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

$LiAlH_4$

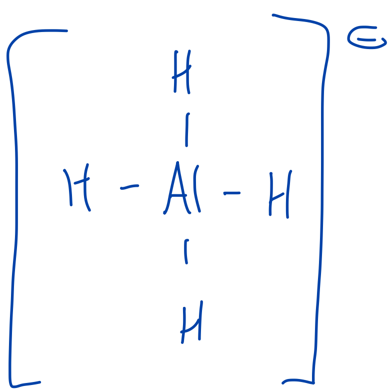
lithium aluminum hydride

extremely reactive

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

and can be dangerous

~ $H:^{\ominus}$

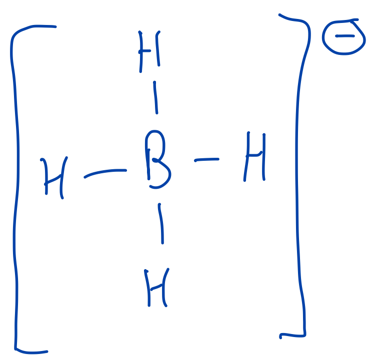


$NaBH_4$

sodium borohydride

Fully reduces ketones, aldehydes, and acid chlorides to alcohols. Does not reduce esters, carboxylic acids, and amides

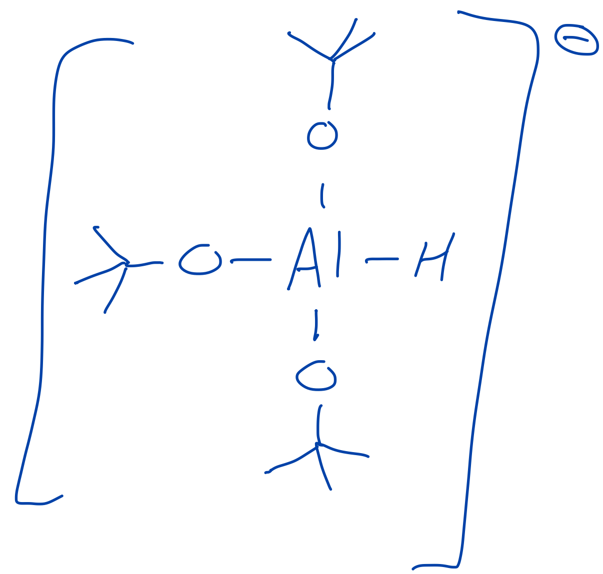
~ $H:^{\ominus}$



$LiAl[OC(CH_3)_3]_3H$

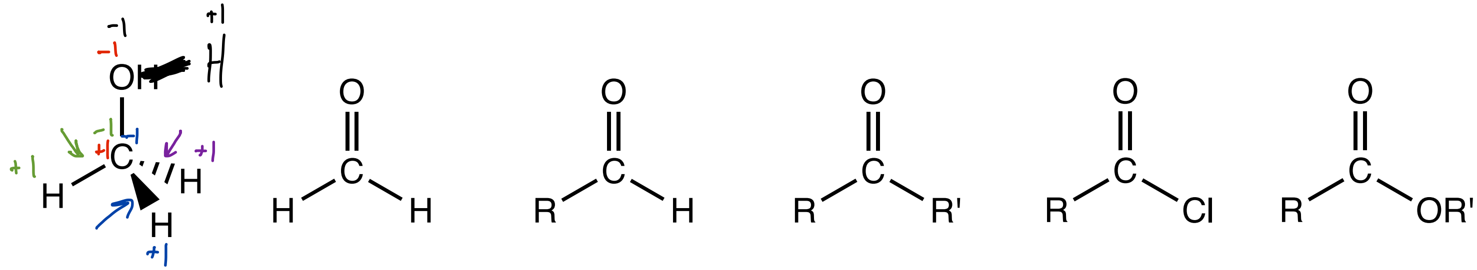
lithium tri-tertbutoxyaluminum hydride

Reduces acid chlorides to aldehydes

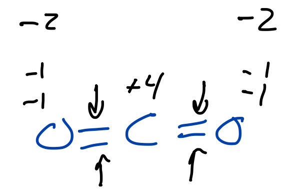


$\overset{-4}{CH_4} + 2\overset{0}{O_2} \rightarrow \overset{+4}{CO_2} + 2H_2O$

−1
−1
−1
+1
———
−2



−2 0 +1 +2 +3 +3



+1
+1
+1
+1

oxidation # of C

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.

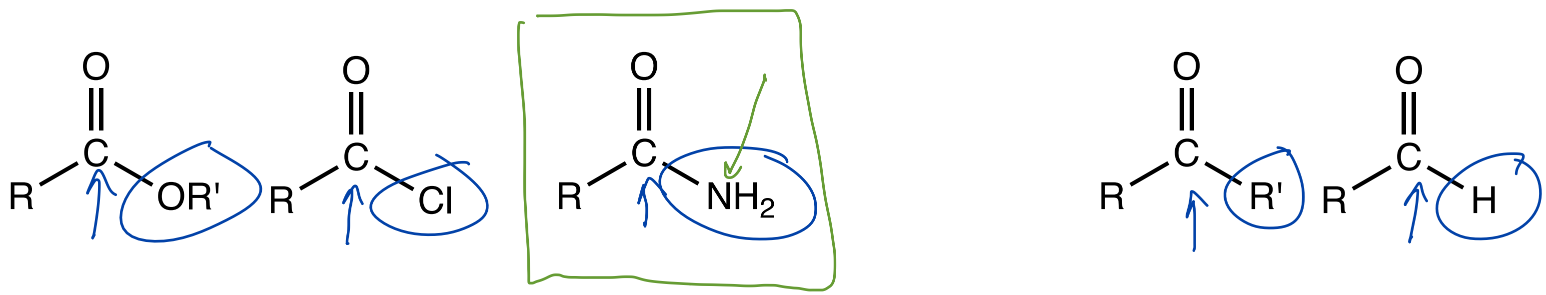
oil rig
leo say ger

$2Mg + O_2 \rightarrow 2MgO$

0 + 0 0 → +2 −2

Mg lost 2 e^- and became Mg^{2+} oxidation

O gained 2 e^-'s an became O^{2-}

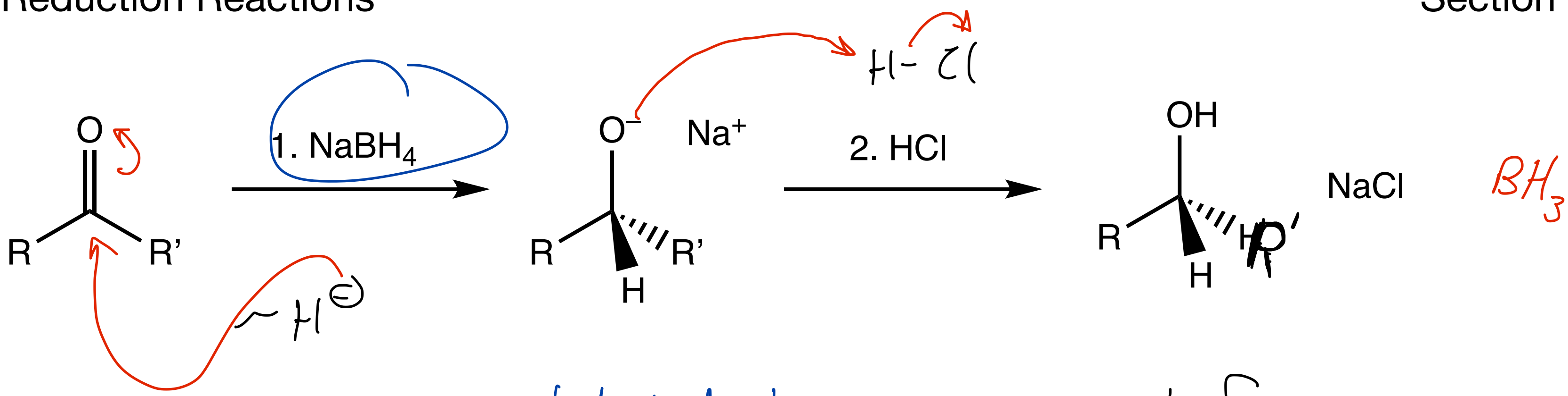


Carbonyl compounds with leaving groups

Carbonyl compounds without leaving groups

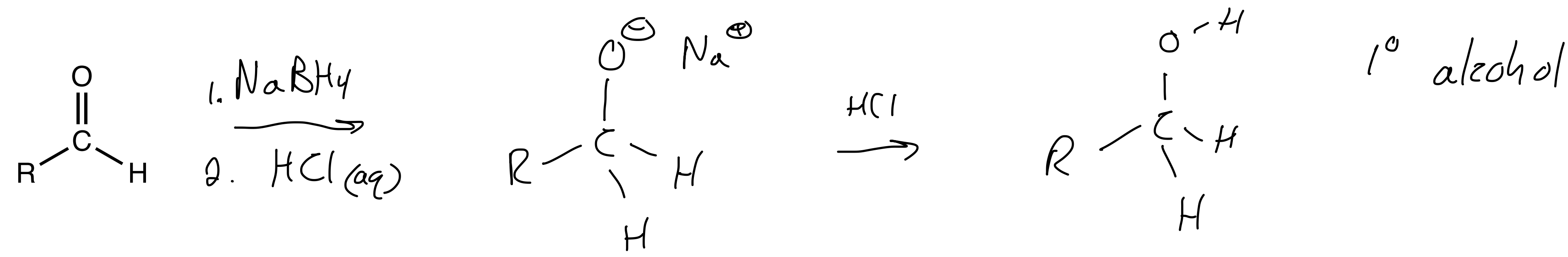
all our carbonyls are electrophilic

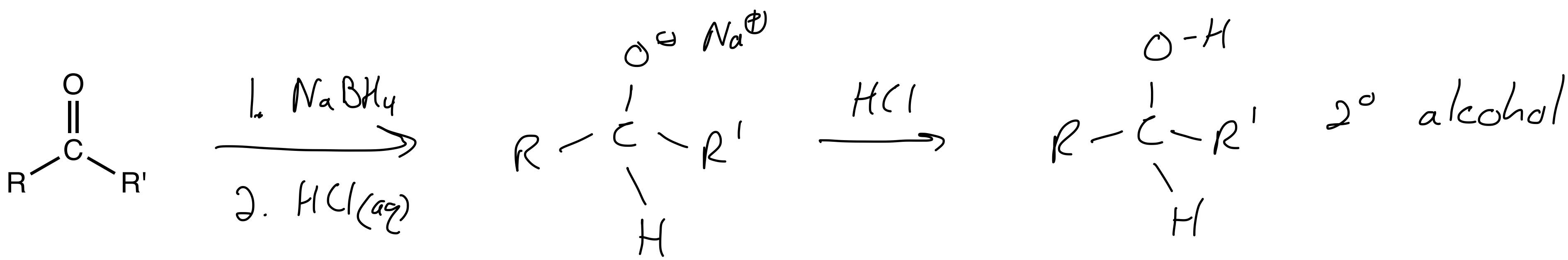
leaving groups means that these will behave differently as compared to these

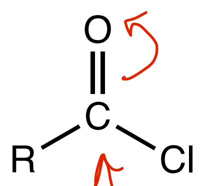


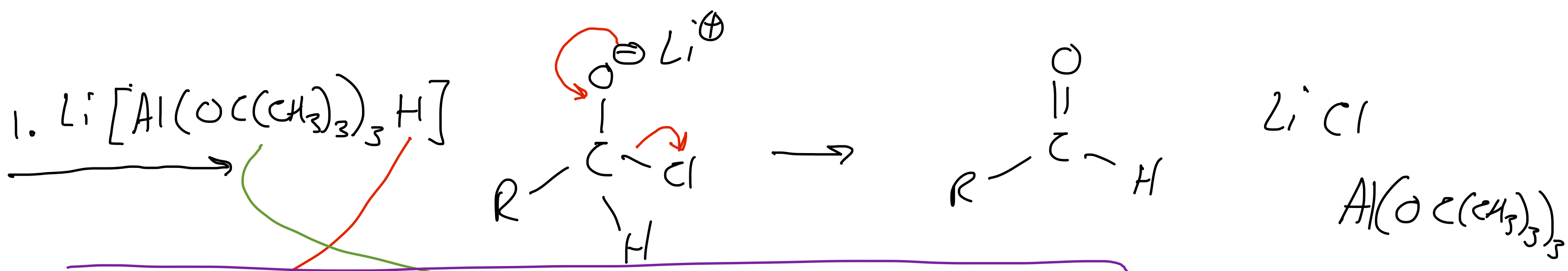
tetrahedral
C atom
forms ...
and since
there aren't
2 eneg atoms
bonded to it
it is stable

simple 1 step reaction
convert alkoxide to more convenient alcohol
in a second reaction


O
R
C
H
1. NaBH4
2. HCl (aq)
O⊖ Na⊕
HCl
O-H
1° alcohol


O
R
C
R'
1. NaBH4
2. HCl(aq)
O⊖ Na⊕
HCl
O-H
2° alcohol





acid chlorides are more reactive than aldehydes + ketones

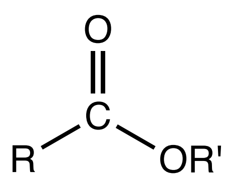
1.2 equiv NaBH4
2. HCl

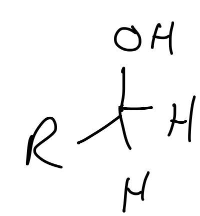
less reactive than acid chloride

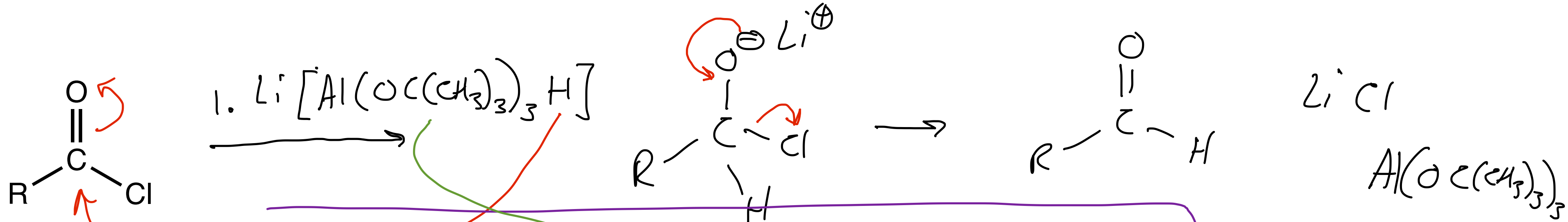
what could we use to convert acid chloride to the alcohol

remember we said this isn't strong enough to react with aldehyde or ketone

NaBH4 can reduce aldehyde! so







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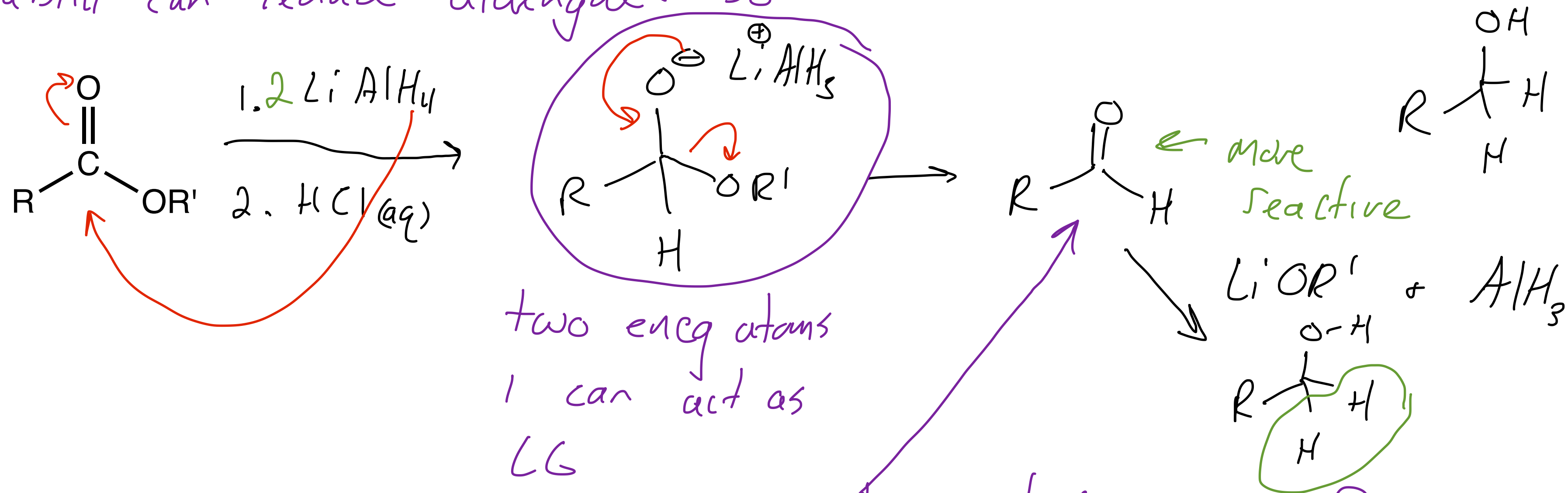


two eneg atoms
1 can act as LG

can we catch this intermediate

stopping here could be useful

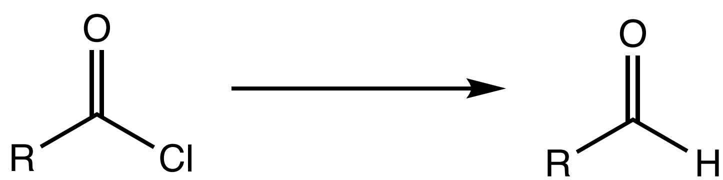
Oxidation-Reduction Reactions - Selective Reductions
Stopping at an Aldehyde

$LiAlH_4$

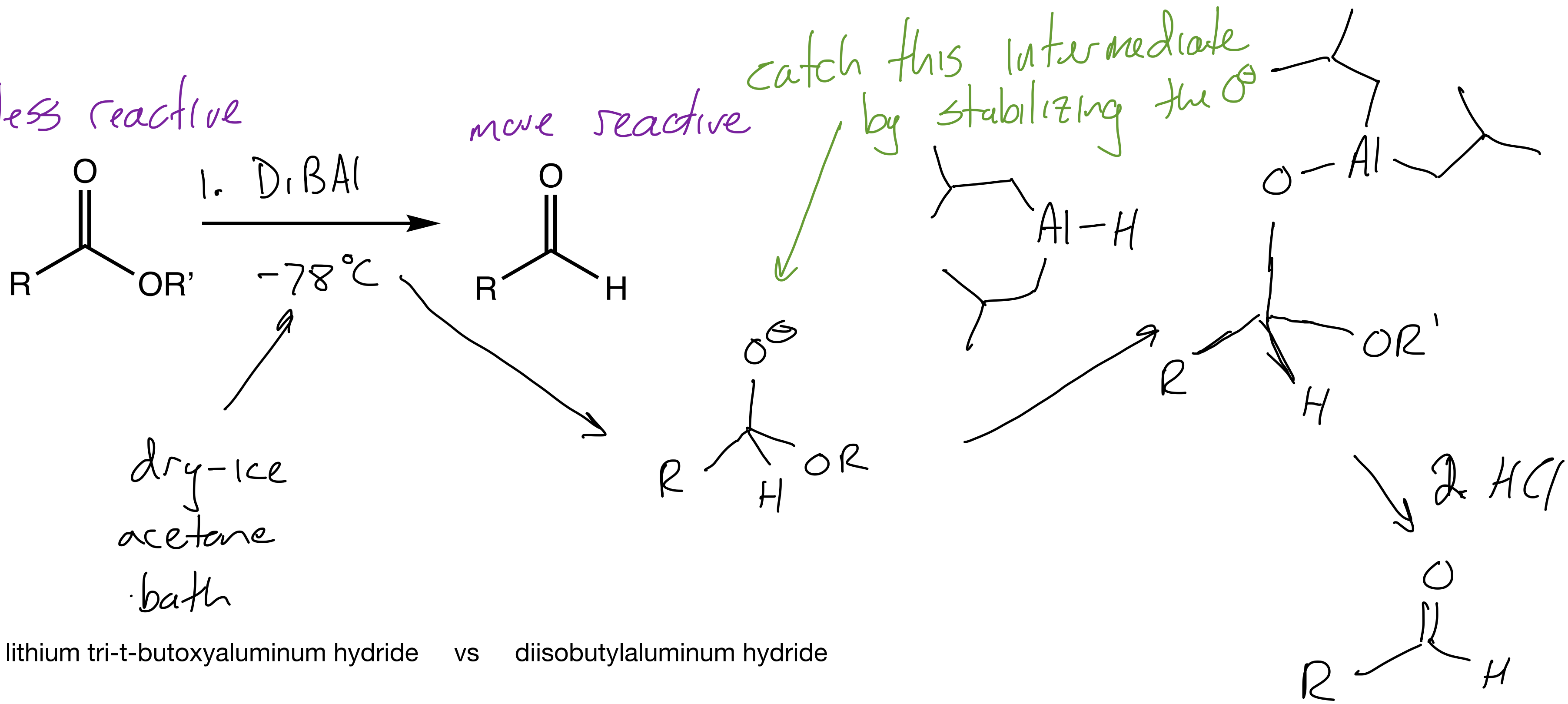
$NaBH_4$

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

less reactive product .... nerf the reducing agent to stop reaction after 1st reduction. O atoms help stabilize hydride donor



less reactive — more reactive



lithium tri-t-butoxyaluminum hydride vs diisobutylaluminum hydride