Today

Reductions and Reactions with Hydride
Sections 16.5 - 16.7

Next Class

Reactions with Nitrogen Nucleophiles
Section 16.8

Reactions with Oxygen Nucleophiles
Section 16.9

Protecting Groups
16.10

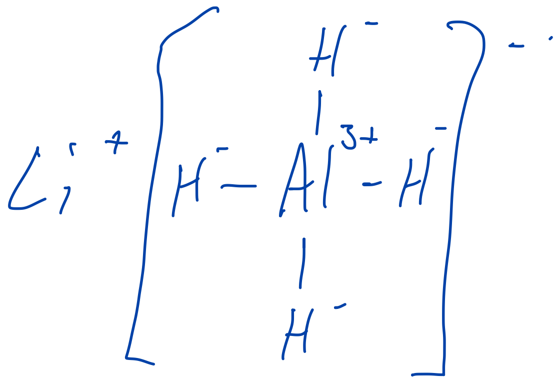
Rework Test 2 by Wednesday, April 6

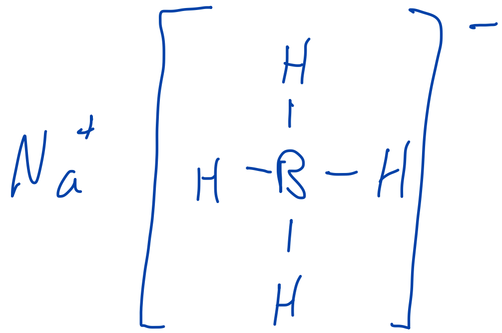
Reactions with Hydrogen Nucleophiles

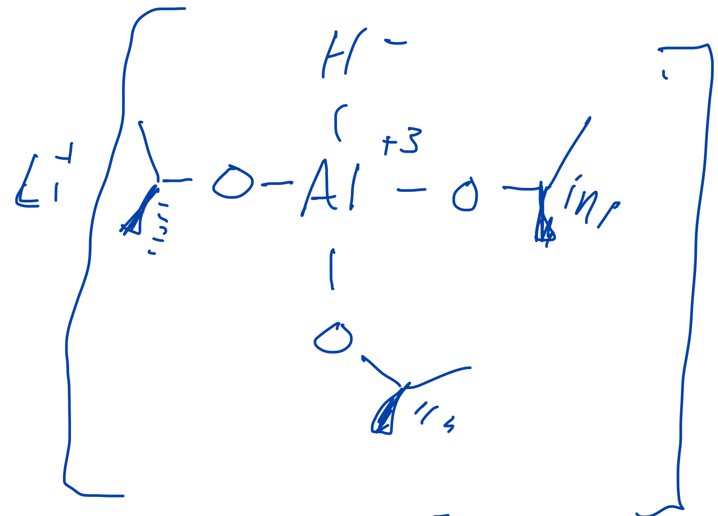
Section 16.5

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

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

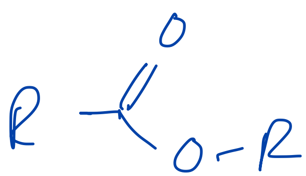


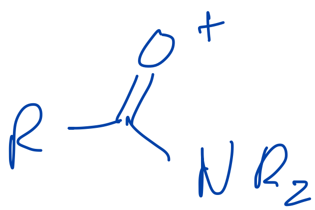




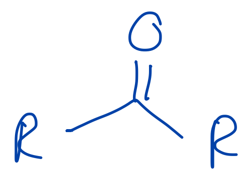
$H:^-$	$H:^-$	$H:^-$
extremely reactive	reactive but not as reactive as LAH	alcoxides lower the reactivity of the $H:^-$ donor
strongest		mildest

$LiAlH_4$	$NaBH_4$	$LiAl(OC(CH_3)_3)_3H$
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	Reduces acid chlorides to aldehydes

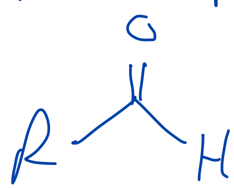


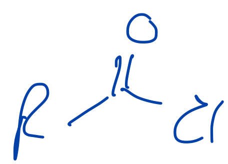


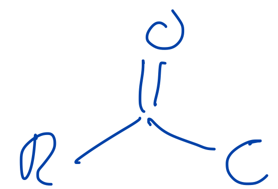
needs LAH



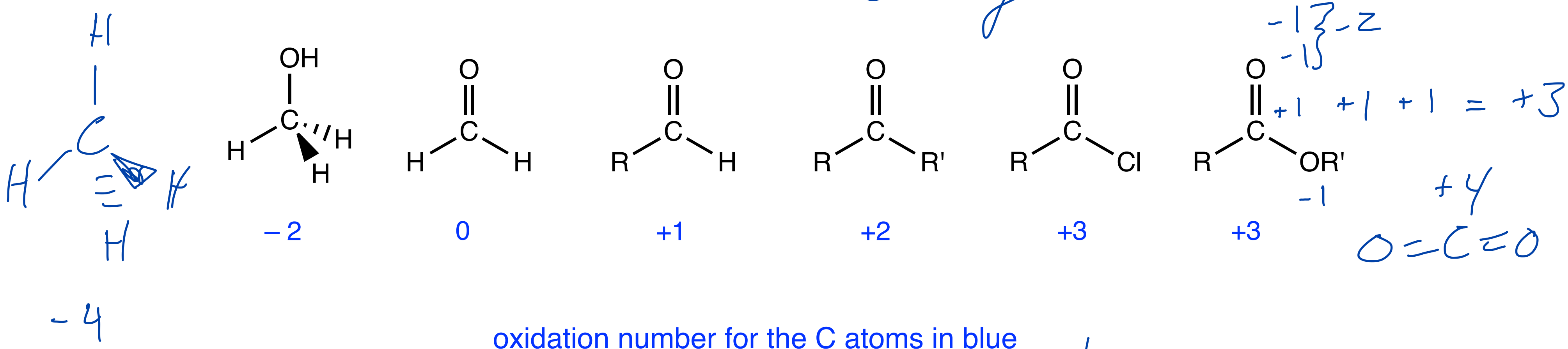
R ≠ H



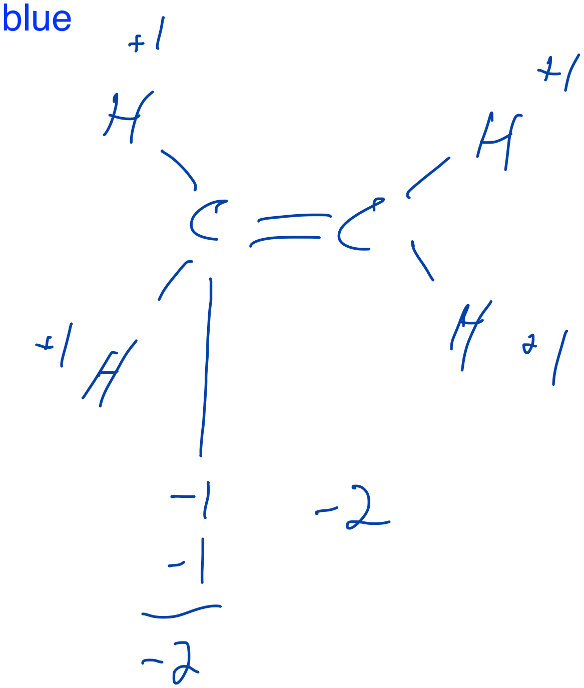




oil rig gaining e^- reduction
losing e^- oxidation



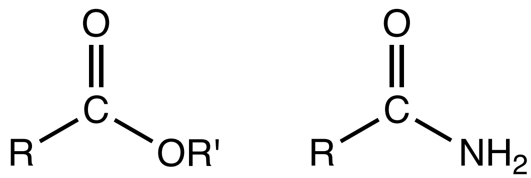
oxidation number for the C atoms in blue

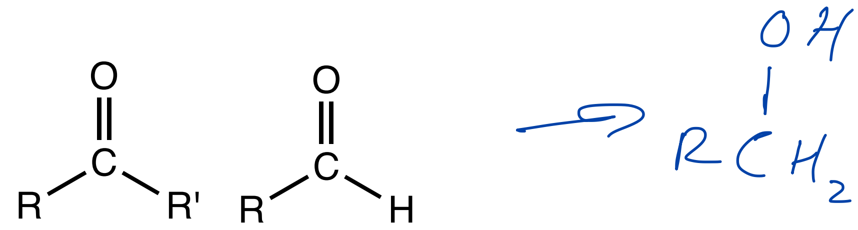


For each bond, assign
- –1 to the more electonegative atom and
- +1 to the less electronegative atom
- 0 if the electronegativities are the same

For each atom sum the assigned charges.

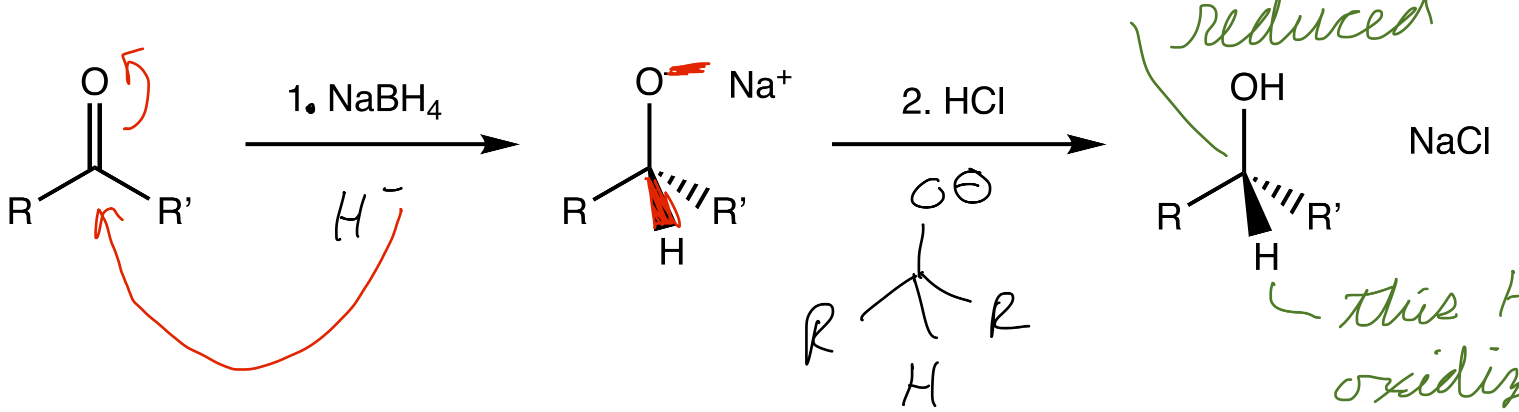
That number is the oxidation number for the atom.





each molecule has a LG on it

no LG on aldehyde or ketone

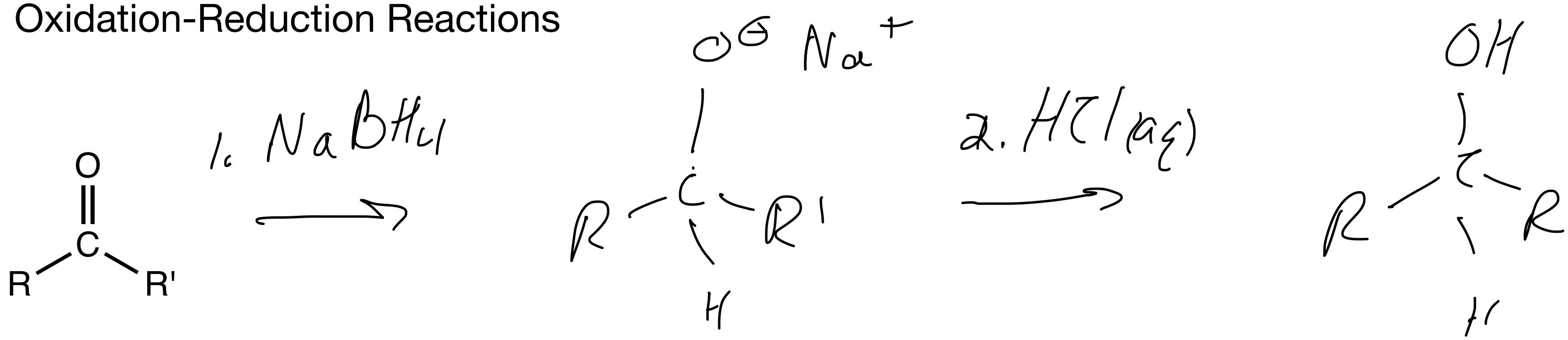


The e⁻ rich H:⁻ bonds with the carbonyl C and an alkoxide is formed.

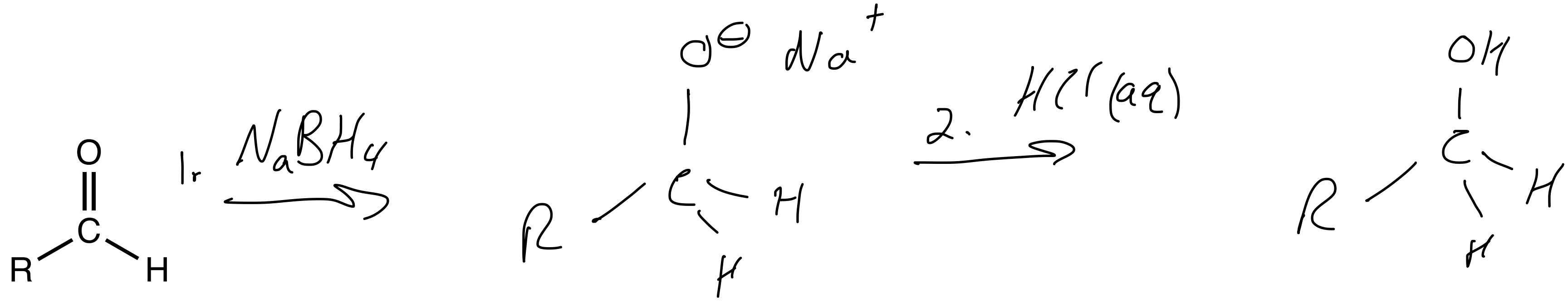
Add some dilute acid to convert alkoxide to an alcohol.

If R + R' are different the C atom will become a chirality center, but we have no control: both R + S will form

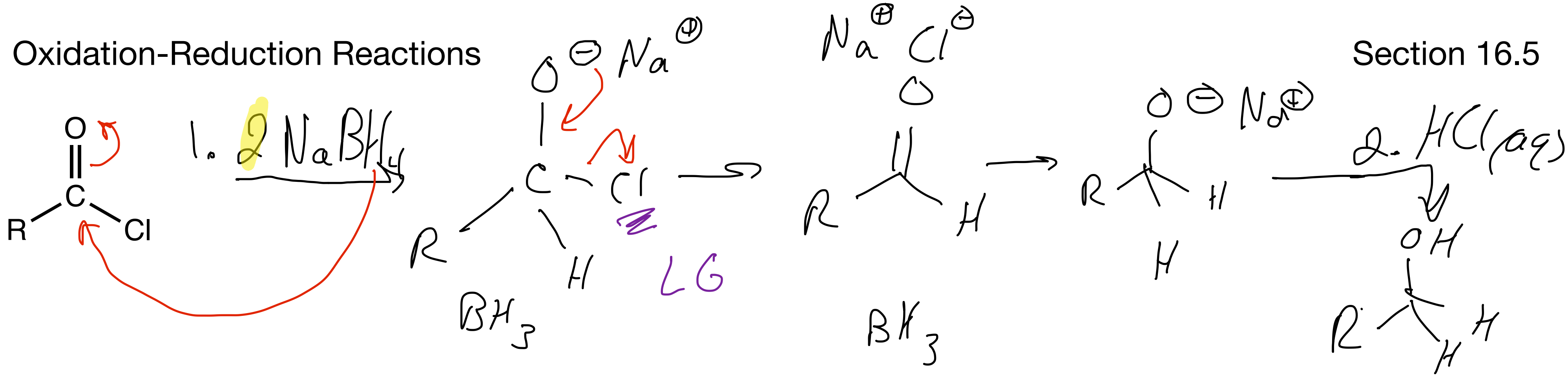
Oxidation-Reduction Reactions

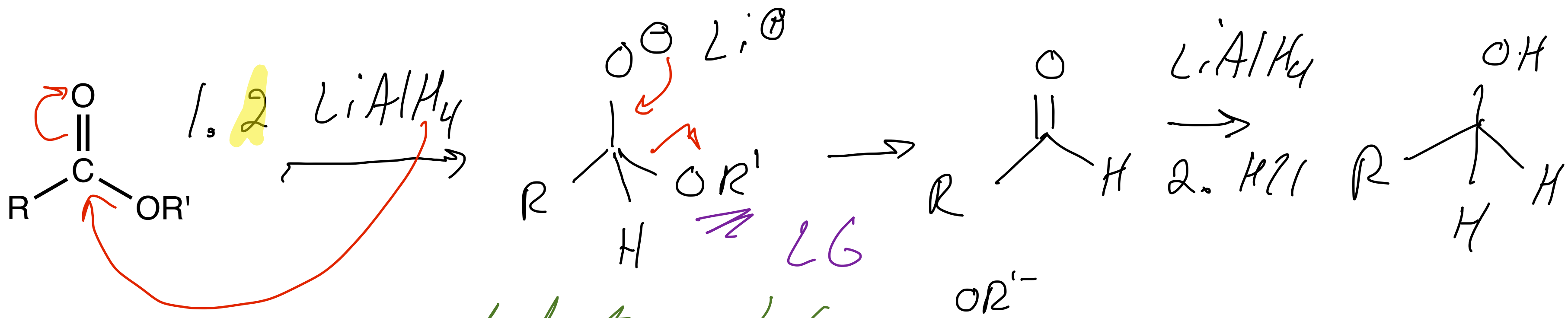


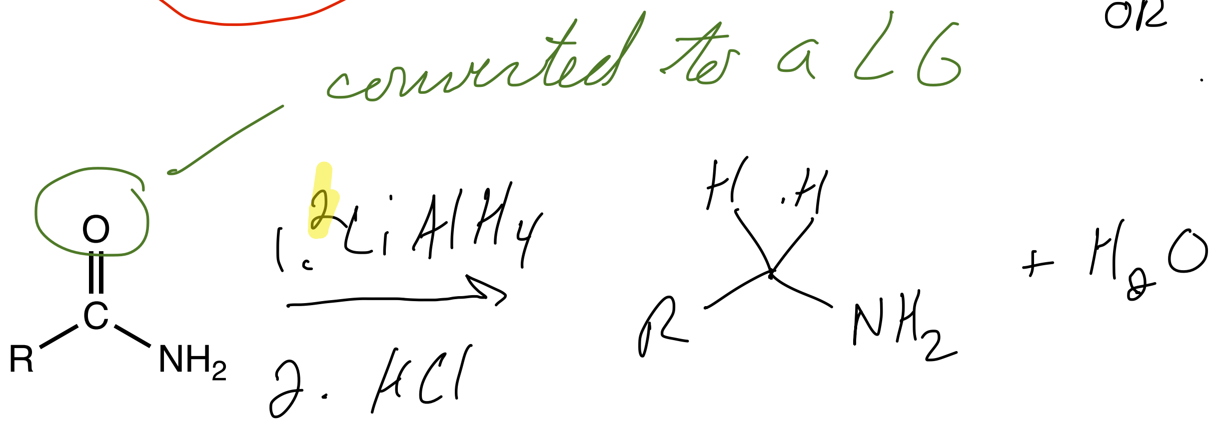
2° alcohol

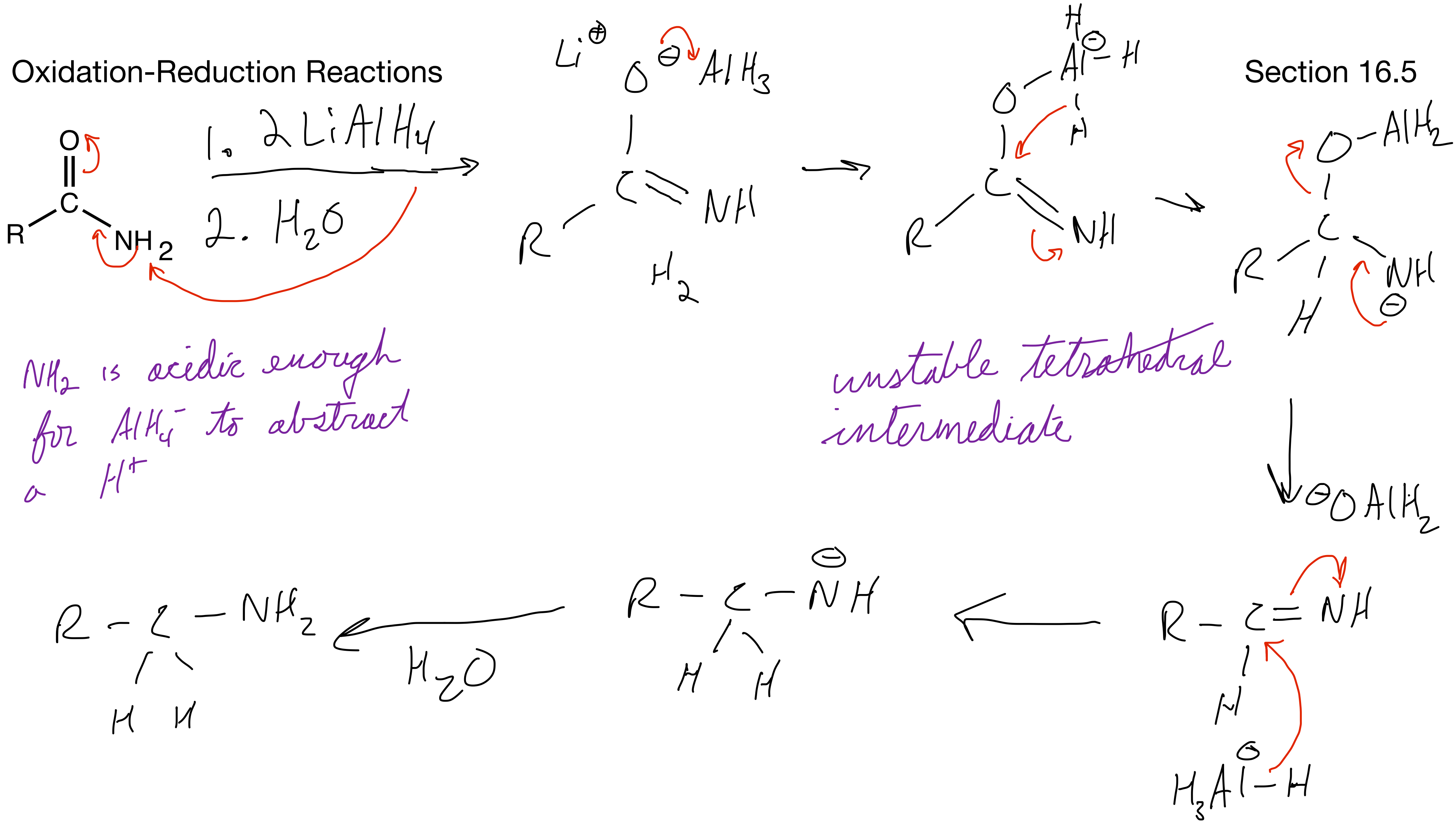


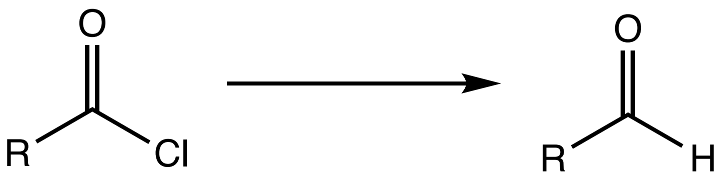
1° alcohol


O
C
R
Cl
1. 2 NaBH4
LG
BH3
Na⊕ Cl⊖
2. HCl(aq)
OH


O
C
R
OR'
1. 2 LiAlH4
LG
OR'⁻
LiAlH4
2. HCl
OH

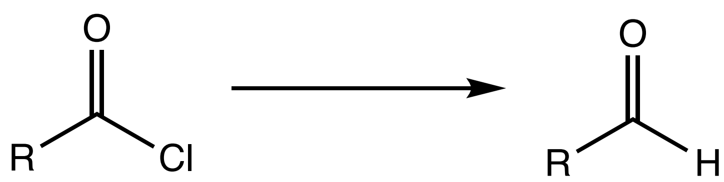

converted to a LG
O
C
R
NH2
1. 2 LiAlH4
2. HCl
NH2
+ H2O


1. 2 LiAlH4
2. H2O
NH2 is acidic enough for AlH4- to abstract a H+
unstable tetrahedral intermediate
H2O



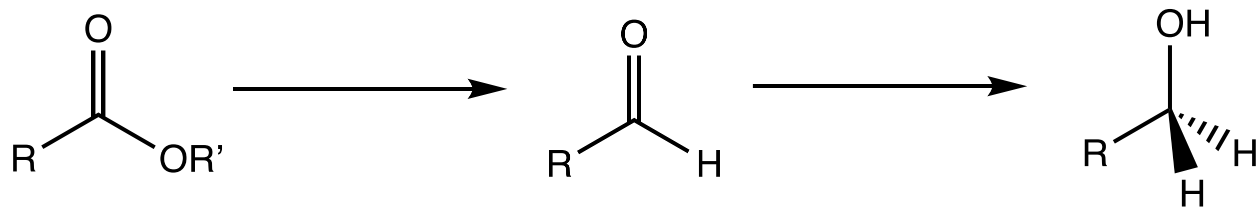
lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

Stopping at an Aldehyde

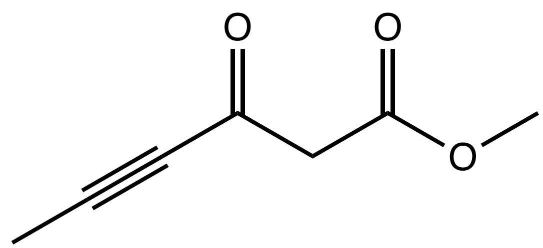


lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride

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



lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride


O
O
O