

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

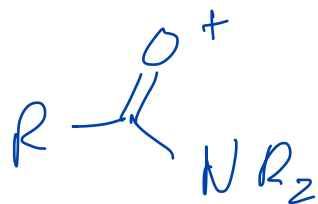
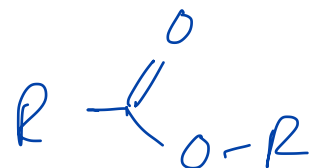
Protecting Groups
16.10

Rework Test 2 by Wednesday, April 6



lithium aluminum hydride

Fully reduces esters,
carboxylic acids,
and amides to
alcohols and amines

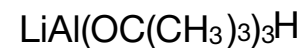
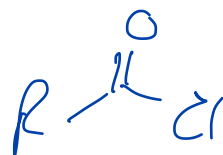


needs
LAH



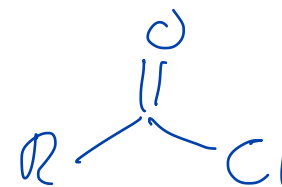
sodium borohydride

Fully reduces
ketones,
aldehydes, and
acid chlorides
to alcohols



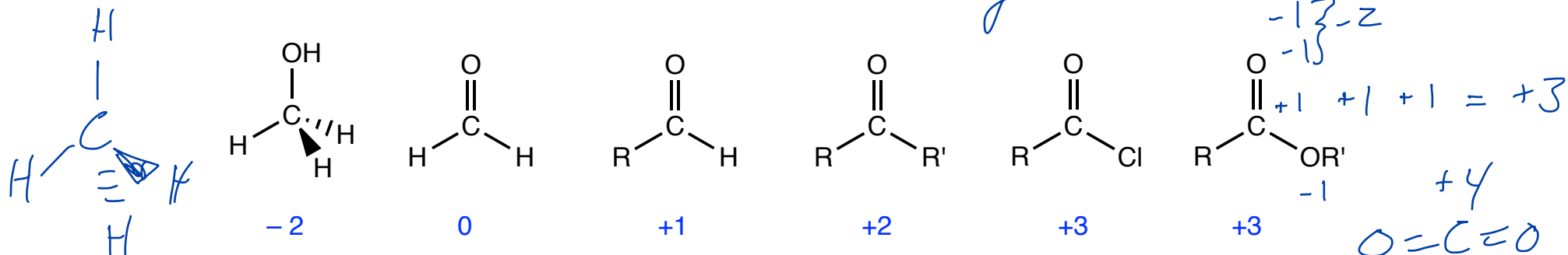
lithium tri-tertbutoxyaluminum hydride

Reduces acid
chlorides to
aldehydes



Oxidation-Reduction Reactions

oil rig gaining e⁻ reduction
 losing e⁻ oxidation

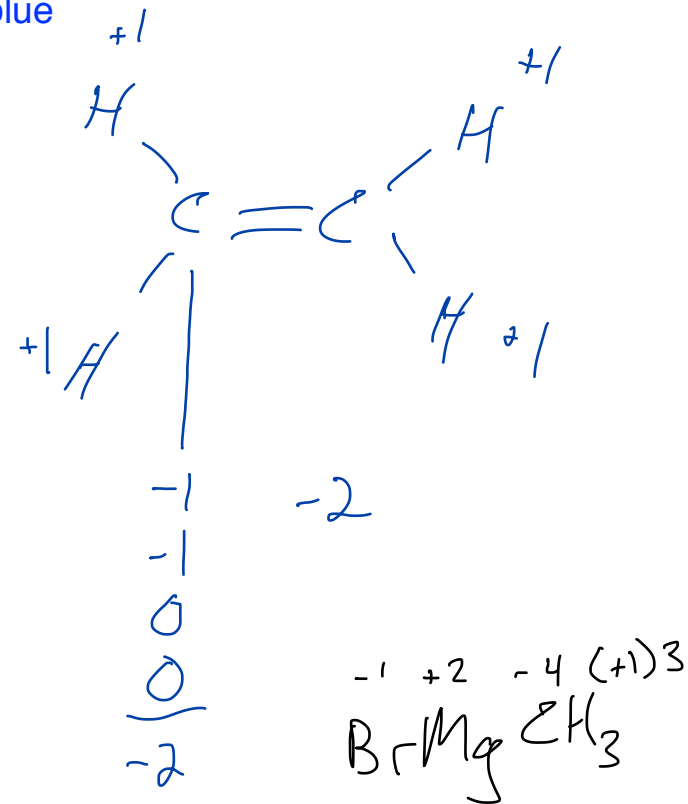


oxidation number for the C atoms in blue

For each bond, assign
 -1 to the more electronegative 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.

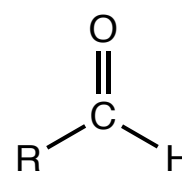
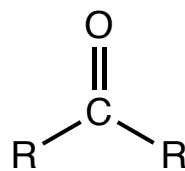
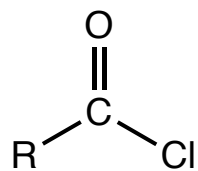
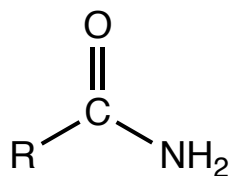
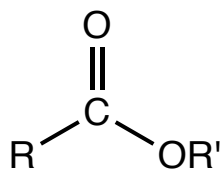


redox rxn



Oxidation-Reduction Reactions

Section 16.5

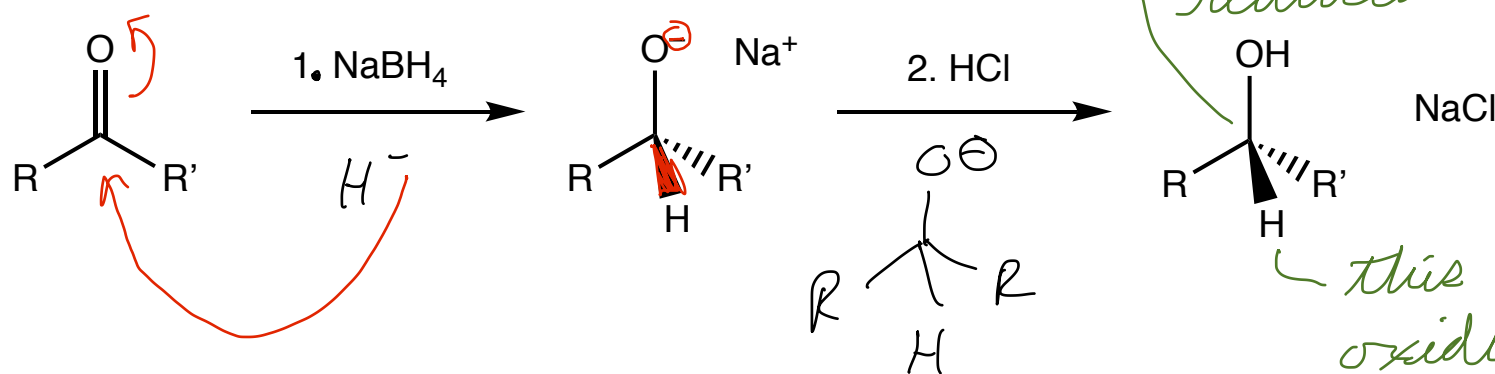


each molecule has
a LG on it

no LG on
aldehyde or
ketone

Oxidation-Reduction Reactions

Section 16.5

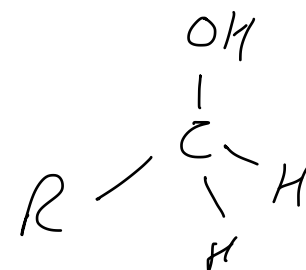
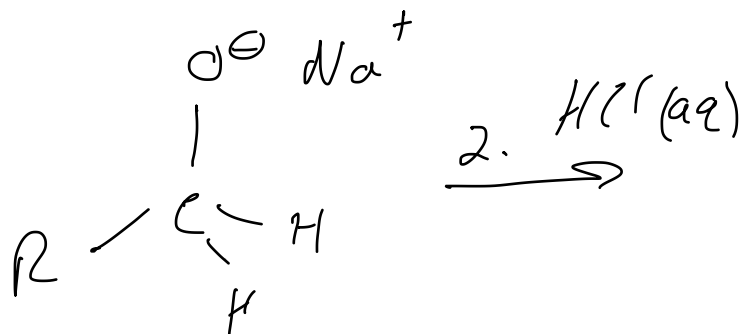
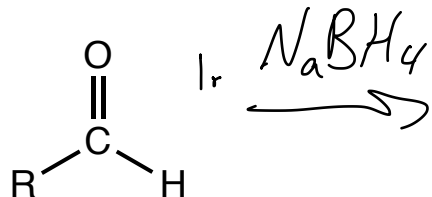
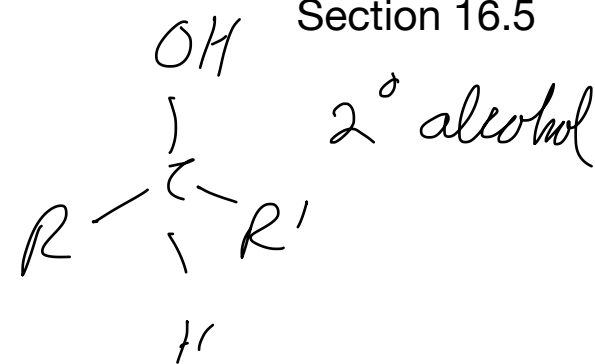
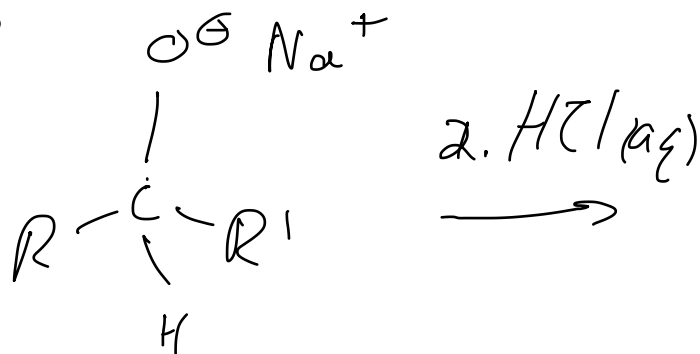
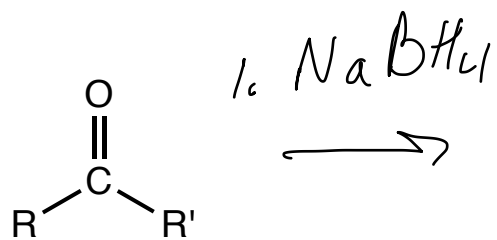


The e^- rich H^- bonds with the carbonyl C and an alkoxide is formed. Add some dilute acid to convert alkoxide to an alcohol.

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

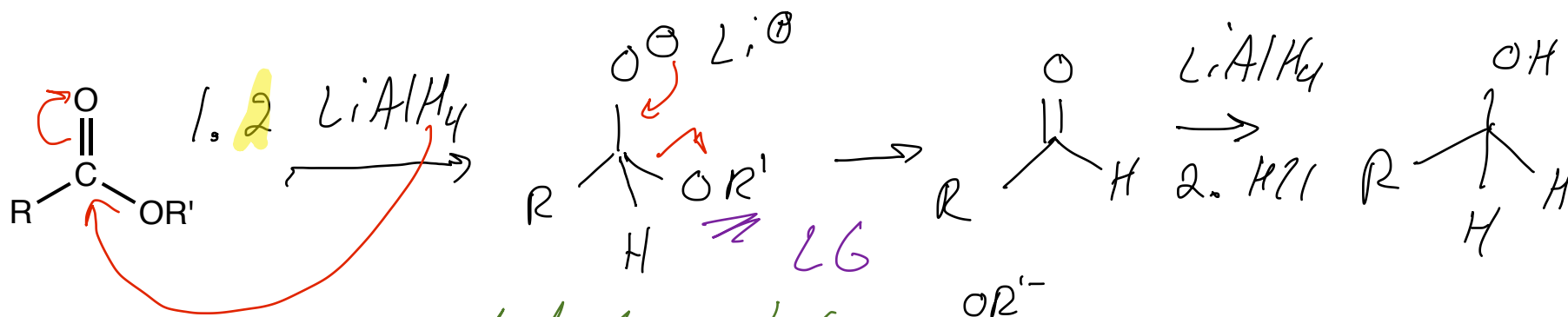
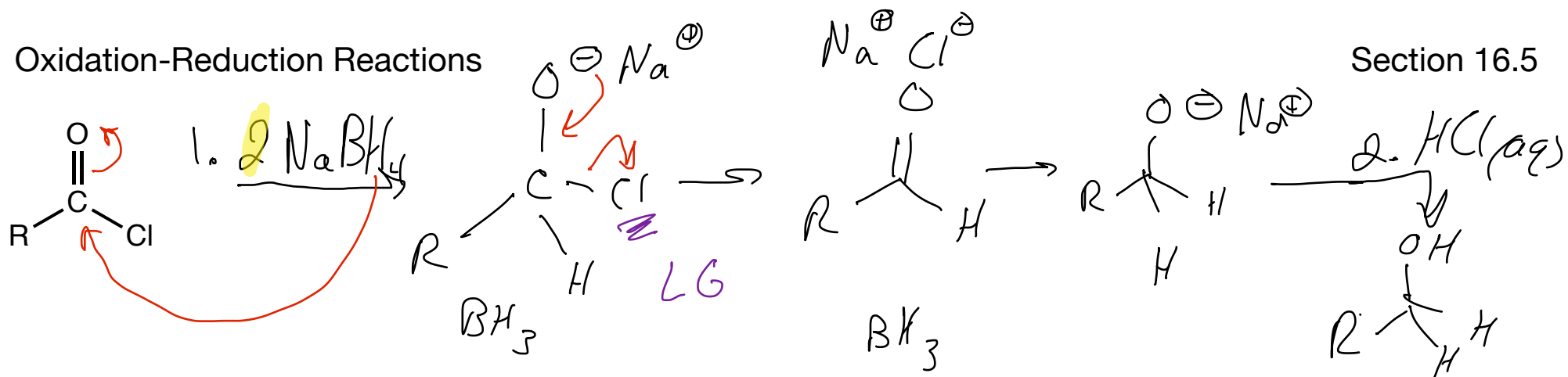
Oxidation-Reduction Reactions

Section 16.5

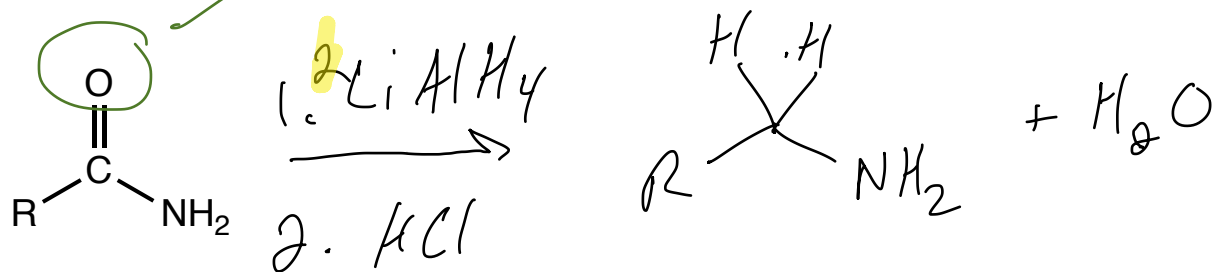


1° alcohol

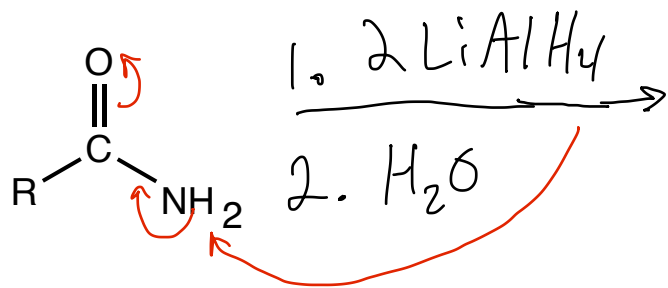
Oxidation-Reduction Reactions



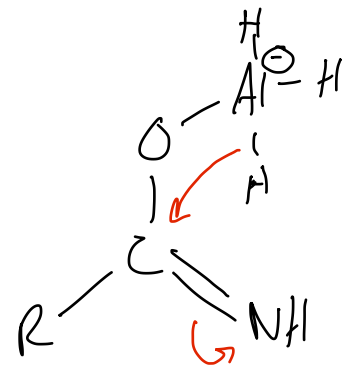
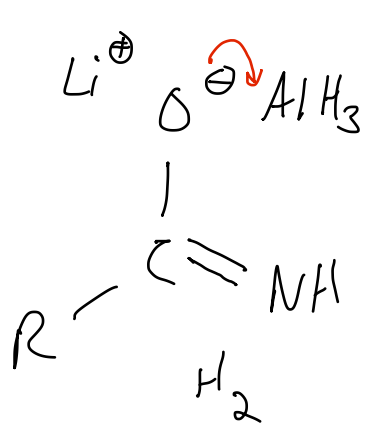
converted to a LG



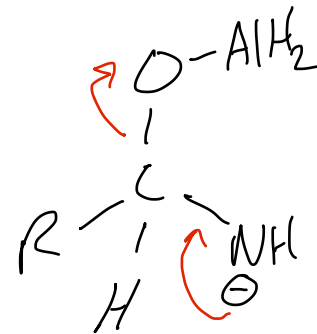
Oxidation-Reduction Reactions



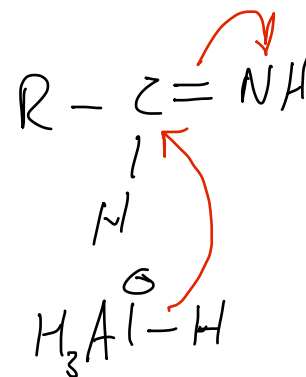
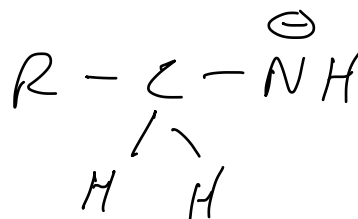
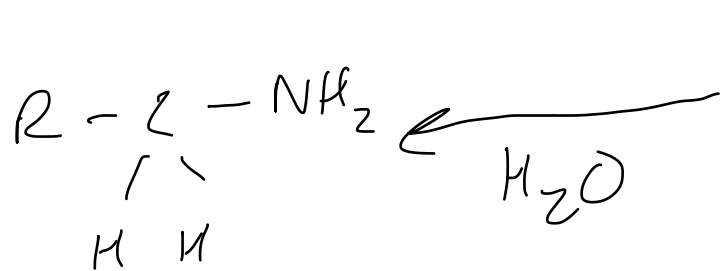
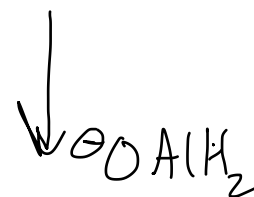
NH₂ is acidic enough for AlH₄⁻ to abstract a H⁺



Section 16.5



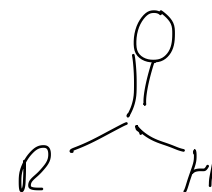
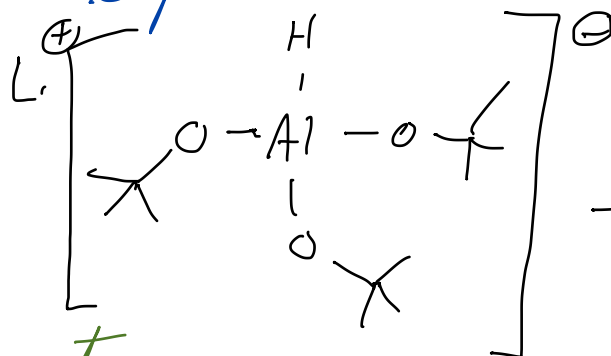
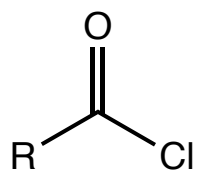
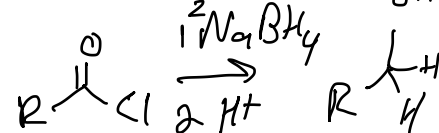
unstable tetrahedral intermediate



Oxidation-Reduction Reactions - Selective Reductions
 Stopping at an Aldehyde

Section 16.5 ΔH

Al is oxophilic

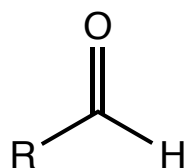
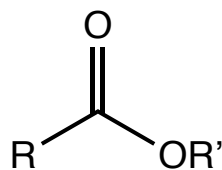


less reactive so rxn stops here

extremely reactive

less reactive than acid chloride

strategy is to find an H⁻ donor that is reactive enough to react with acid chloride but not the aldehyde



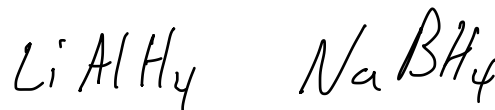
this is a new problem.

When the ester reacts and forms the aldehyde a more reactive molecule is made.

So a weaker reducing agent won't do the trick

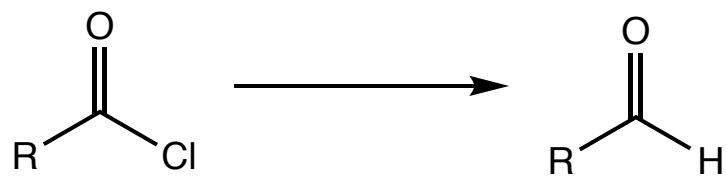
lithium tri-*t*-butoxyaluminum hydride

vs diisobutylaluminum hydride



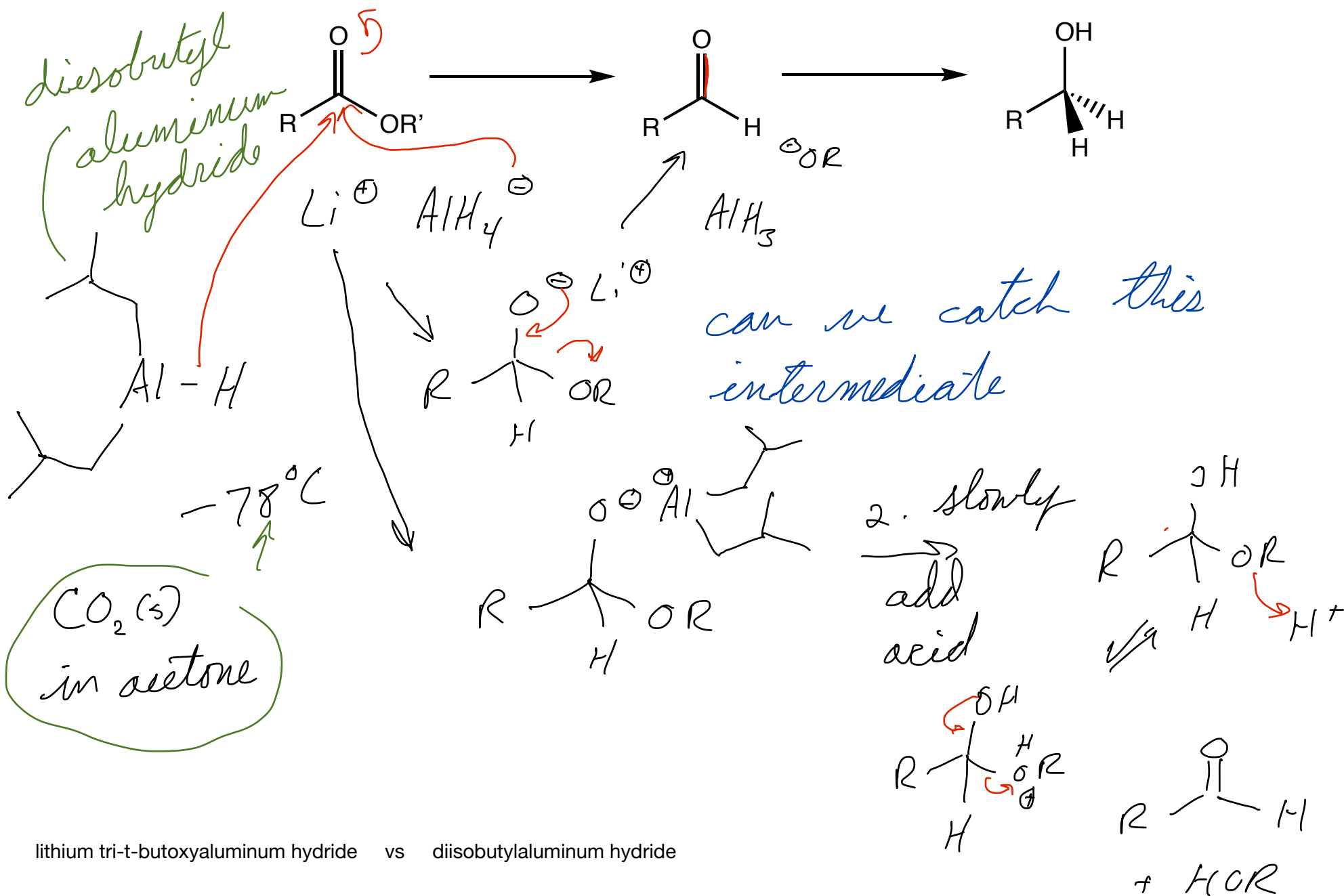
Oxidation-Reduction Reactions - Selective Reductions Stopping at an Aldehyde

Section 16.5 16

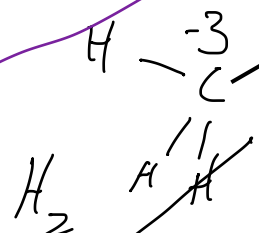
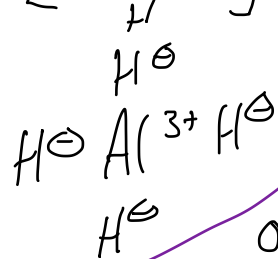
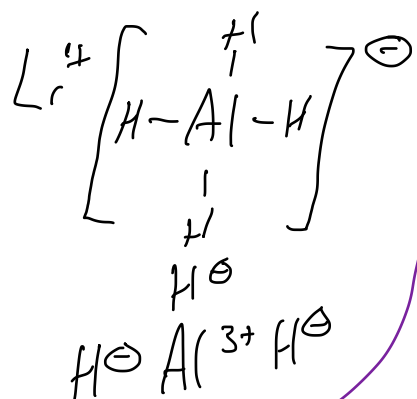
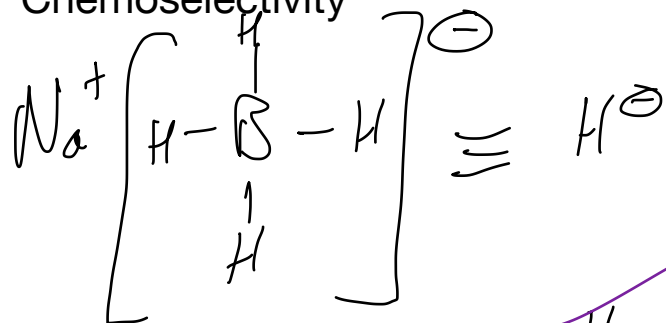


lithium tri-*t*-butoxyaluminum hydride vs diisobutylaluminum hydride

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

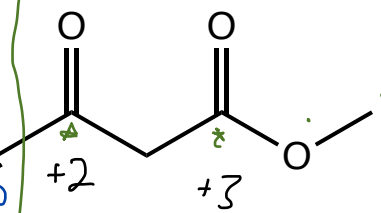


Oxidation-Reduction Reactions - Selective Reductions
Chemoselectivity



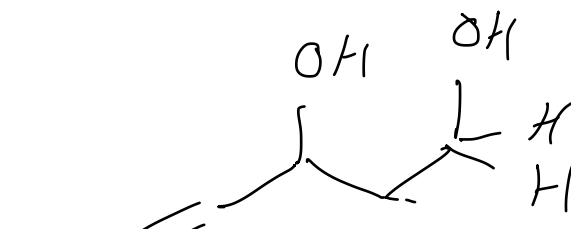
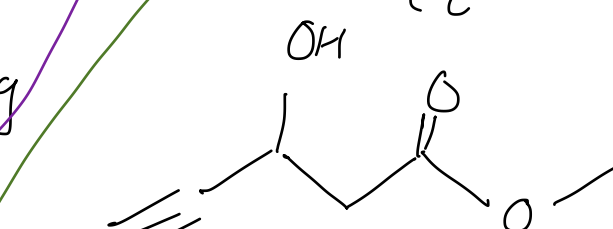
cat.
Raney
Ni

targets for
reduction



1. $\downarrow \text{NaBH}_4$
2. $\downarrow \text{H}^+ (\text{aq})$

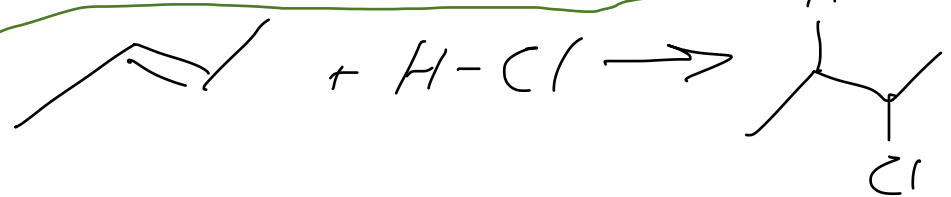
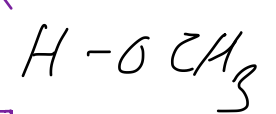
1. $\text{LiAlH}_4 \text{ (H}^-)$
2. $\text{H}^+ (\text{aq})$

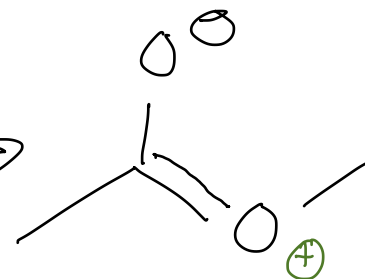
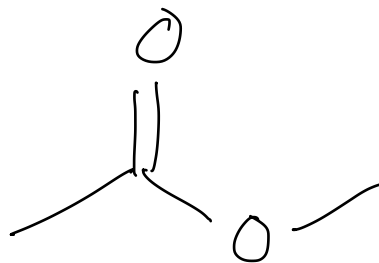


use a weak
acid to preserve C to C
 π bond

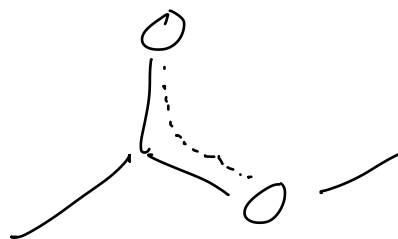
HOCH_3

not covered





|||



π bond character
makes ester less
reactive to
nucleophiles

Topic

Section

Topic

Section

