Acid Chlorides & Anhydrides

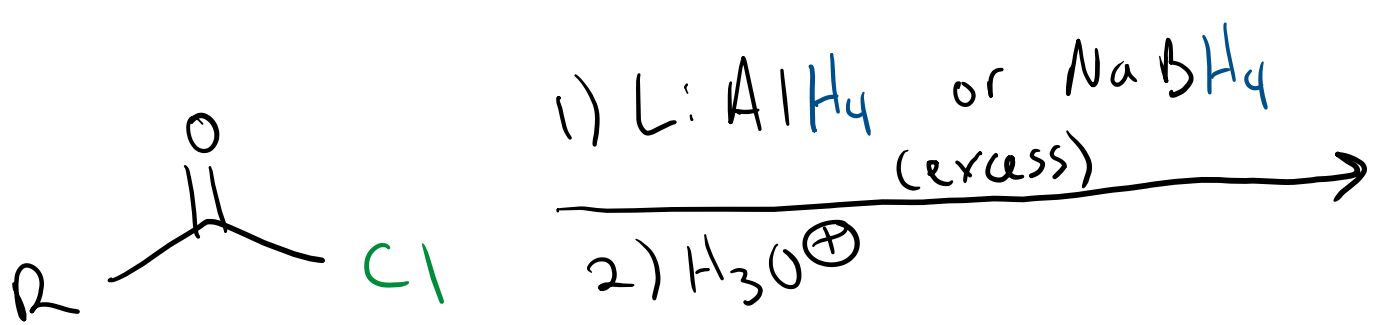
Esters

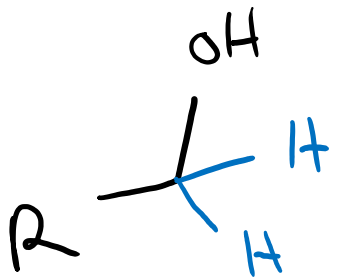
2/27/2023

Reactions of Acid Chlorides

With Reducing Agents:

Hydride transfer agents

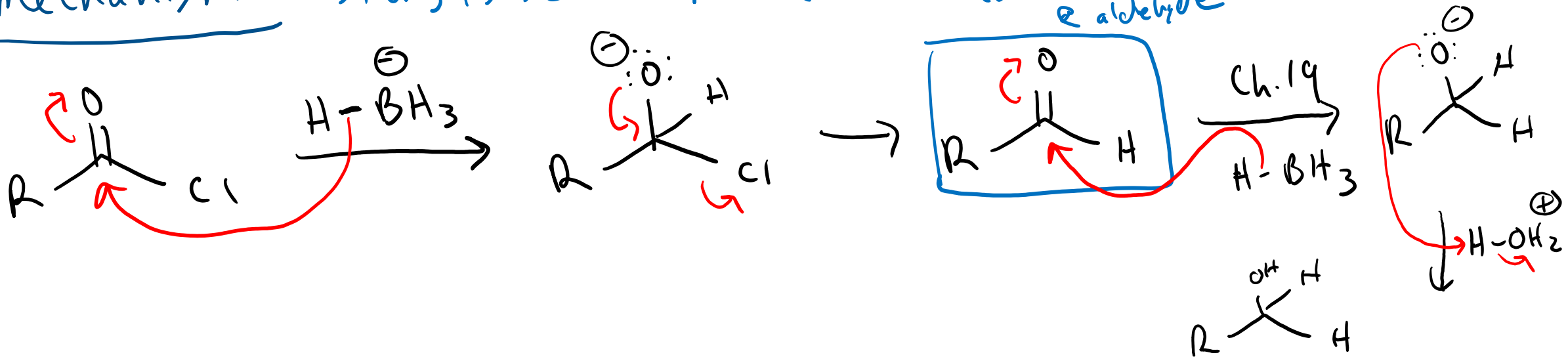




2 H's added (as w/ carboxylic acid)

mechanism: strong, basic nucleophile (anionic)

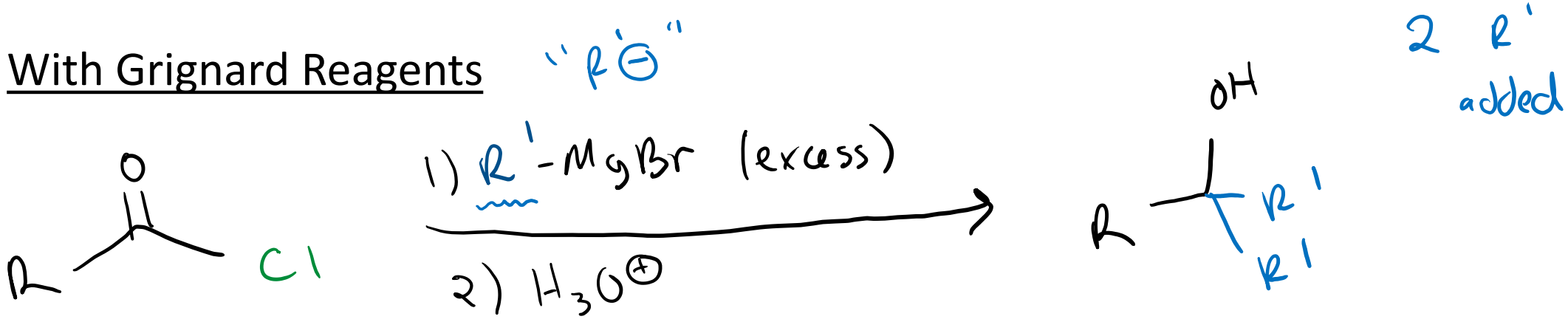
can't stop @ aldehyde



Reactions of Acid Chlorides

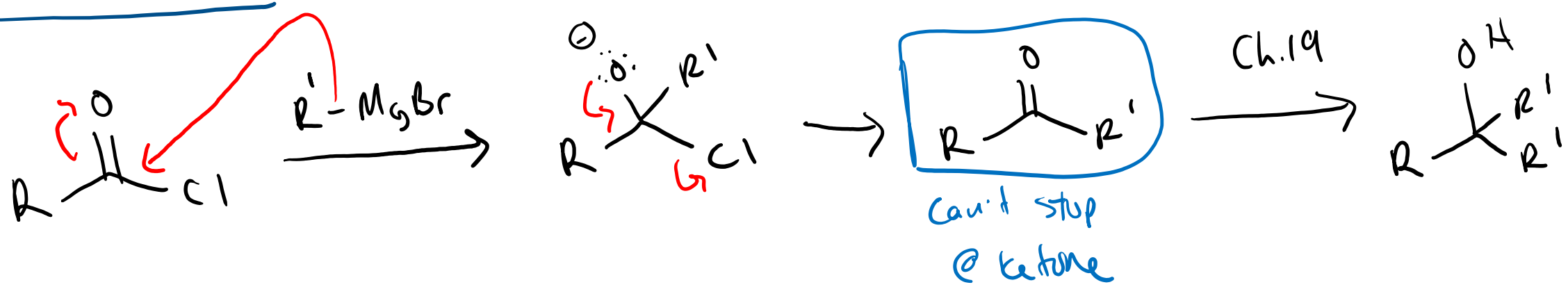
With Grignard Reagents

"$R^{\ominus}$"



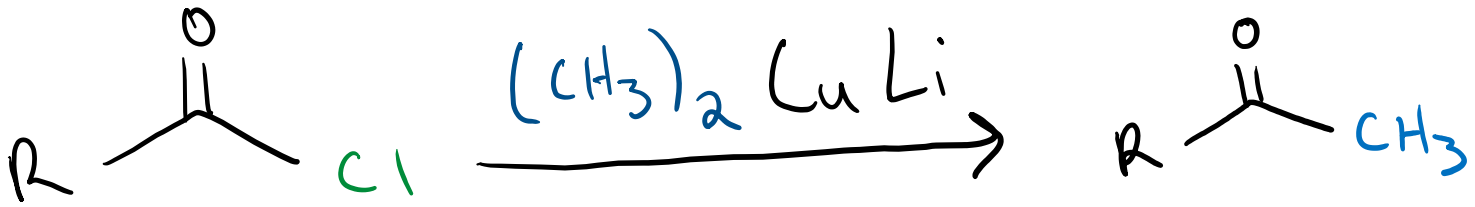
2 R' added

mechanism: acyl transfer, strong base (anion) nucleophile



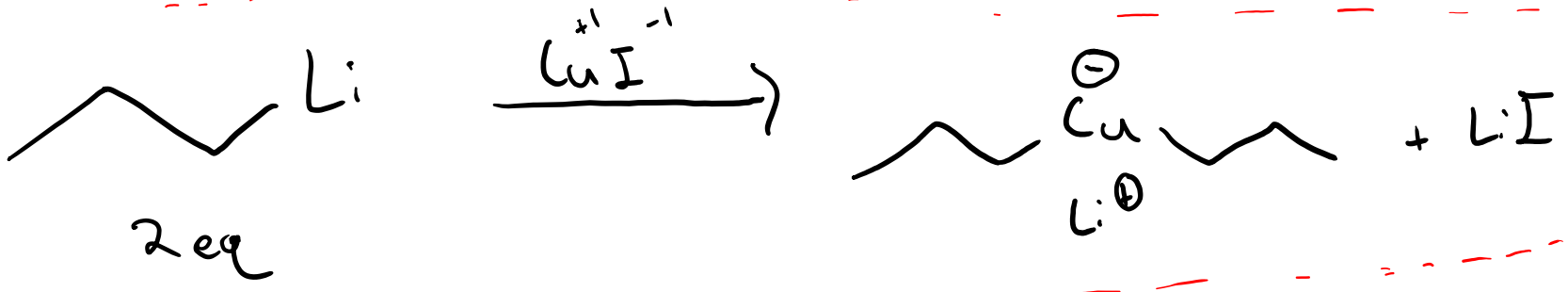
Reactions of Acid Chlorides

With Organocuprates ("Gilman Reagents"): R'_2CuLi - acts like "milder" Grignard / Alkyllithium



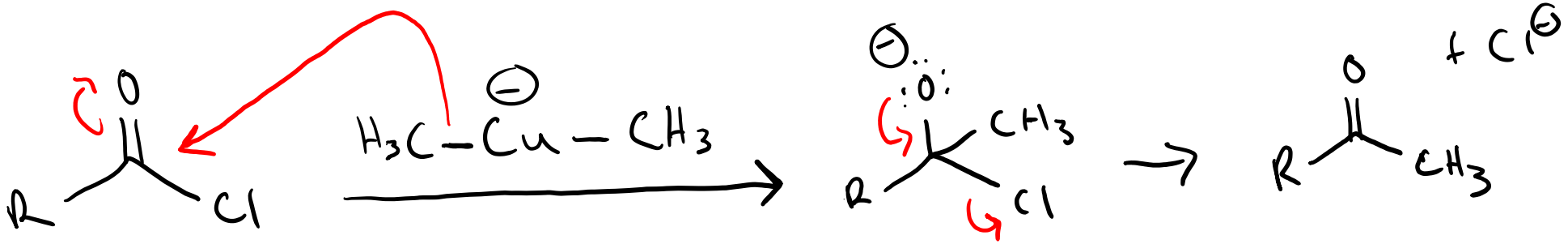
stops @ ketone!

making the organocuprate



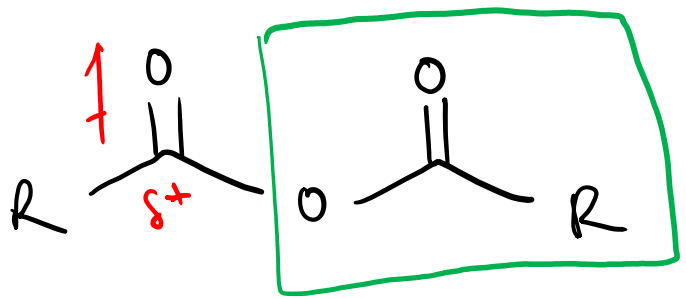
(strong, basic anionic)

acyl transfer mechanism:

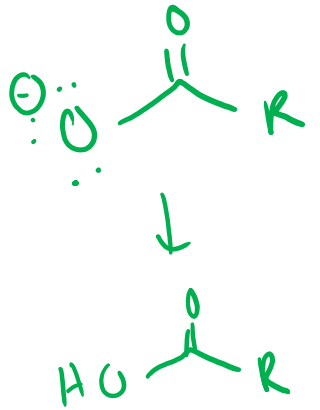


Anhydrides (20.9)

almost as $E^{\oplus}$ as acid chloride



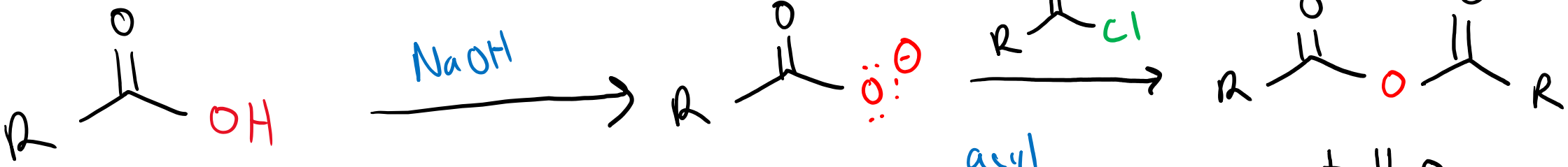
reacts like acid chloride



"pretty good" L.G.

pka ~5

Synthesis of Anhydrides:



proton transfer

acyl transfer

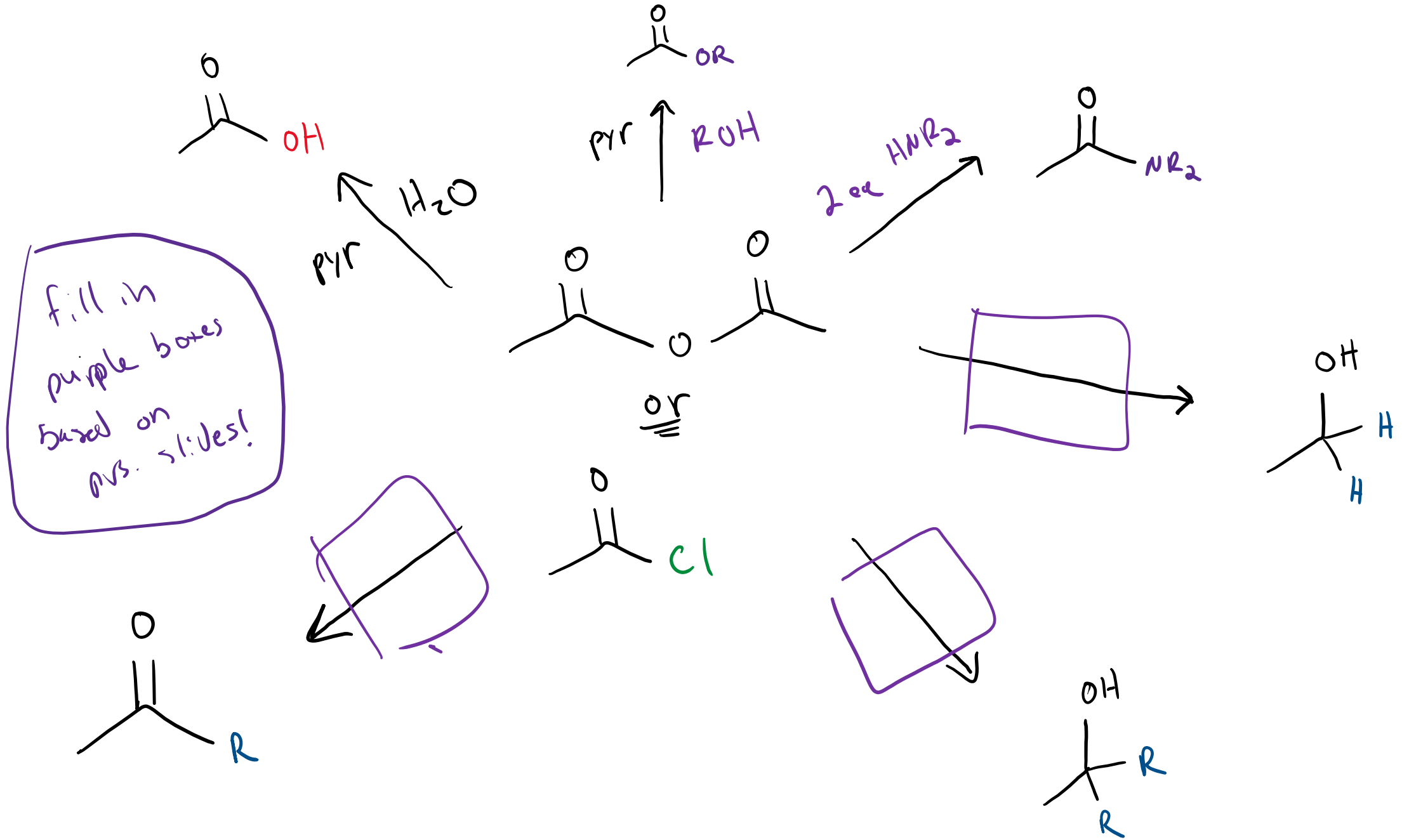
base (carbonyl) nucleophile

+ H_2O

+ $Na^{\oplus}$

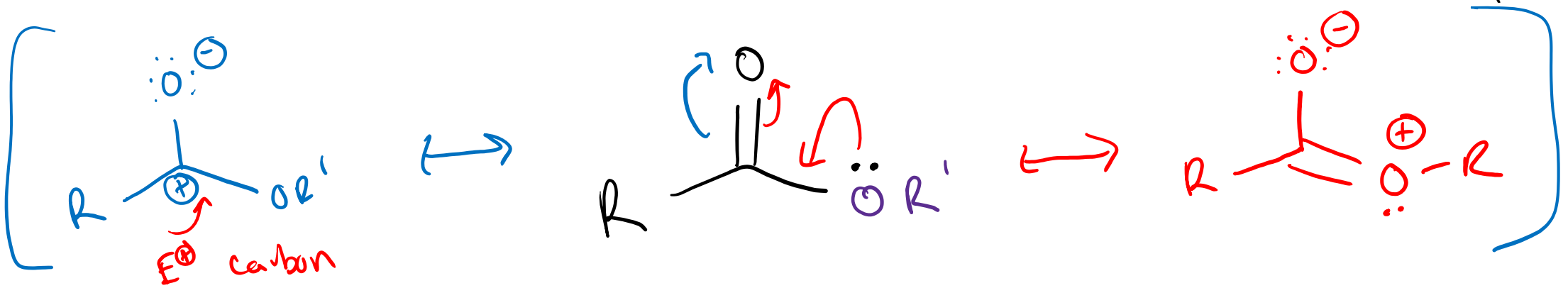
+ $Cl^{\ominus}$

Reactions of Anhydrides & Acid Chlorides: Recap

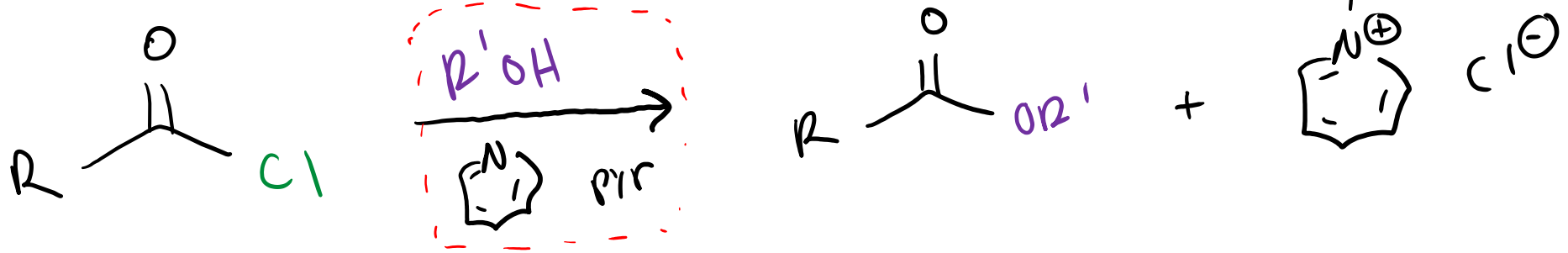


Esters

(20.10-11)



Synthesis of Esters:



mechanism:

acyl transfer

weak nuc

weak base

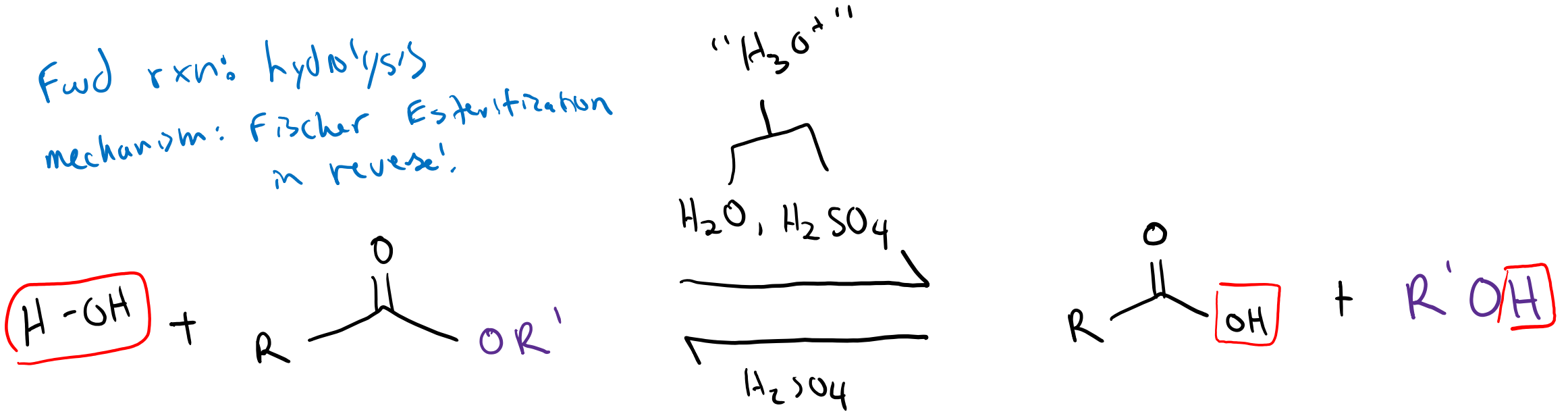
or Fischer Esterification

or S_N2 — See lecture #15

Hydrolysis of Esters: Acidic Conditions

Fwd rxn: hydrolysis

mechanism: Fischer Esterification in reverse!



(remove R'OH

use excess H_2O
(as solvent))

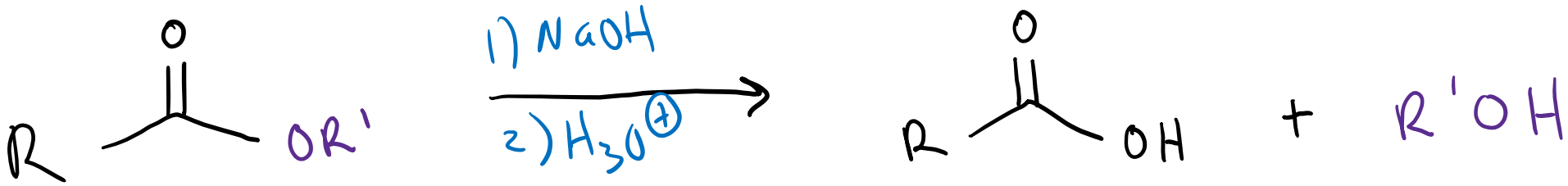
Reverse reaction:

Fischer Esterification

mechanism: acid-catalyzed acyl transfer

(remove H_2O, use excess ROH)

Hydrolysis of Esters: Basic Conditions



mechanism: