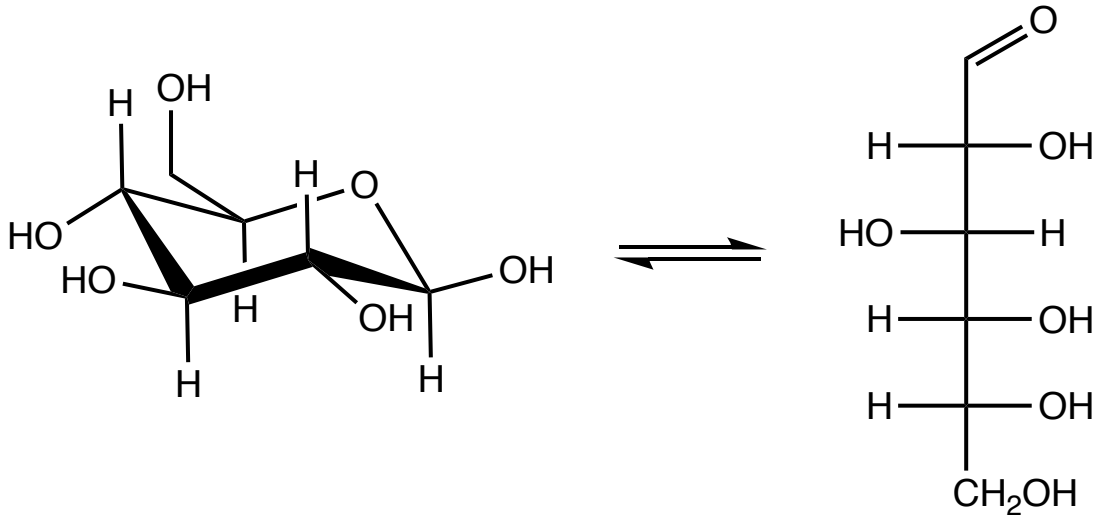

electron poor C
electron rich N
trace H+
:base
stable tetrahedral
C? nope...
more than 1 eneg element bonded to C
imine a.k.a. Schiff base

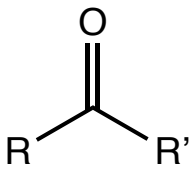

O
R
R'
H
N
R
R
OH
R
N
R
R'
R
R
R
N
'R
R
OH

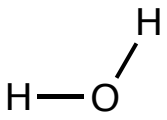

O
R
R'
H
H
N
R"
R"
N
R
R'
H
H
O

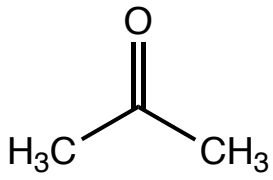

O
R
C
H2
R'
R
H
N
R
R'
R
C
H
NR2
H
H
O

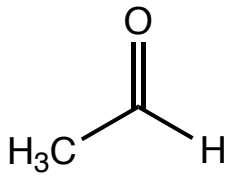

O
R
R'
R"
R"
N
R"

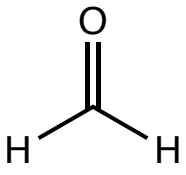

H
OH
H
O
HO
HO
OH
H
OH
H
H
O
H
OH
HO
H
H
OH
H
OH
CH2OH

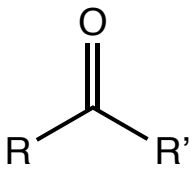

O
R
R'

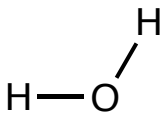

H
H
O

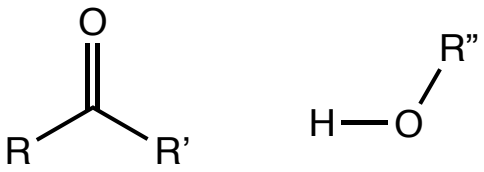

O
H3C
CH3


O
H3C
H


O
H
H


O
R
R’


H
H
O


O
R
R’

R”
H
O