File:Dream Team Basketball 1992 Olympic Games Barcelona.jpg

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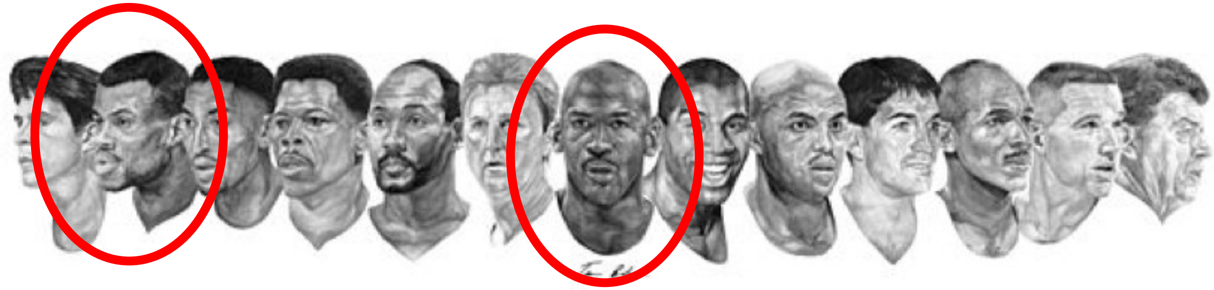
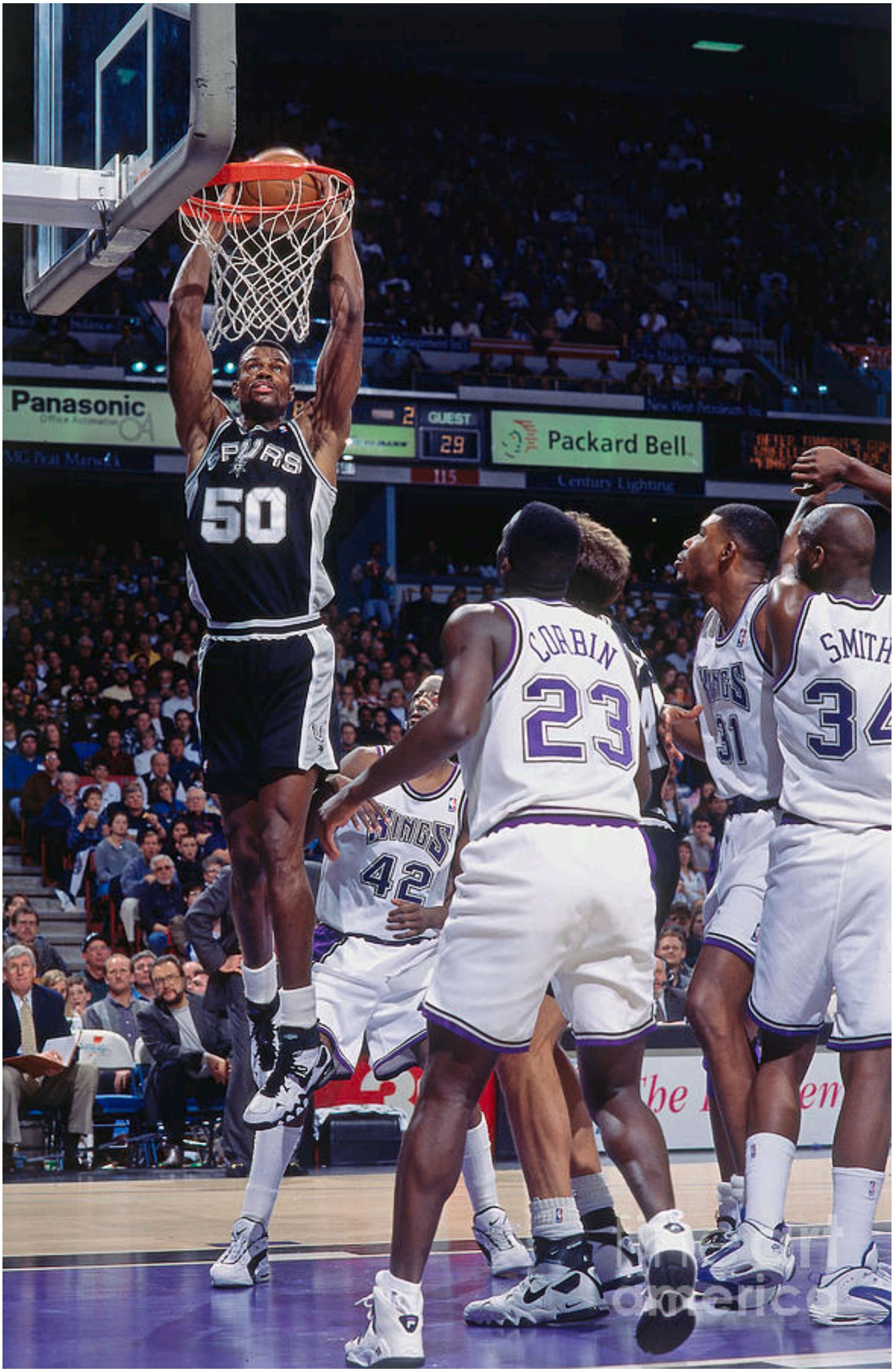


Michael

Robinson

Iverson


JORDAN
9
6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KINGS
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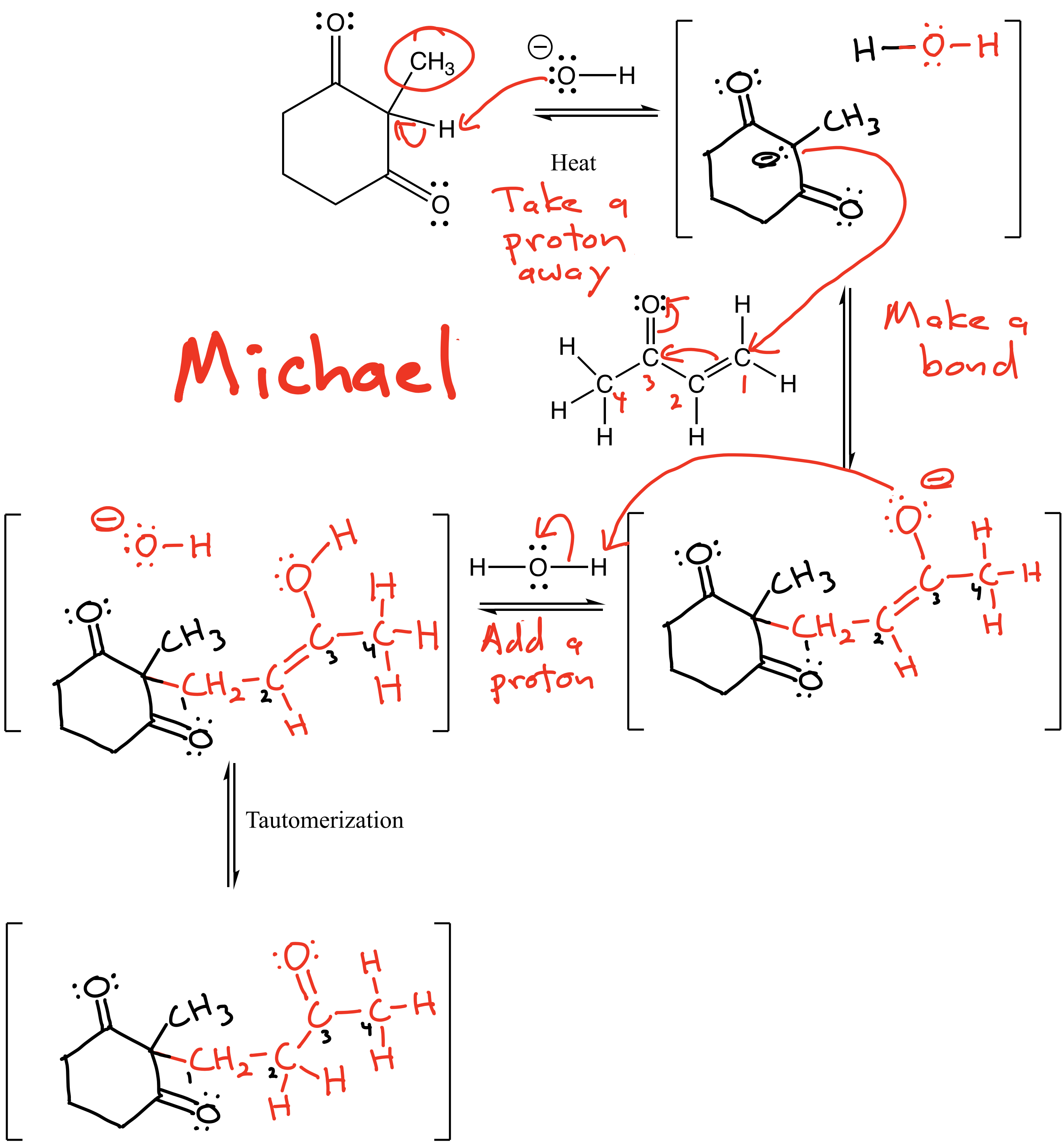
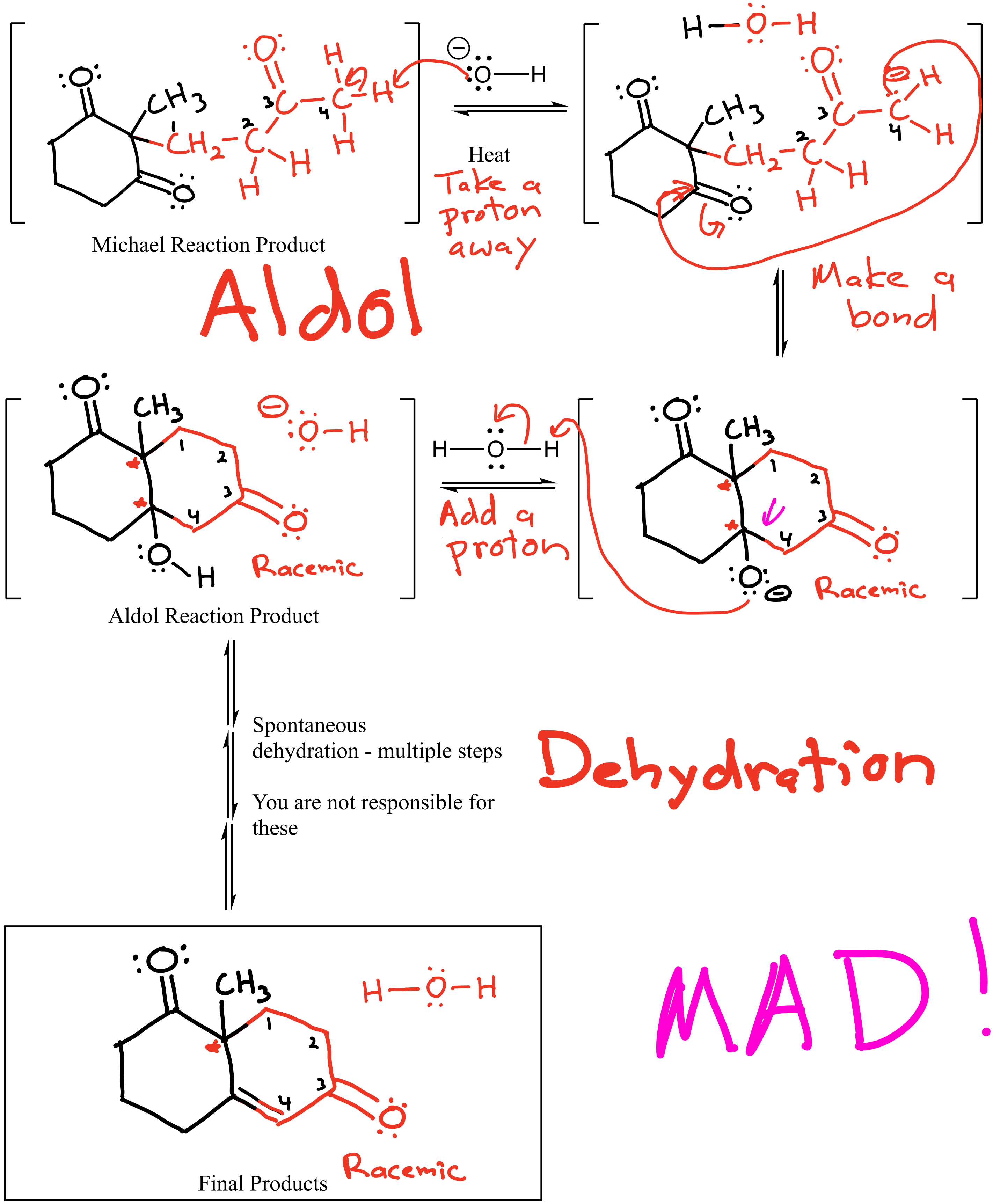
Robinson Annulation Part 1 - Michael Reaction Steps

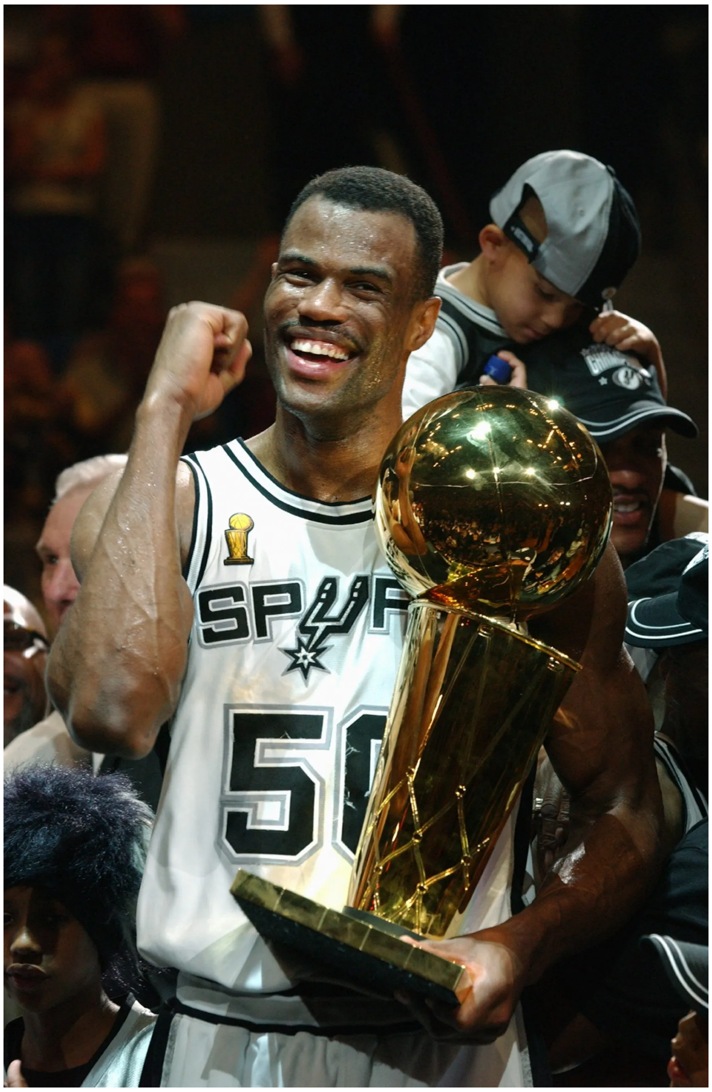


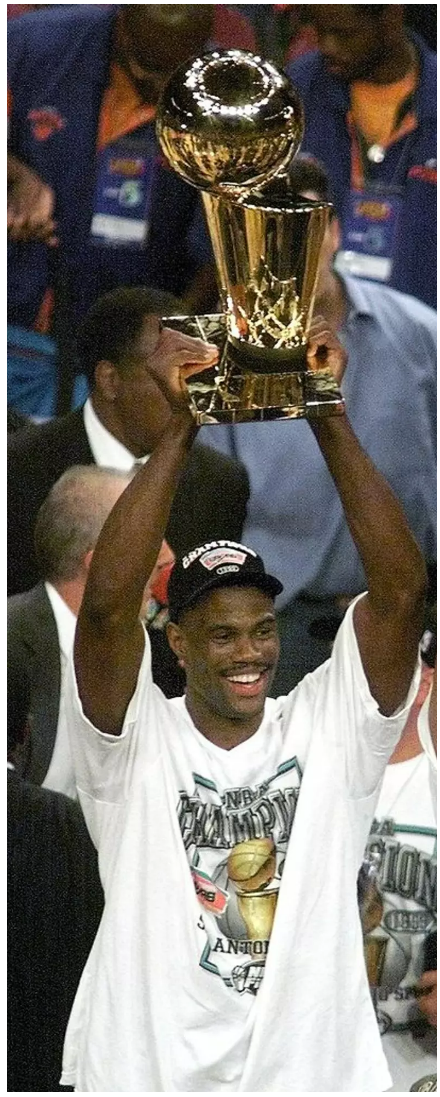
Michael Reaction Product

Robinson Annulation Part 2 - Aldol and Dehydration Steps



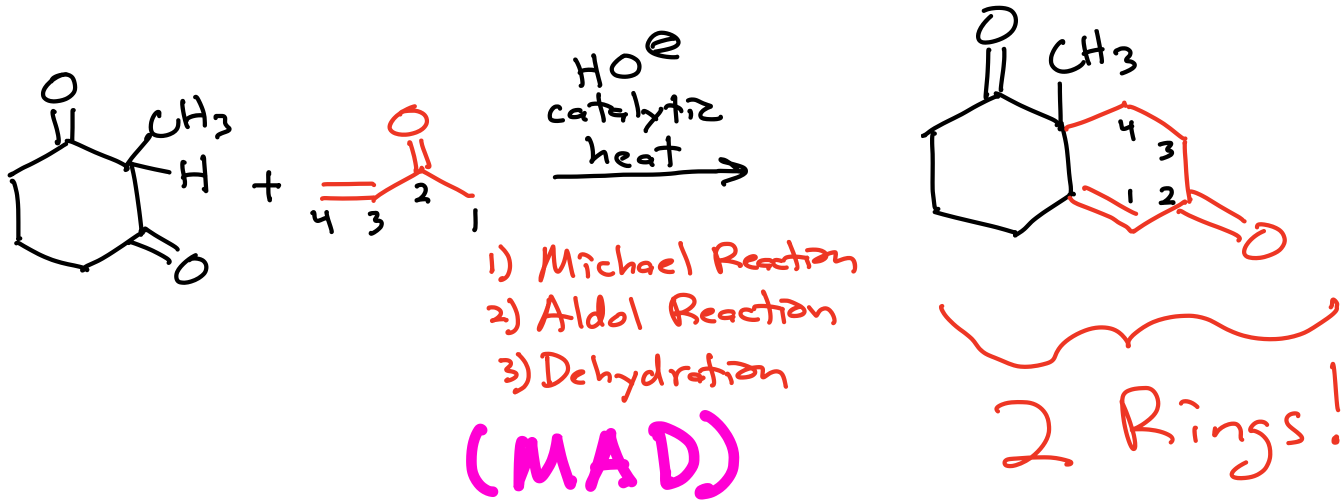

SPALDING
IVERSON
3
20





David Robinson earned 2 NBA Championship Rings!

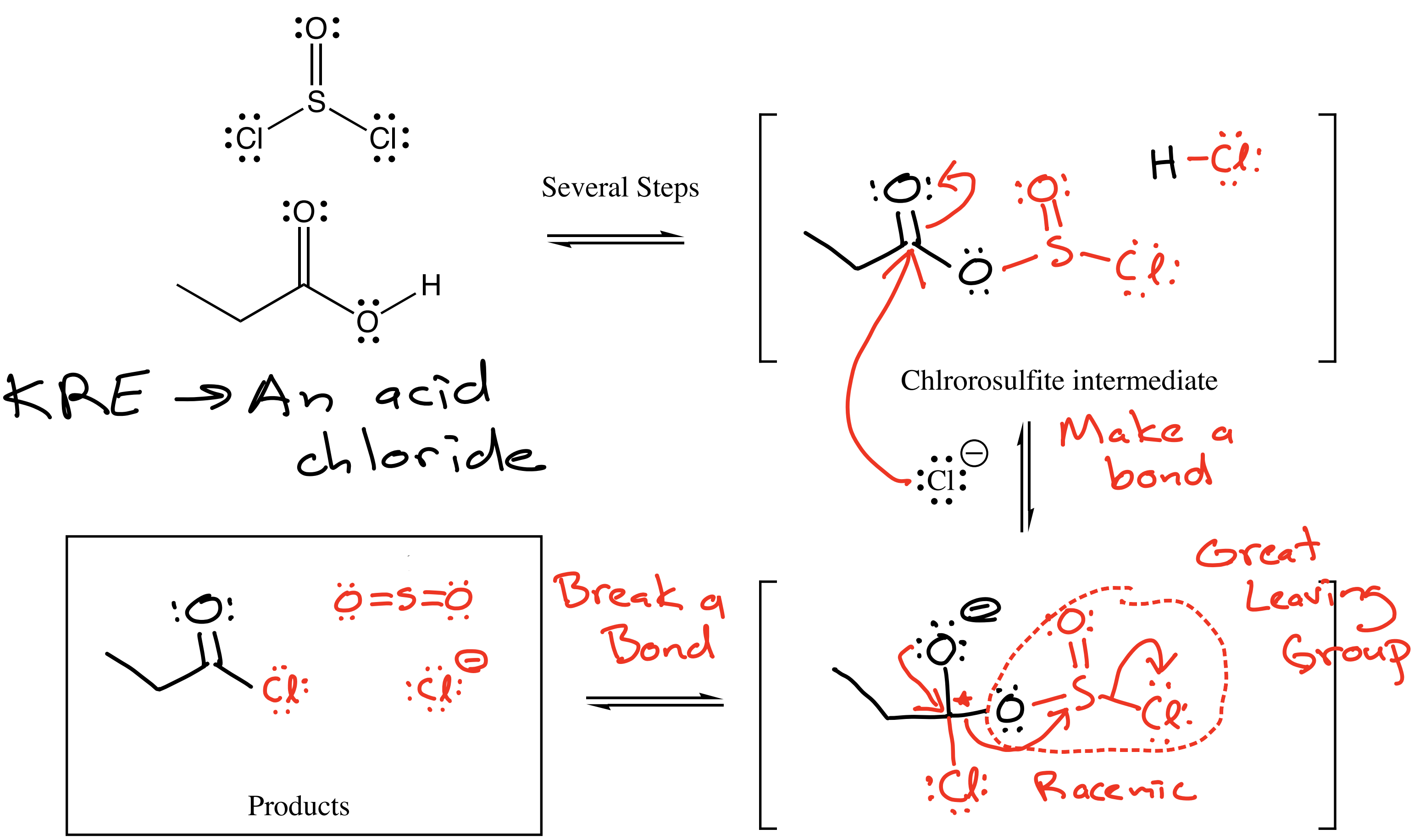
This is the only Robinson annulation reaction you will see on exams



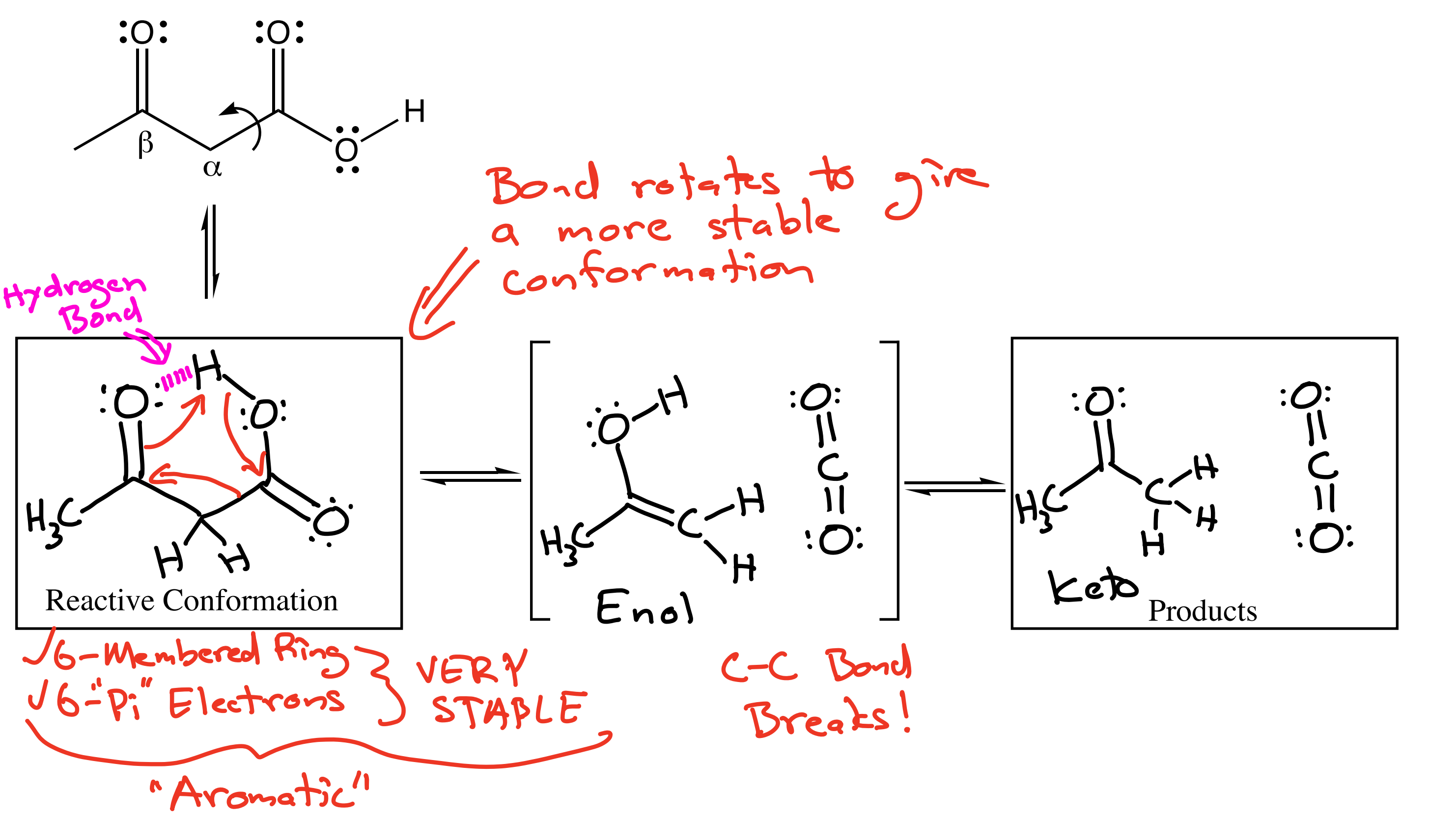
Note how the only Robinson annulation you will see in this class creates a product with

2 Rings!

Reaction with Thionyl Chloride



Decarboxylation of a β-Keto Acid

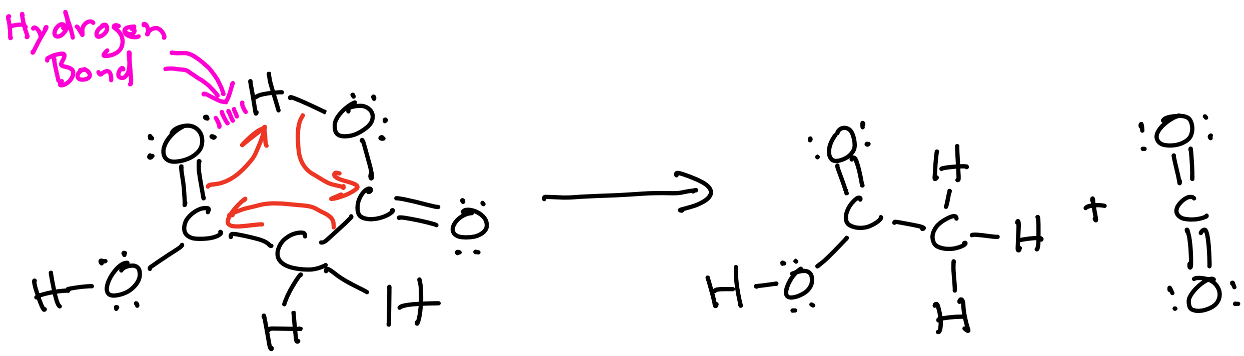


KRE → Ketone and CO_2

Time capsule →

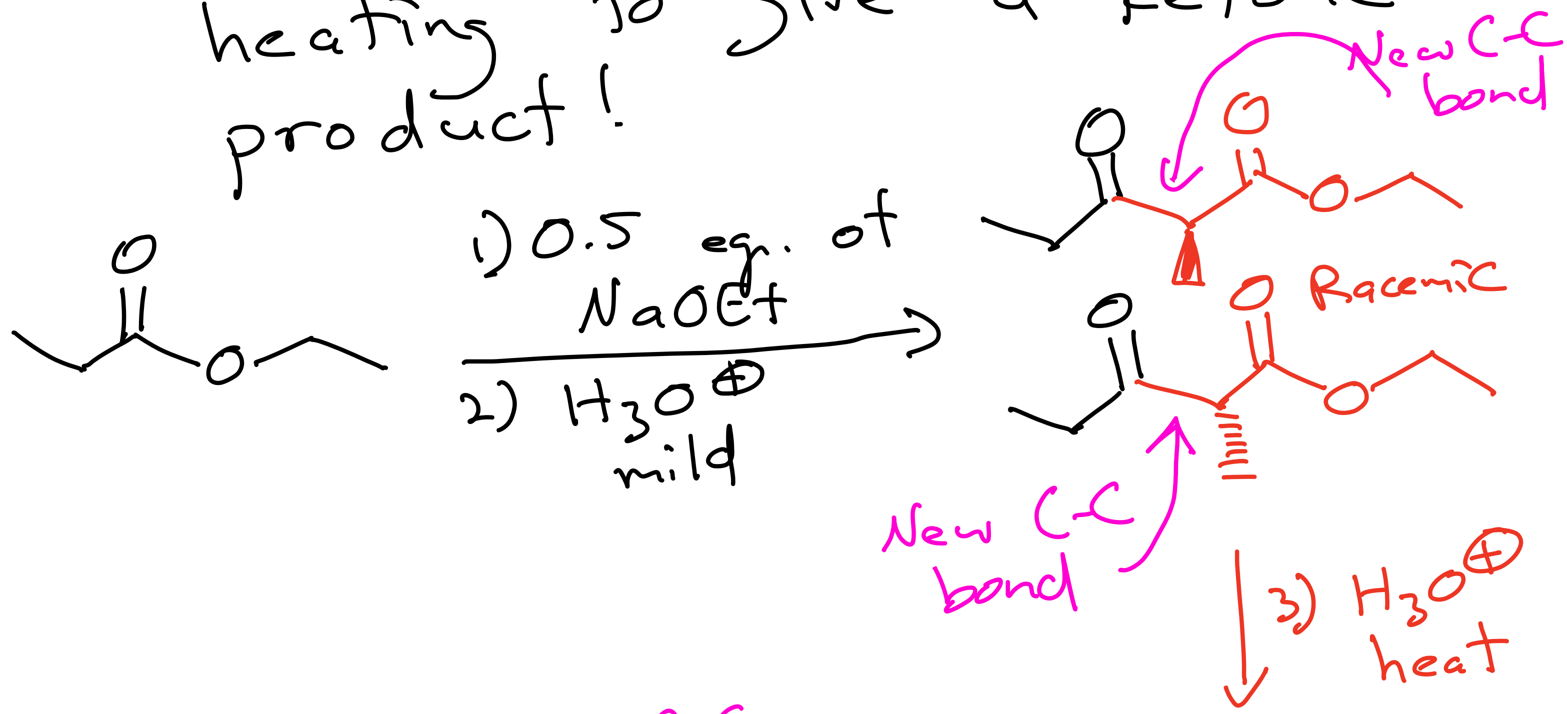
Important for products of the Claisen reaction

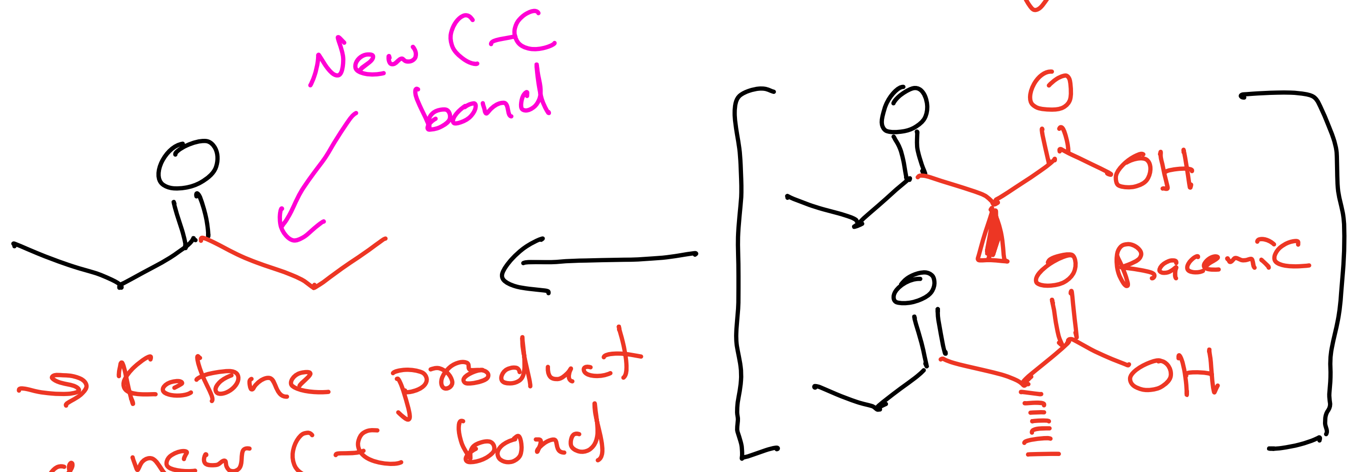
This also works with β-diacids



Decarboxylation of Claisen reaction products

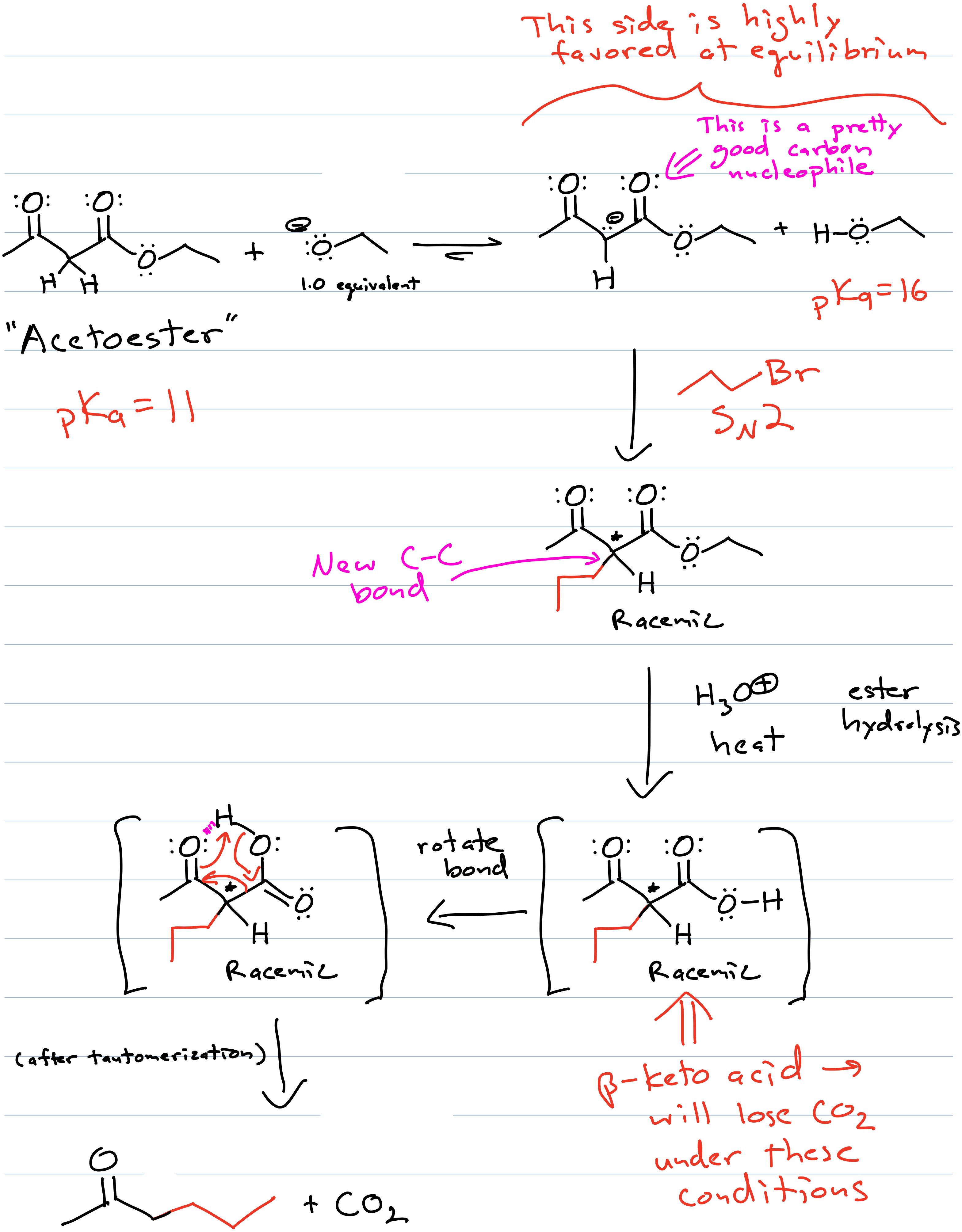
You can hydrolyze the ester of a Claisen product to give the β-keto acid, that will decarboxylate upon heating to give a ketone product!



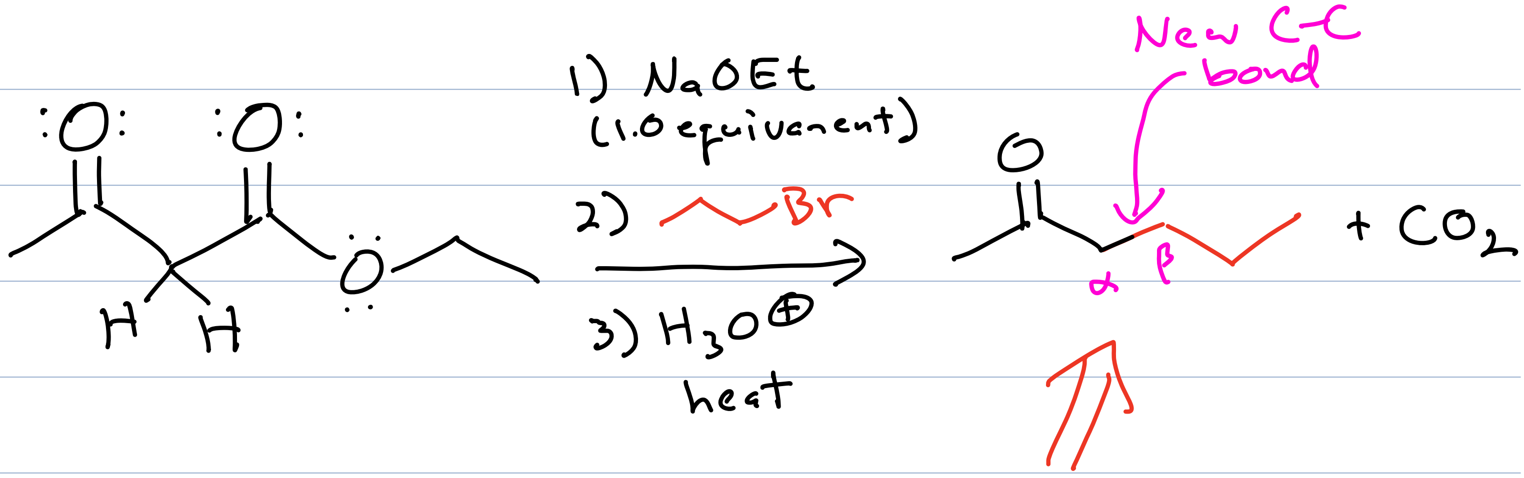


A β-keto acid!

KRE → Ketone product with a new C-C bond at C=O carbon


This side is highly favored at equilibrium
This is a pretty good carbon nucleophile
"Acetoester"
pKa = 11
1.0 equivalent
pKa = 16
Br
SN2
New C–C bond
Racemic
H3O⊕
heat
ester hydrolysis
rotate bond
Racemic
Racemic
β-keto acid → will lose CO2 under these conditions
(after tautomerization)
+ CO2

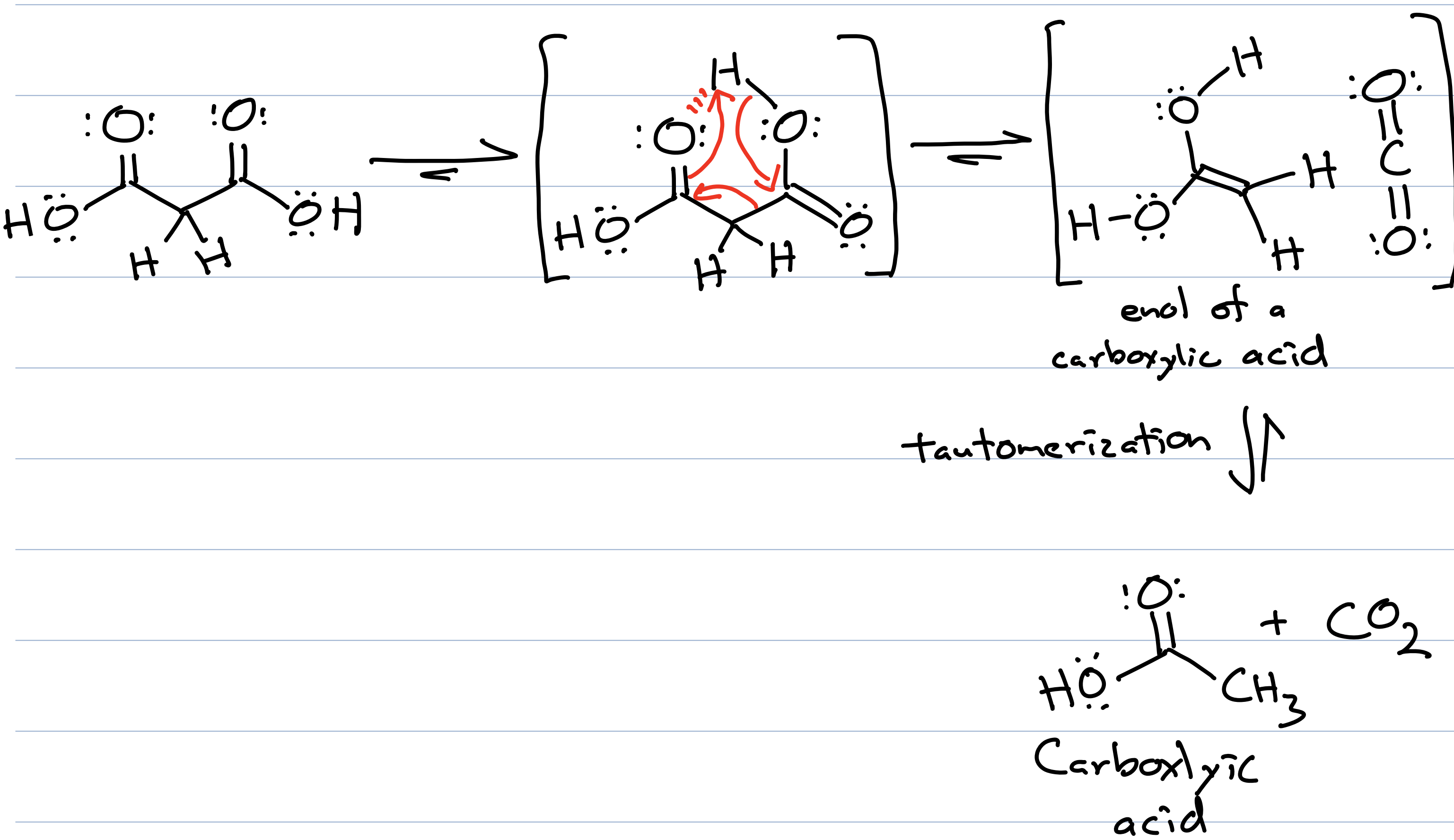
Acetoester Synthesis Summary



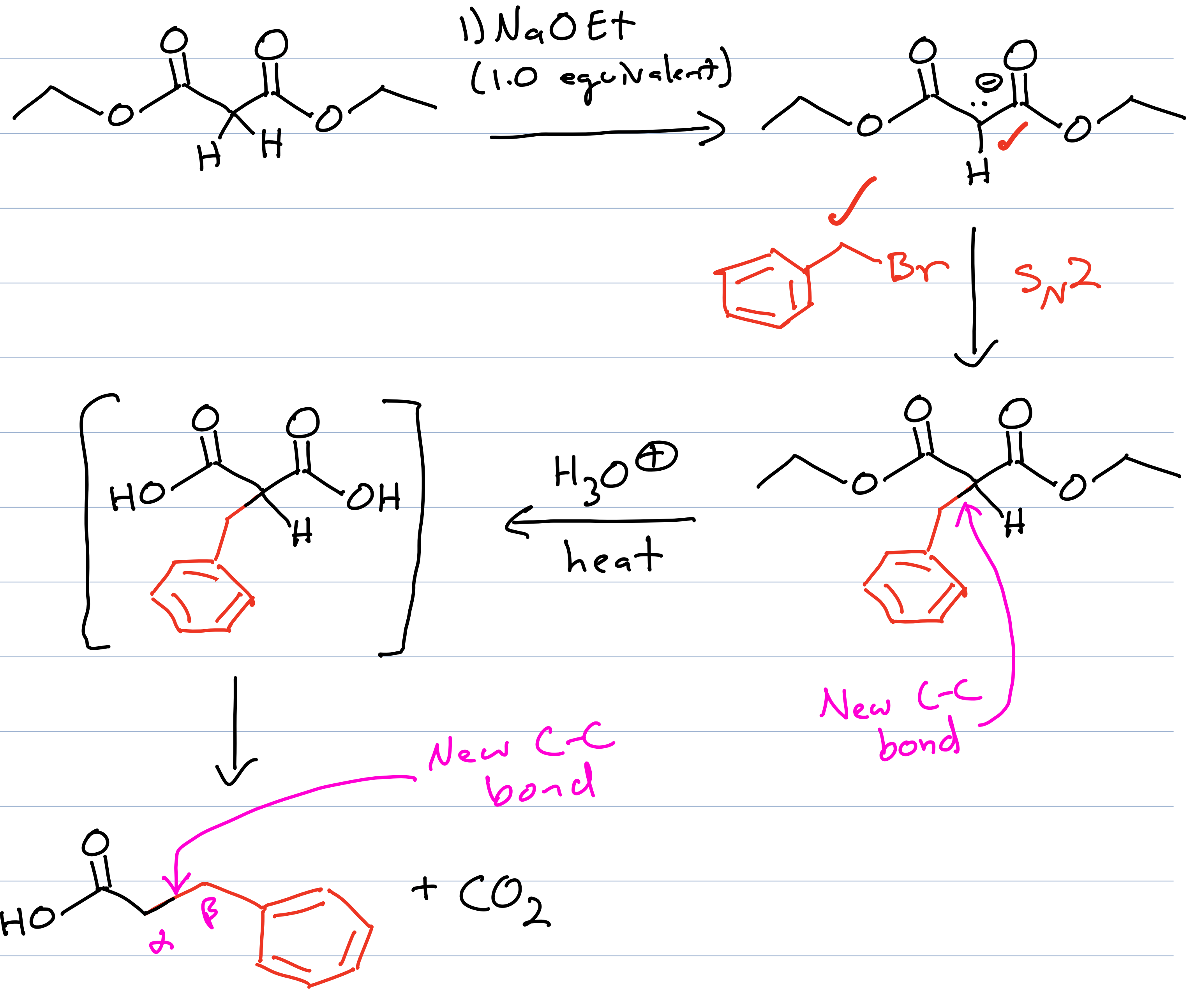
KRE – A methyl ketone with a new C-C bond between the α and β carbon atoms

Malonic Ester Synthesis

Malonic acid decarboxylates with heat to give a carboxylic acid and CO_2



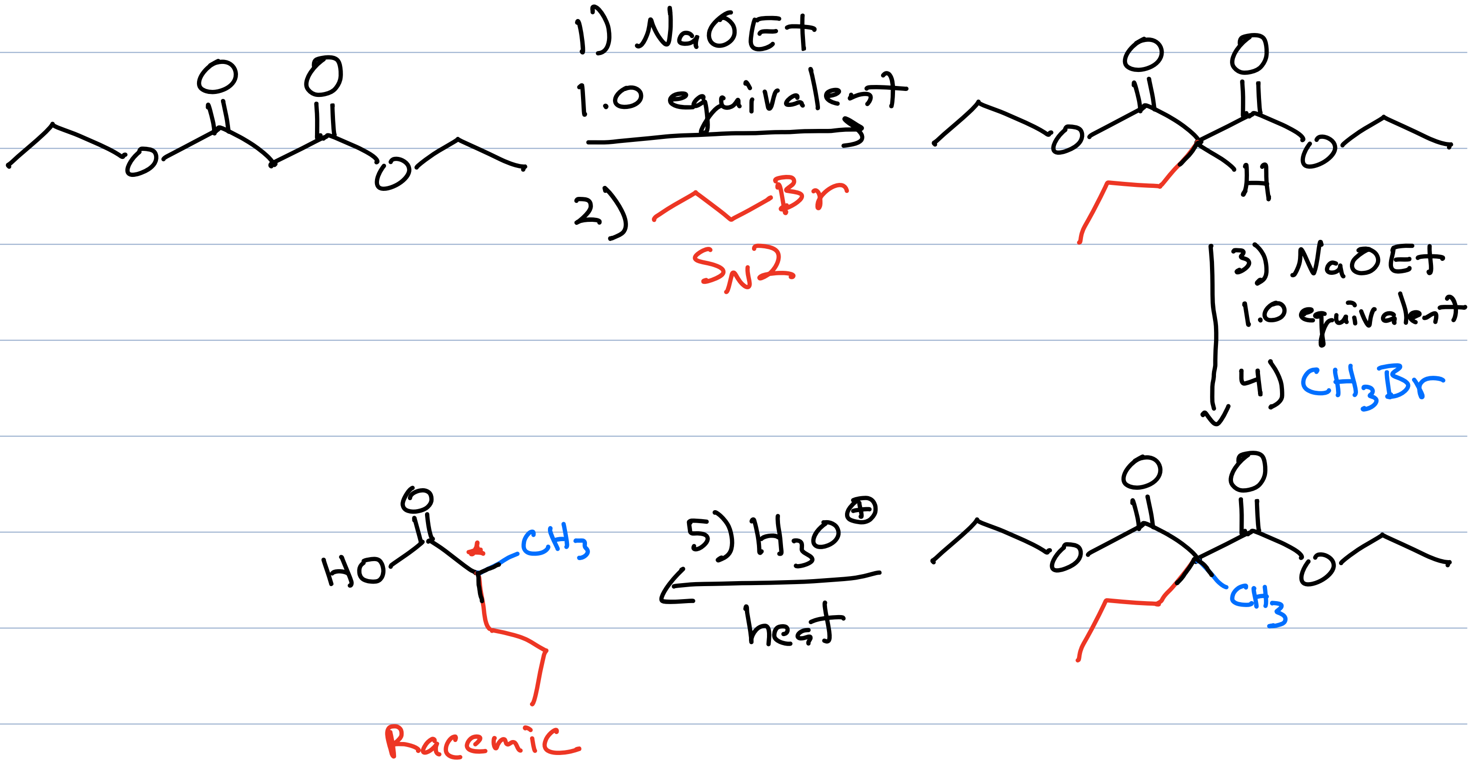
We start with diethyl malonate



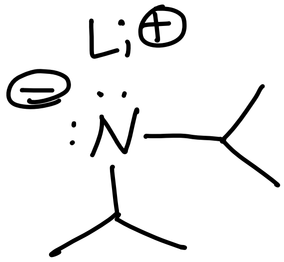
KRE → A carboxylic acid with a new C-C bond between the α and β carbon atoms

CH_3Br
CH_3I
These are so small they can react with enolates that are already substituted — applies to acetoester and malonic ester syntheses

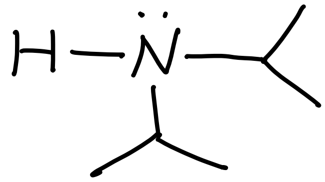
Any group that is larger cannot react due to steric strain



The wicked strong base that changes things



NOT a nucleophile

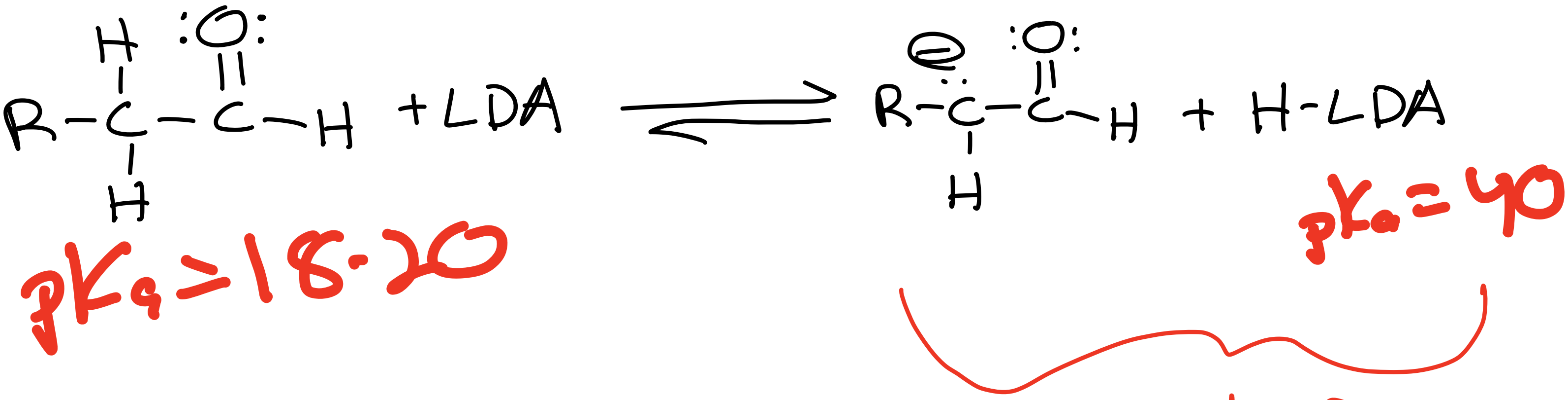


Lithium Diisopropylamide $pK_a \cong 40$

"LDA" "H-LDA"

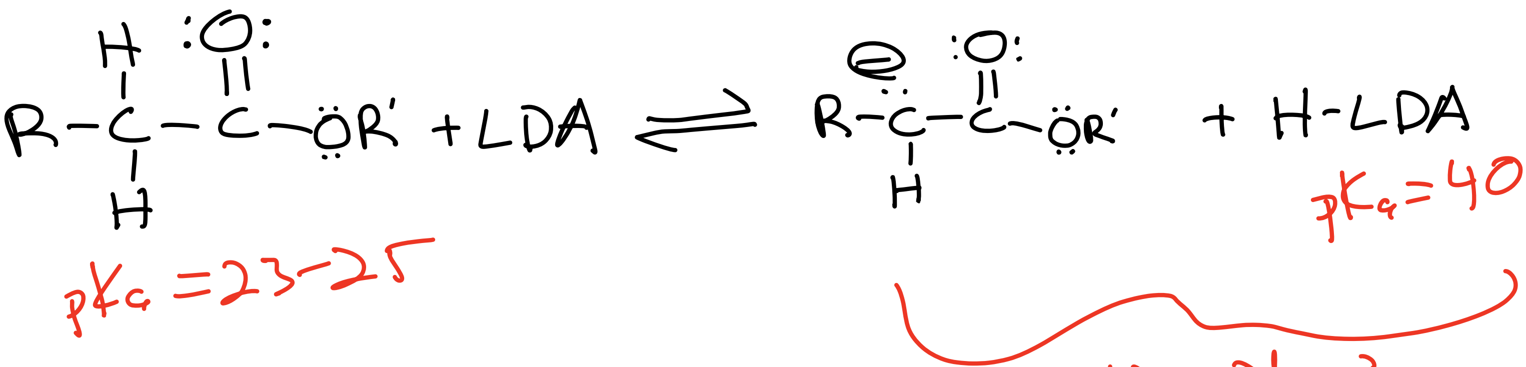
LDA will quantitatively deprotonate aldehydes, ketones and esters to make enolates!

Aldehydes



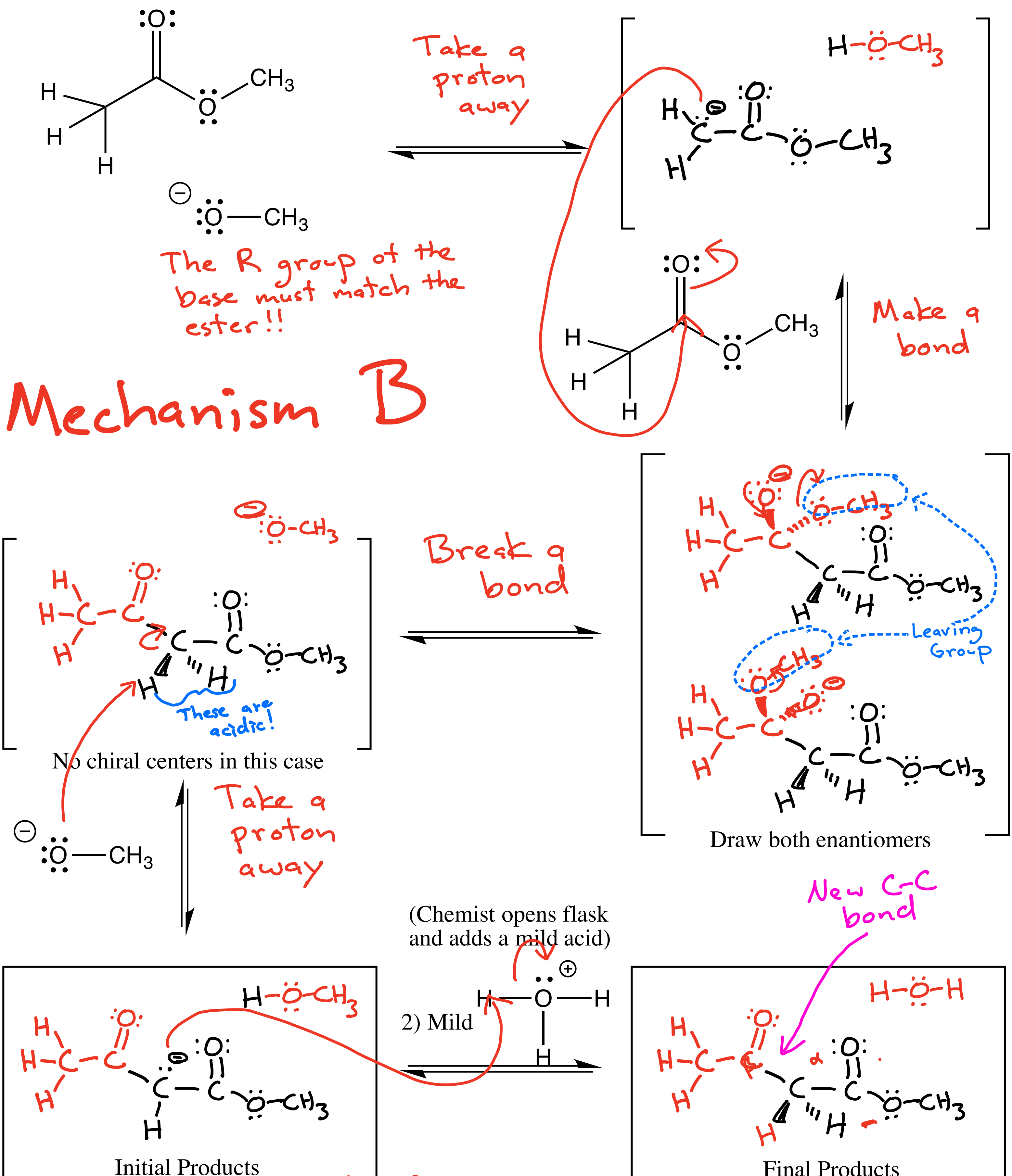
This side is favored by ~10^{20}!

Esters



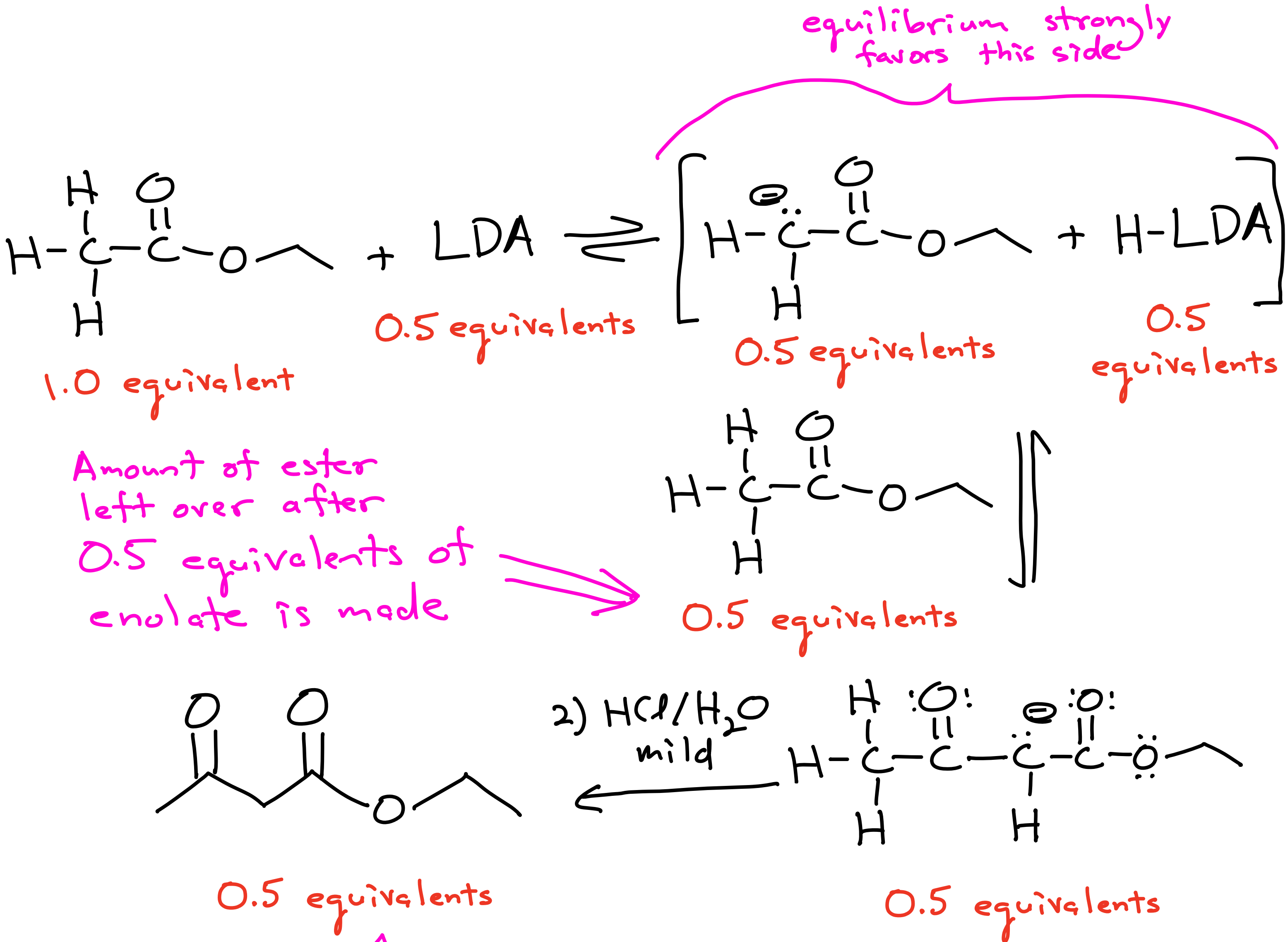
This side is favored by ~10^{15}!

Claisen Condensation → "Aldol with Esters"



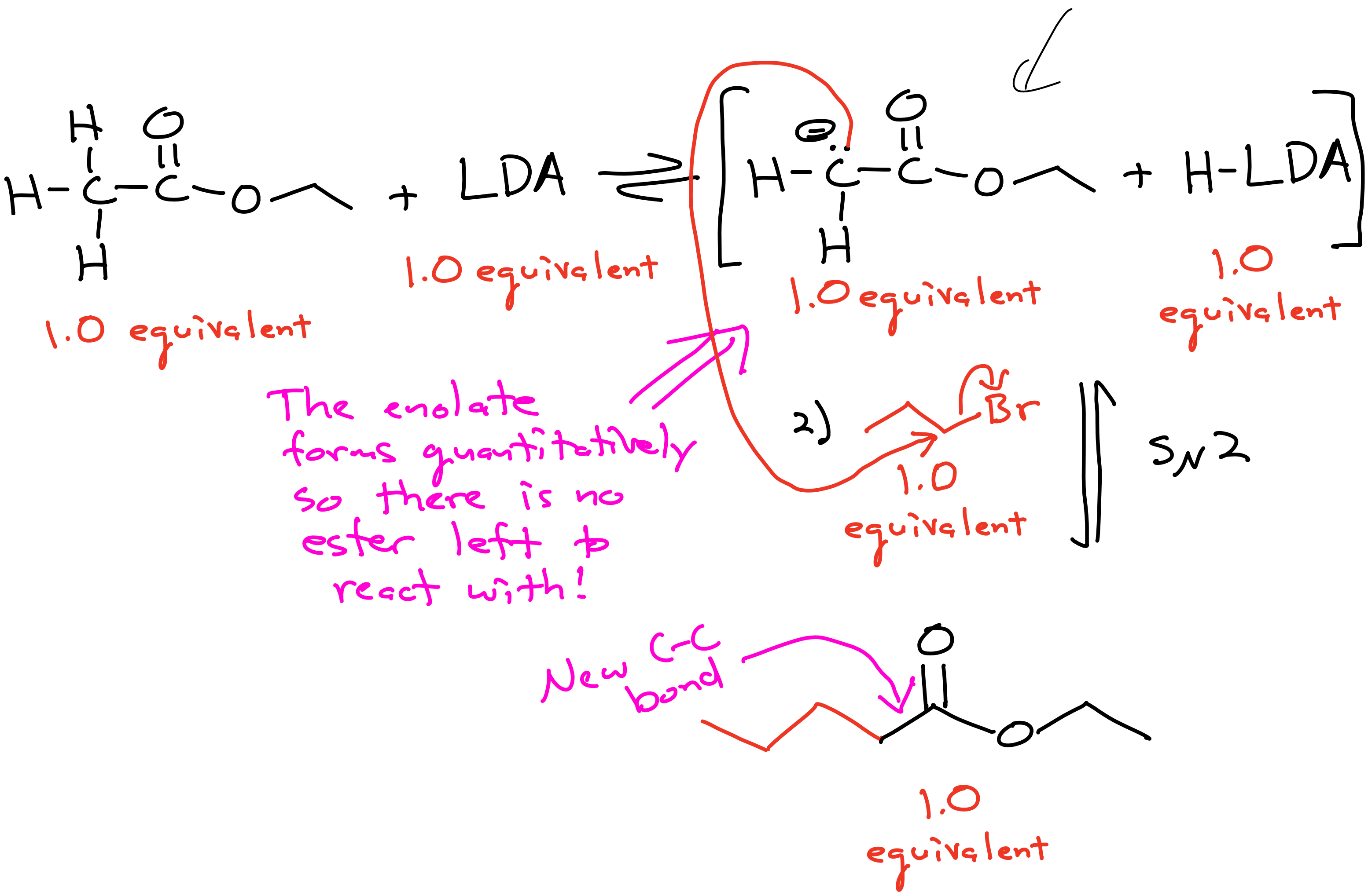
This is a much more stable anion compared to ⊖OCH3, providing a strong driving force (motive) for the Claisen condensation reaction

What if we use 0.5 equivalents of LDA with an ester?



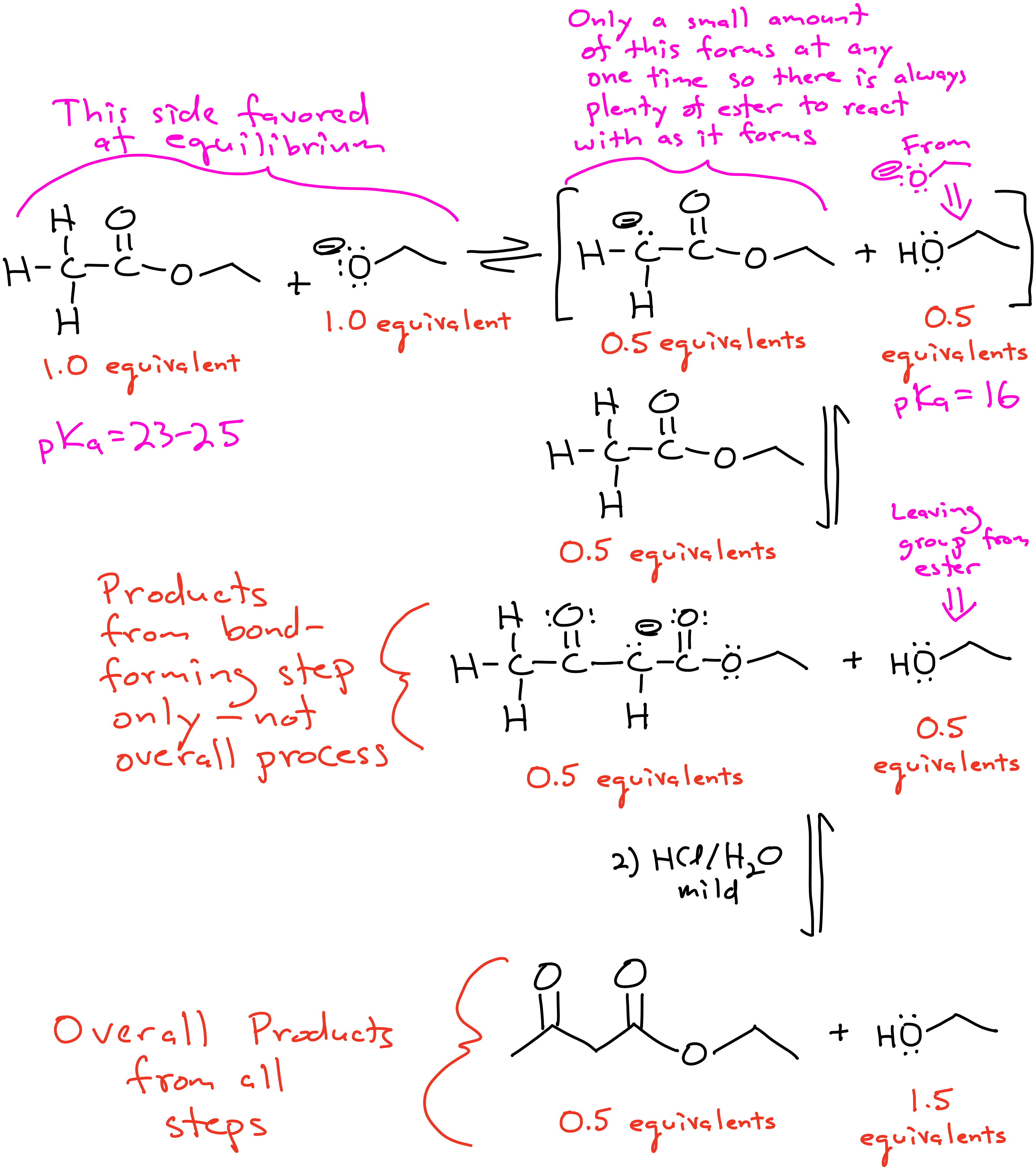
(There are 2 ester molecules used for each product molecule so there can only be half the number of product molecules compared to starting ester molecules)

What if we use 1.0 equivalent of LDA with an ester?

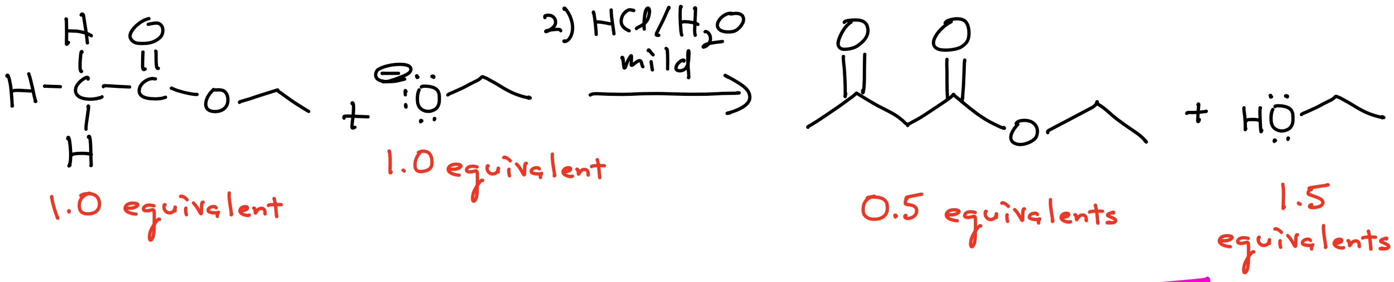


All of the starting ester molecules end up as a the same number of product molecules with a new C-C bond!

What if we use 1.0 equivalent of ⊖:Ö⁀ with an ester?



Overall Reaction



0.5 equivalents comes from first step, formation of the enolate

0.5 equivalents comes from second step, loss of $^{\ominus}$:Ö⌒ leaving group from ester (see mechanism)

0.5 equivalents is left over from original $^{\ominus}$:Ö⌒ that was not used