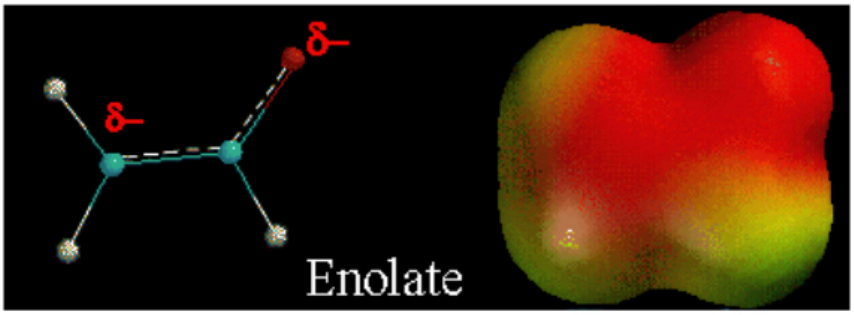
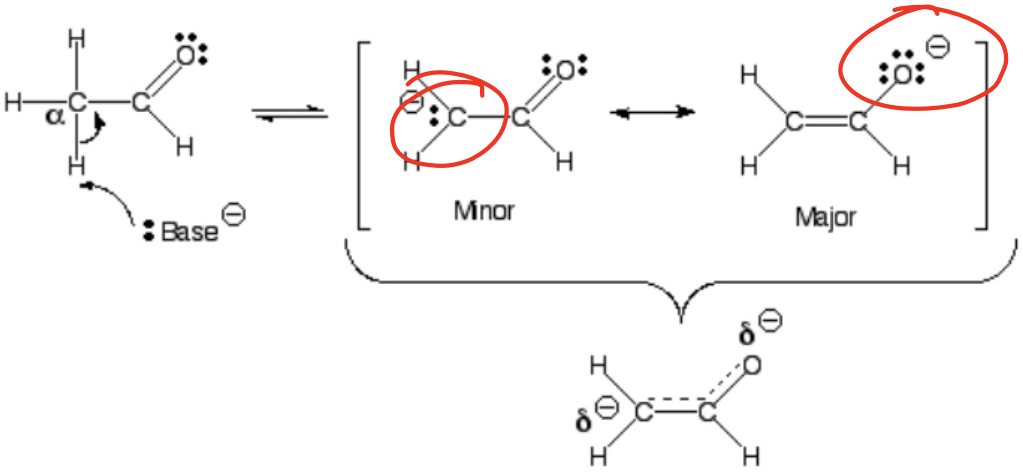

Search "moo deng"
@MsMojo
Subscribe
Top 10 Stars Who Adopted Their Animal Co-Stars
Moo Deng Being Absolutely Adorable
mojo

Enolates as nucleophiles



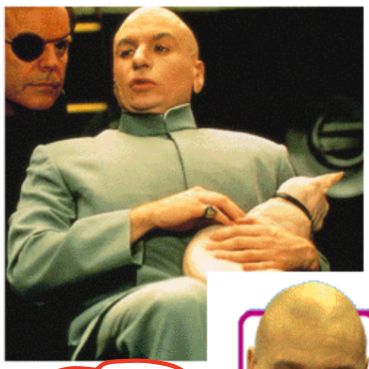


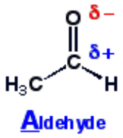
A) Enolates are resonance stabilized, with a partial negative charge on carbon and oxygen.

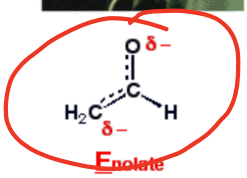
B) Enolates are nucleophiles, so they could react at either the carbon atom or oxygen atom. The partial negative charges give them the **opportunity** to react at either the carbon or oxygen.

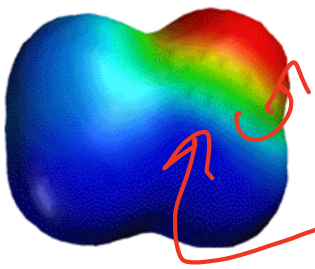
C) Reaction at the carbon atom gives the final product a C=O bond, while reaction at the oxygen atom gives the final product a C=C bond. However, C=O bonds are stronger than C=C bonds, so the **motive** is to react at the carbon atom with most electrophiles.

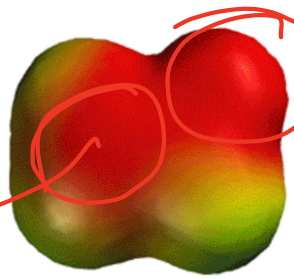
Once Again, A Movie Ripping Off Chemistry











Here are the keys to understanding mechanisms in 320N!!

1) There are basically four different mechanisms elements that make up the steps of carbonyl reactions.

A) Make a bond between a nucleophile and an electrophile
B) Break a bond to give stable molecules or ions
C) Add a proton
D) Take a proton away

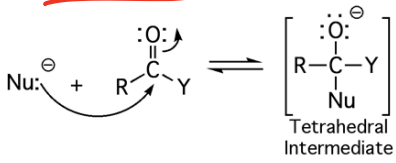
2) These same four mechanism elements describe most of the other mechanisms you have/will learn!!! (Yes, organic chemistry really is this simple if you look at it this way!!)

There are basically four different mechanisms that describe the vast majority of carbonyl reactions and these mechanisms are different combinations/ordering of the four mechanism elements listed above. In this class, I have termed them "Mechanism A", "Mechanism B", "Mechanism C", and "Mechanism D". They all involve a nucleophile attacking the partially positively charged carbon atom of the carbonyl to create a tetrahedral intermediate. Different reaction mechanisms are distinguished by the timing of protonation of the oxygen atom as well as the presence or absence of a leaving group attached to the carbonyl.

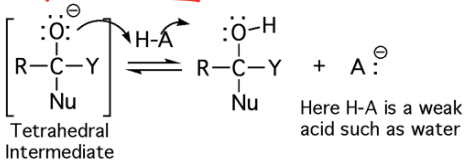
Four Mechanisms for the Reaction of Nucleophiles with Carbonyl Compounds

MECHANISM A: Reaction with a Strong Nucleophile

Step 1 Make a new bond between a nucleophile and electrophile

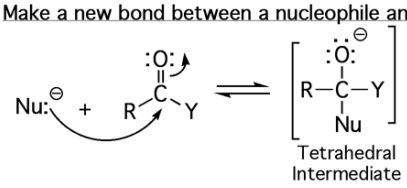


Step 2 Add a proton

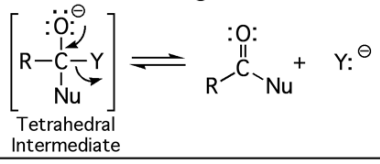


MECHANISM B: Reaction with a Strong Nucleophile When "Y" is a Good Leaving Group (-OR, -Cl, etc.).

Step 1 Make a new bond between a nucleophile and electrophile

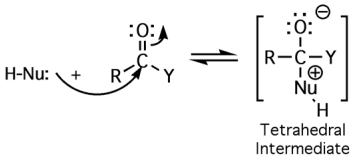


Step 2 Break a bond to give stable molecules or ions

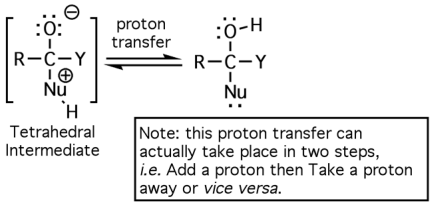


MECHANISM C: Reaction with a Weak Nucleophile

Step 1 Make a new bond between a nucleophile and electrophile

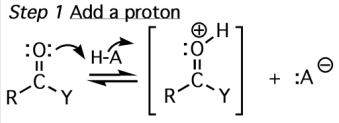


Step 2 Add a proton and Take a proton away

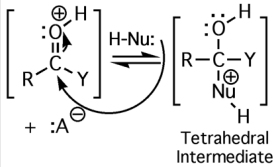


MECHANISM D: Reaction with a Weak Nucleophile in the Presence of Acid (H-A)

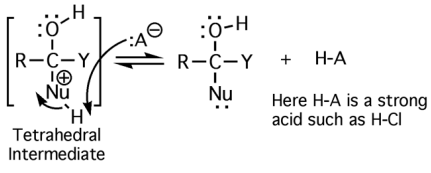
Step 1 Add a proton



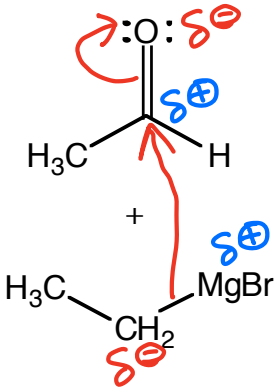
Step 2 Make a new bond between a nucleophile and electrophile



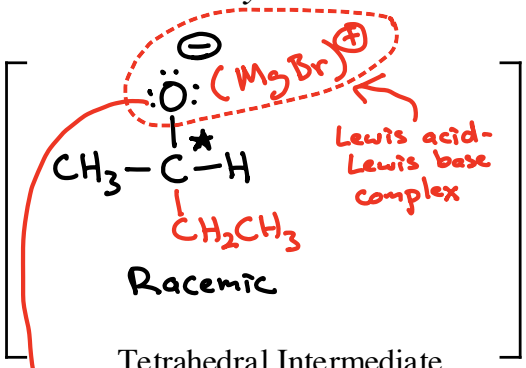
Step 3 Take a proton away



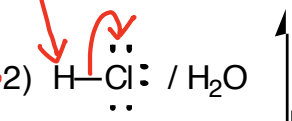
Grignard Reagent Reacting with an Aldehyde or Ketone



Make a bond



Chemist opens the flask

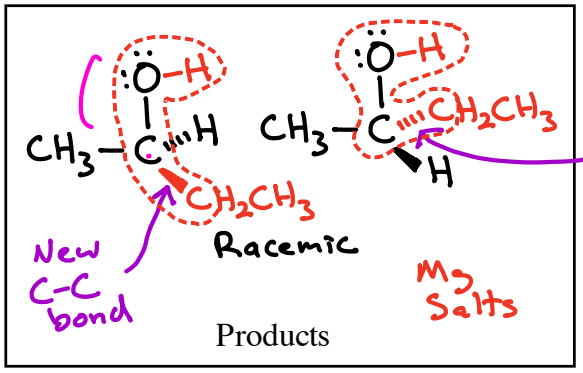


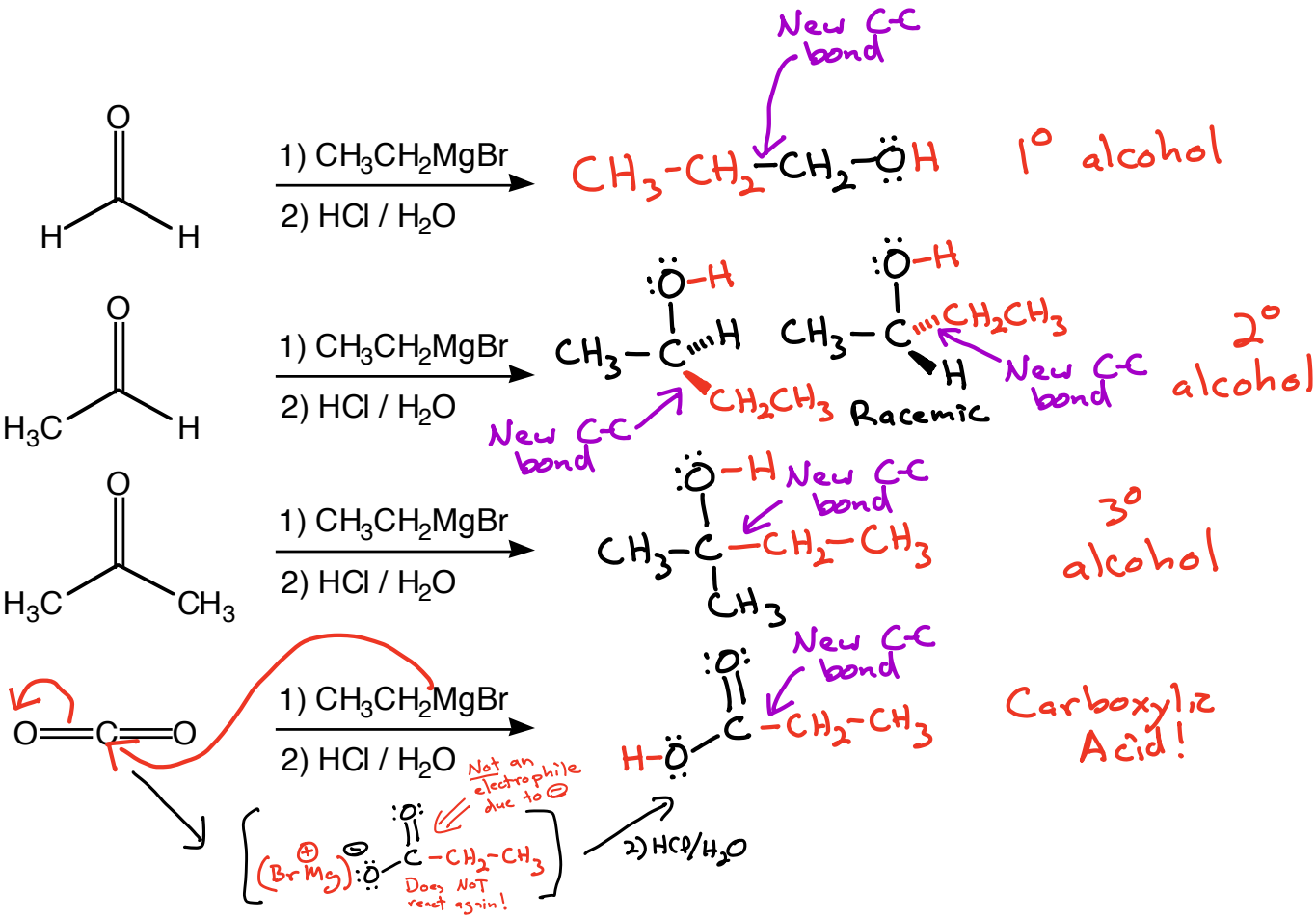
Add a proton

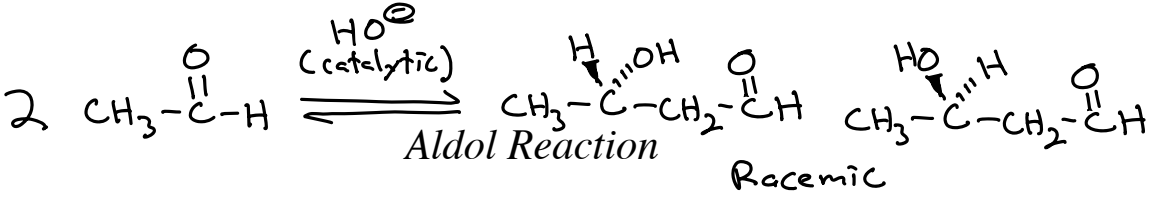
Mechanism A

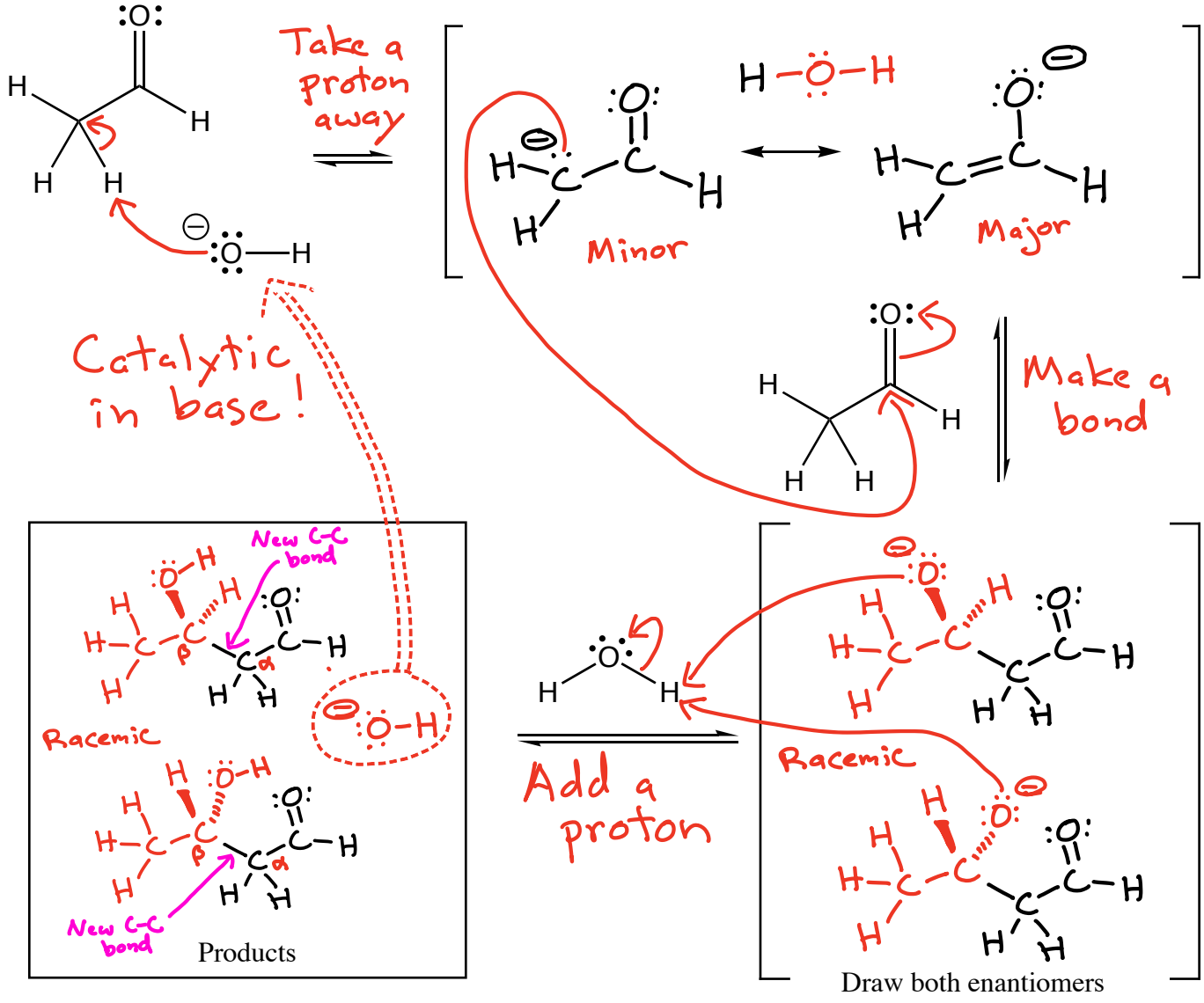
Key Recognition Element (KRE):

-OH group attached the same C atom as a new C-C bond









KRE → β-hydroxy aldehyde with a new C-C bond between the aldehyde α and β carbons

Mechanism A

Here are the keys to understanding mechanisms in 320N!!

1) There are basically four different mechanisms elements that make up the steps of carbonyl reactions.

A) Make a bond between a nucleophile and an electrophile
B) Break a bond to give stable molecules or ions
C) Add a proton
D) Take a proton away

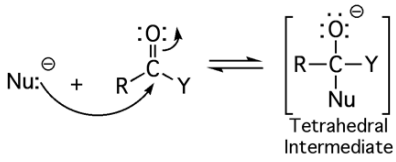
2) These same four mechanism elements describe most of the other mechanisms you have/will learn!!! (Yes, organic chemistry really is this simple if you look at it this way!!)

There are basically four different mechanisms that describe the vast majority of carbonyl reactions and these mechanisms are different combinations/ordering of the four mechanism elements listed above. In this class, I have termed them "Mechanism A", "Mechanism B", "Mechanism C", and "Mechanism D". They all involve a nucleophile attacking the partially positively charged carbon atom of the carbonyl to create a tetrahedral intermediate. Different reaction mechanisms are distinguished by the timing of protonation of the oxygen atom as well as the presence or absence of a leaving group attached to the carbonyl.

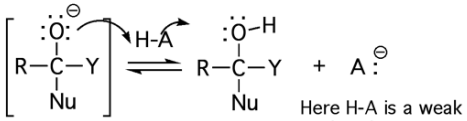
Four Mechanisms for the Reaction of Nucleophiles with Carbonyl Compounds

MECHANISM A: Reaction with a Strong Nucleophile

Step 1 Make a new bond between a nucleophile and electrophile

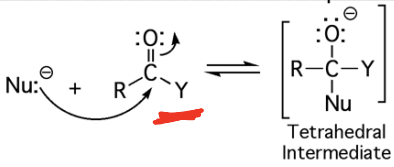


Step 2 Add a proton

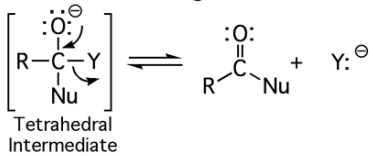


MECHANISM B: Reaction with a Strong Nucleophile When "Y" is a Good Leaving Group (-OR, -Cl, etc.).

Step 1 Make a new bond between a nucleophile and electrophile

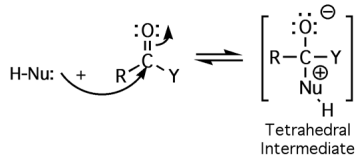


Step 2 Break a bond to give stable molecules or ions

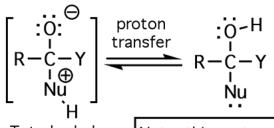


MECHANISM C: Reaction with a Weak Nucleophile

Step 1 Make a new bond between a nucleophile and electrophile



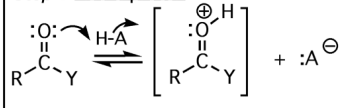
Step 2 Add a proton and Take a proton away



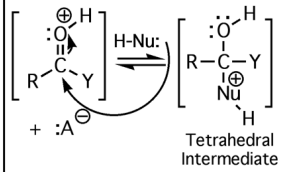
Note: this proton transfer can actually take place in two steps, *i.e.* Add a proton then Take a proton away or *vice versa*.

MECHANISM D: Reaction with a Weak Nucleophile in the Presence of Acid (H-A)

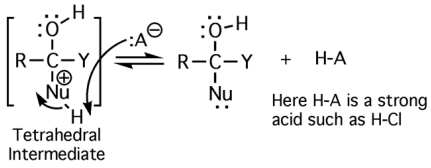
Step 1 Add a proton

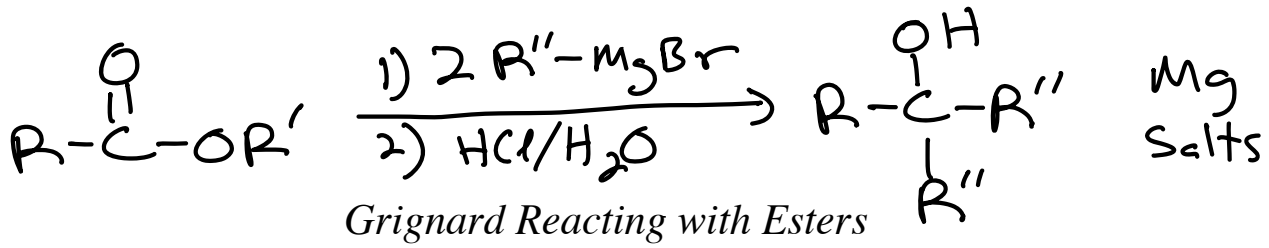


Step 2 Make a new bond between a nucleophile and electrophile

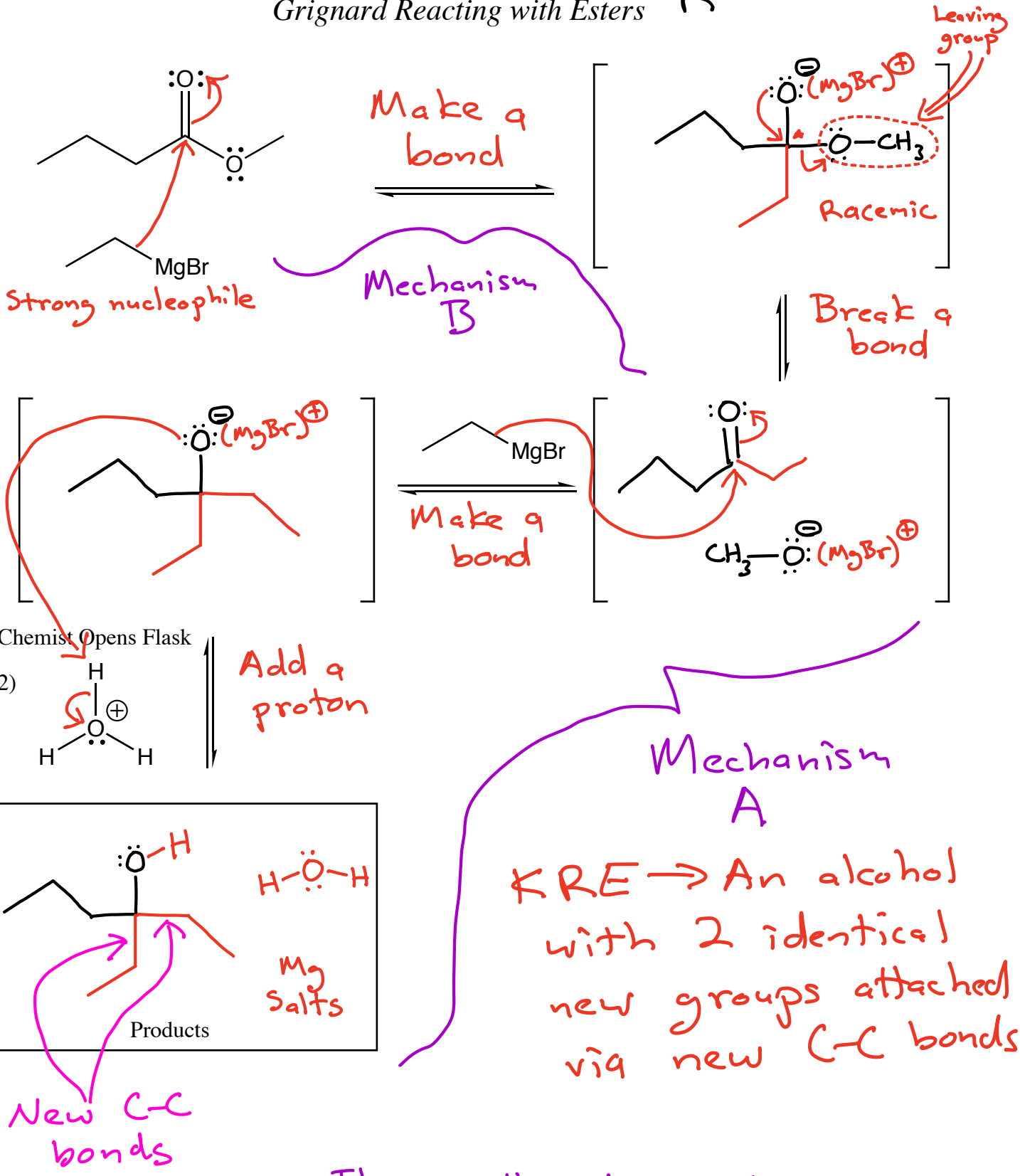


Step 3 Take a proton away

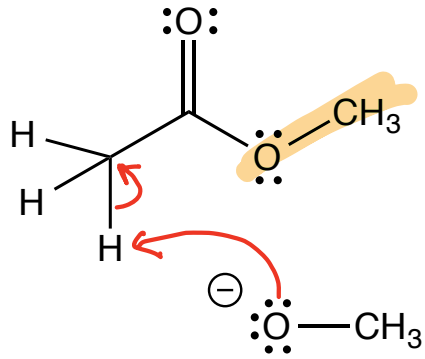




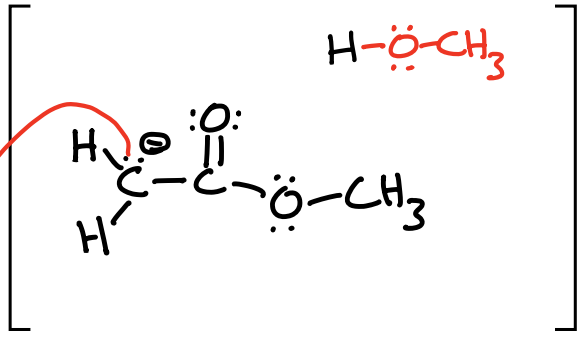
Grignard Reacting with Esters



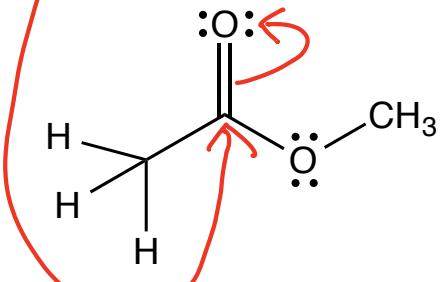
Claisen Condensation → "Aldol with Esters"



Take a proton away

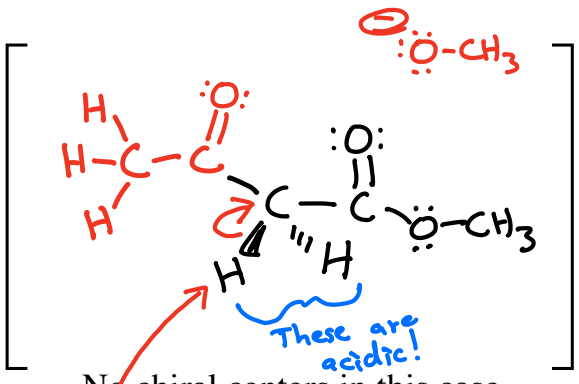


The R group of the base must match the ester!!



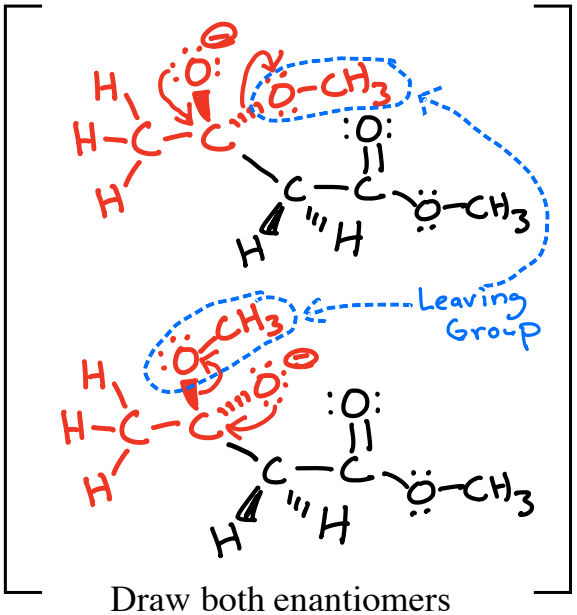
Make a bond

Mechanism B

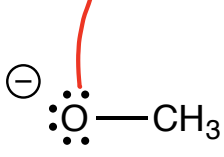


No chiral centers in this case

Break a bond



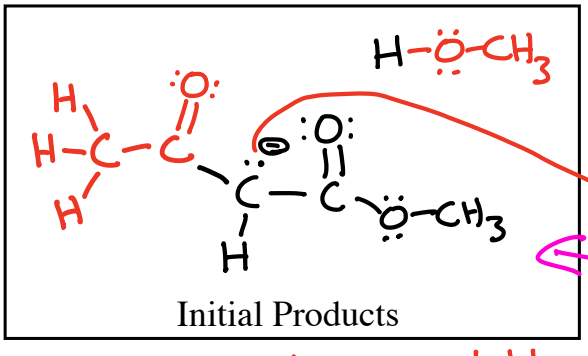
Draw both enantiomers



Take a proton away

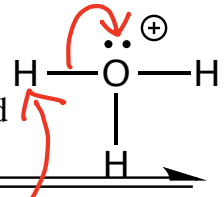
This "drives" the reaction

(Chemist opens flask and adds a mild acid)



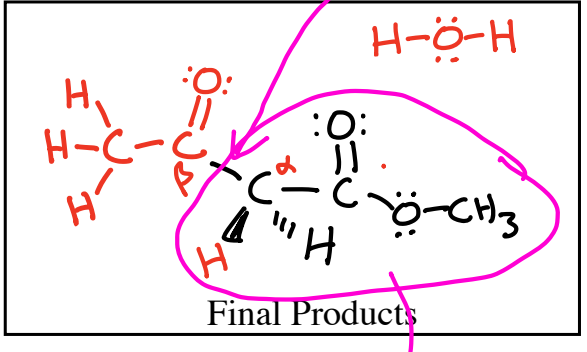
Initial Products

2) Mild



NOT an electrophile

New C-C bond

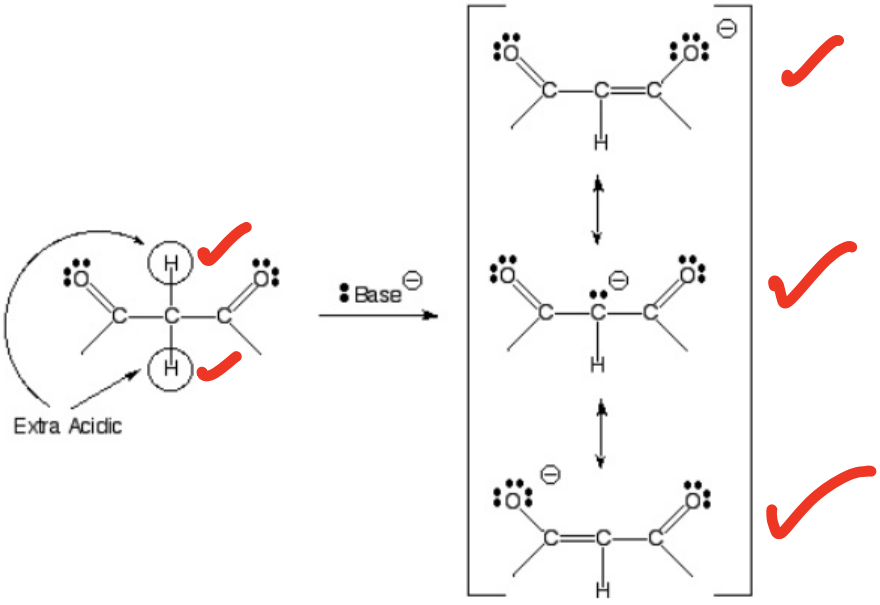


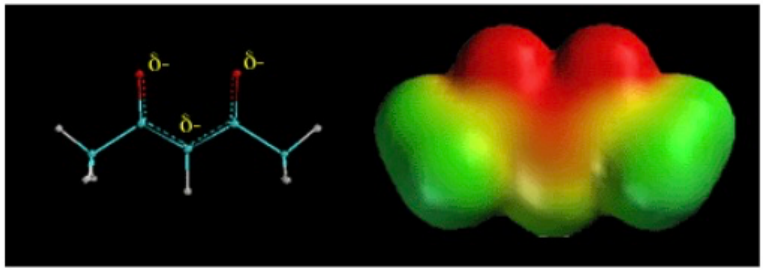
Final Products

This is a much more stable anion compared to $^{\ominus}OCH_3$, providing a strong driving force (motive) for the Claisen condensation reaction

Was an enolate nucleophile

Beta-dicarbonyls have alpha-hydrogens that are extra acidic





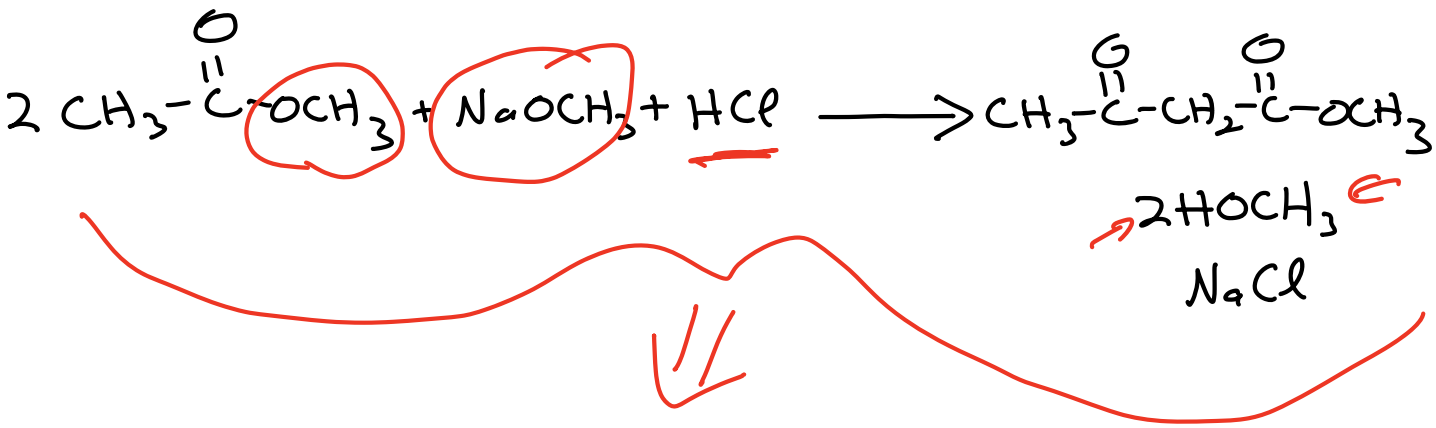
The C-H hydrogen atoms between two carbonyl groups are aven more acidic than normal a hydrogens because the resulting anion is double resonance stabilized. The above electrostatic potential surface shows how the negative charge (red color) is spread over all three atoms as predicted by the three resonance contributing structures.

KRE → A β-keto ester with a new C-C bond between the α and β carbons

Before we add acid → the last step drives the reaction because we make a relatively stable anion.

The "R" for the $^{\ominus}O-R$ must be the same "R" as the starting ester!

Balanced Equation for the Overall Process

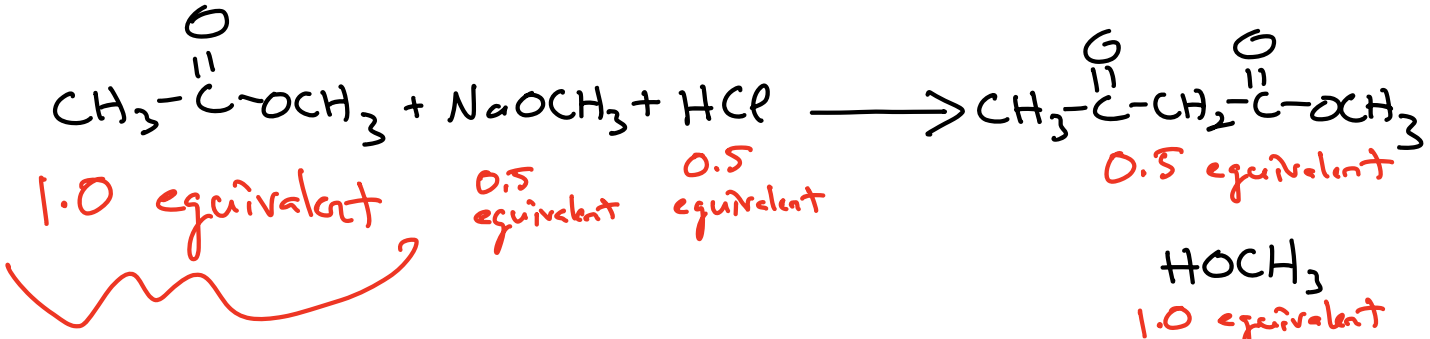


This is the balanced equation that is explained by the mechanism

With the balanced equation in hand we can set up a reaction properly in the lab because we know how much of each reactant is needed → For this we use the notation of "equivalents"

⇓

Notation that you will use on box problems and synthesis problems

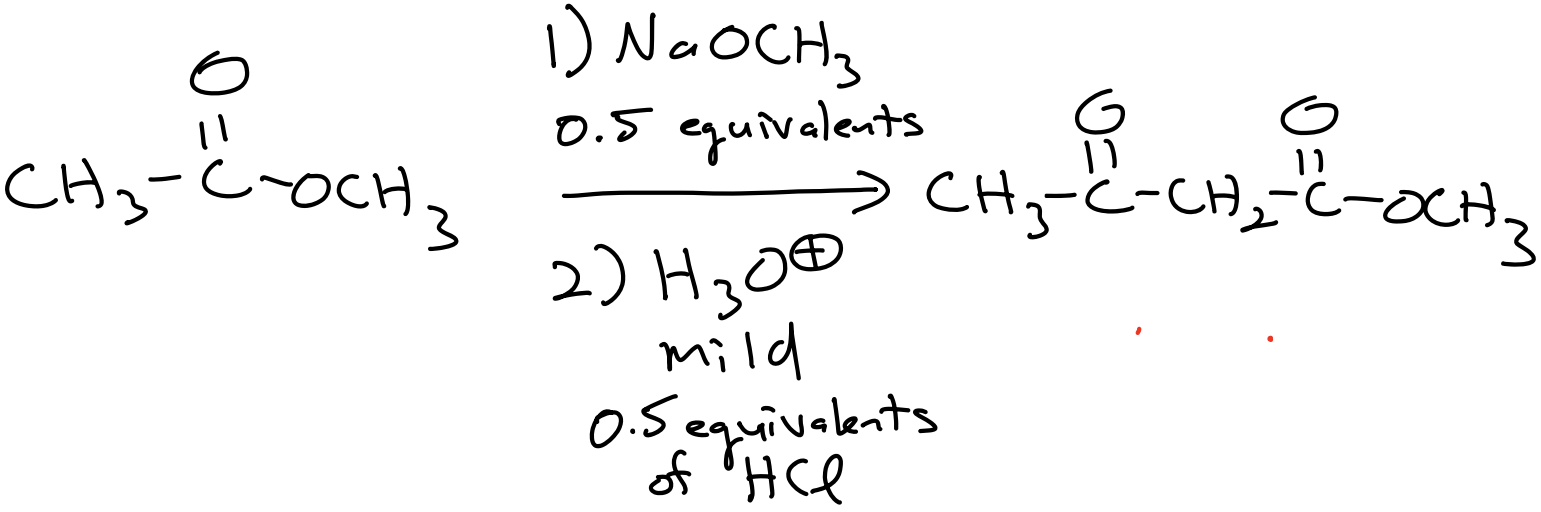


Defined as 1.0 equivalent as the important carbon containing starting material

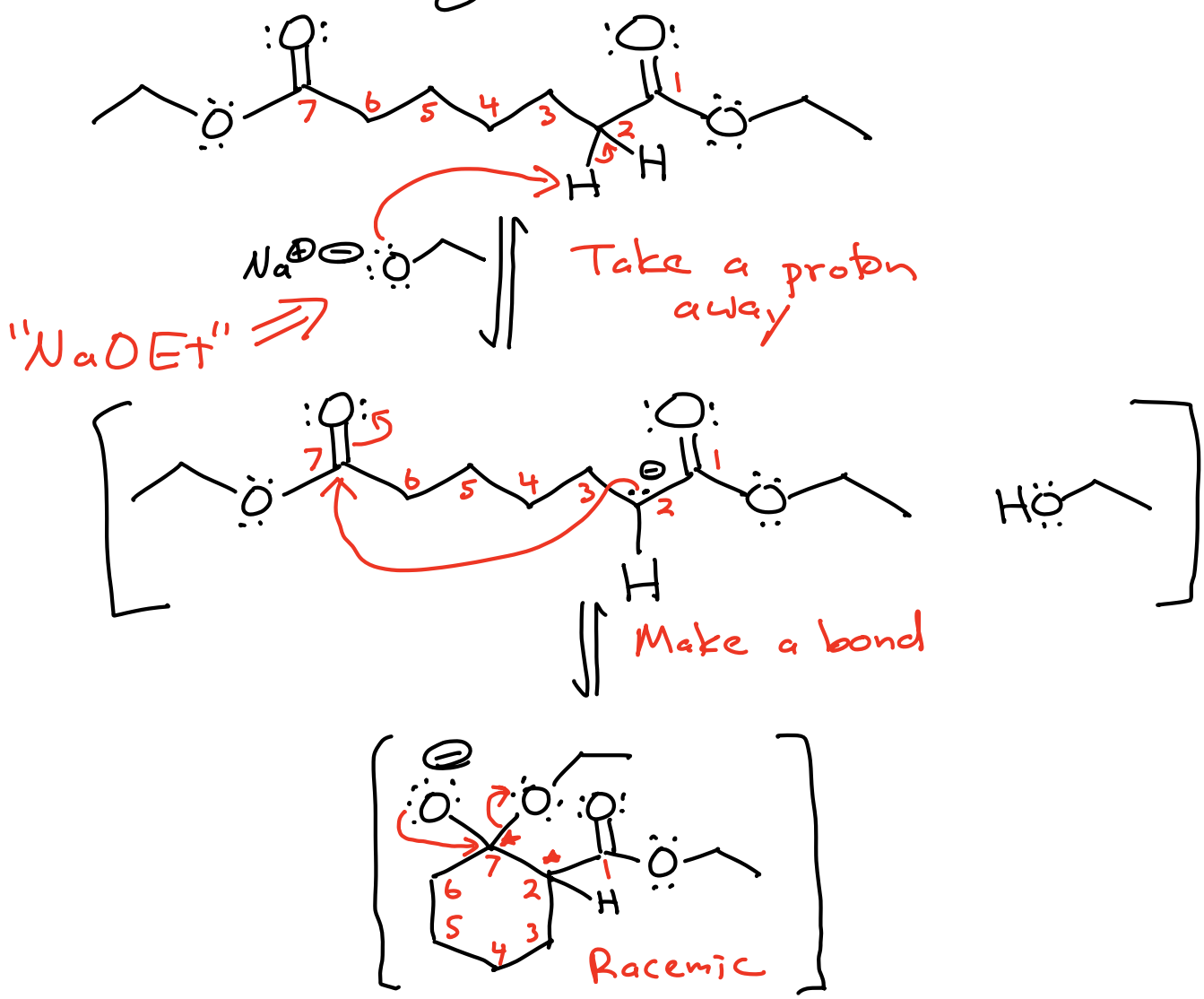
$HOCH_3$
1.0 equivalent

NaCl
0.5 equivalent

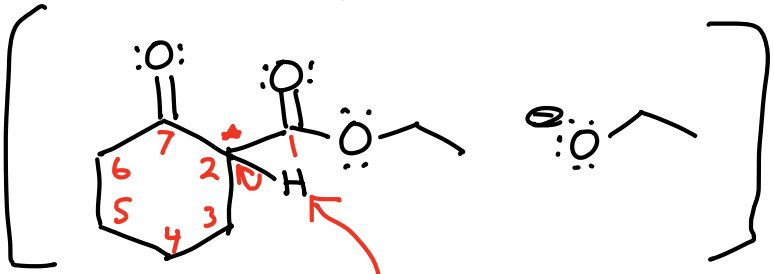
Example of using equivalents



The Dieckmann Condensation → Using a Claisen to make a ring.

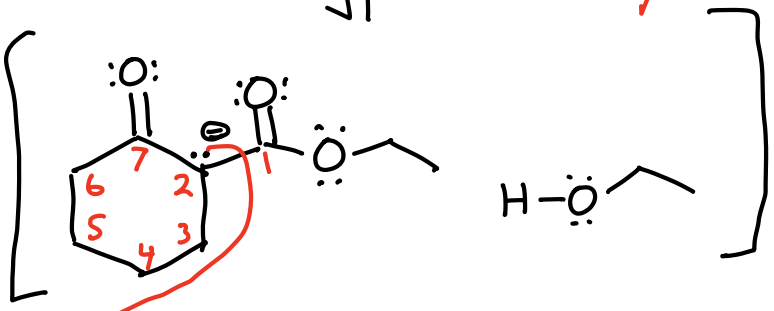


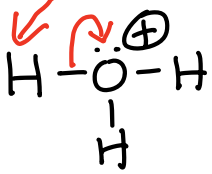
Break a bond



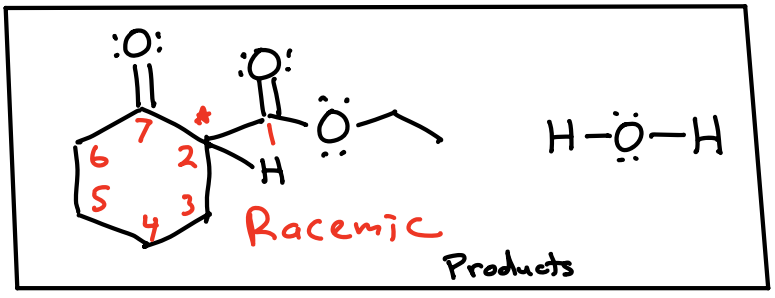
Racemic

Take a proton away



2) 

Add a proton



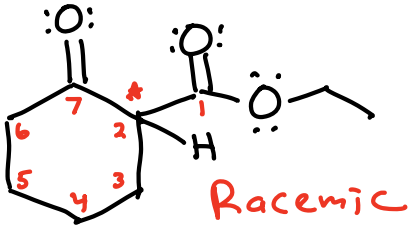
Overall Process

1.0 equivalent

2 esters!

1) NaOEt
1.0 equivalent

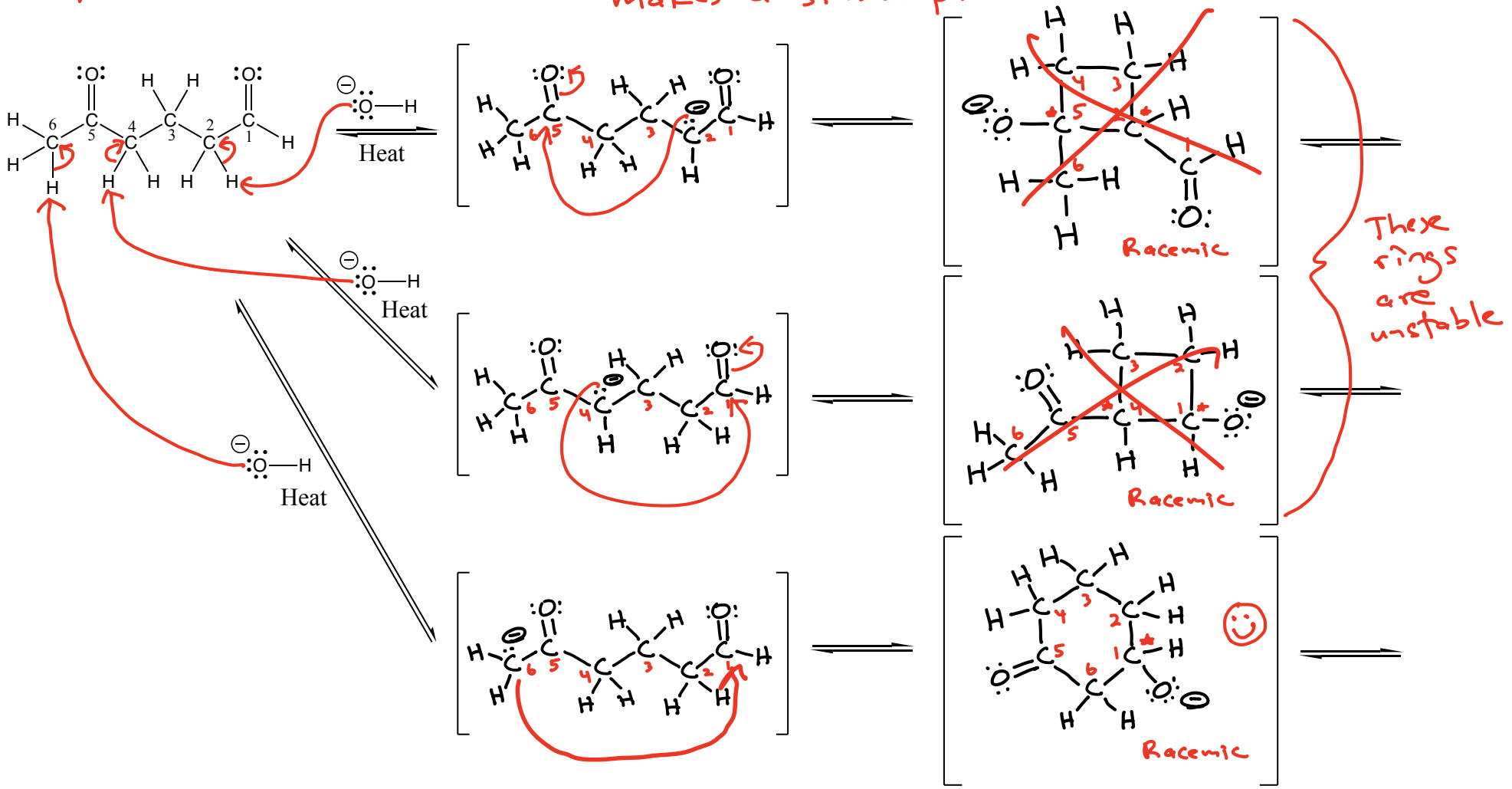
2) $H_3O^{\oplus}$
1.0 equivalent

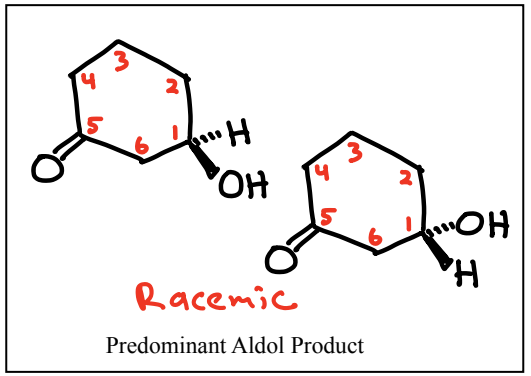


Racemic

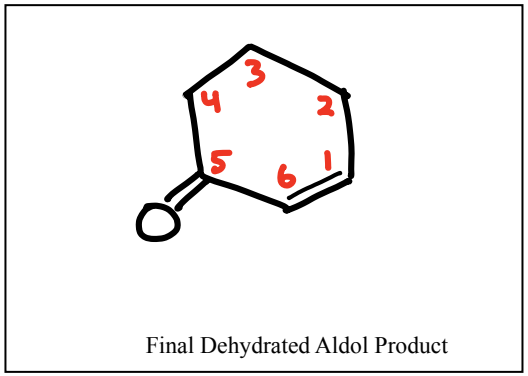
1.0 equivalent

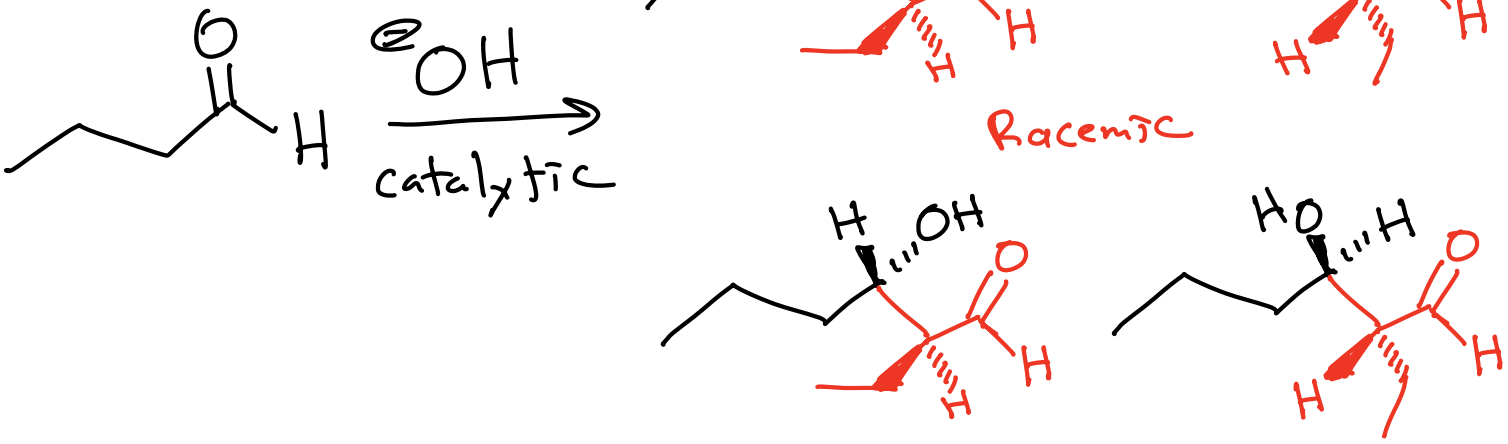
Cyclic Aldol Reaction → 3 different enolates are possible, but only one makes a stable product

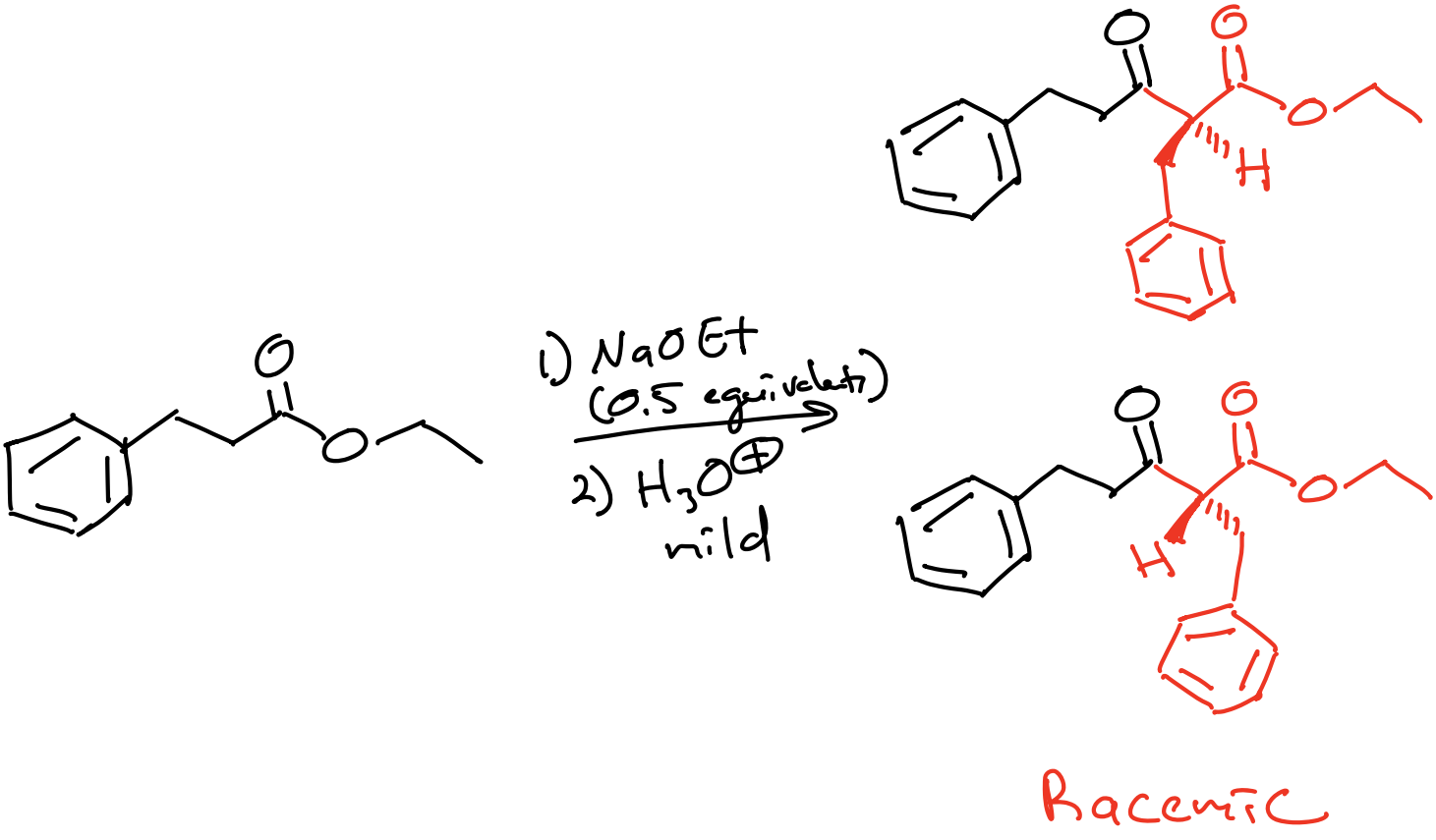


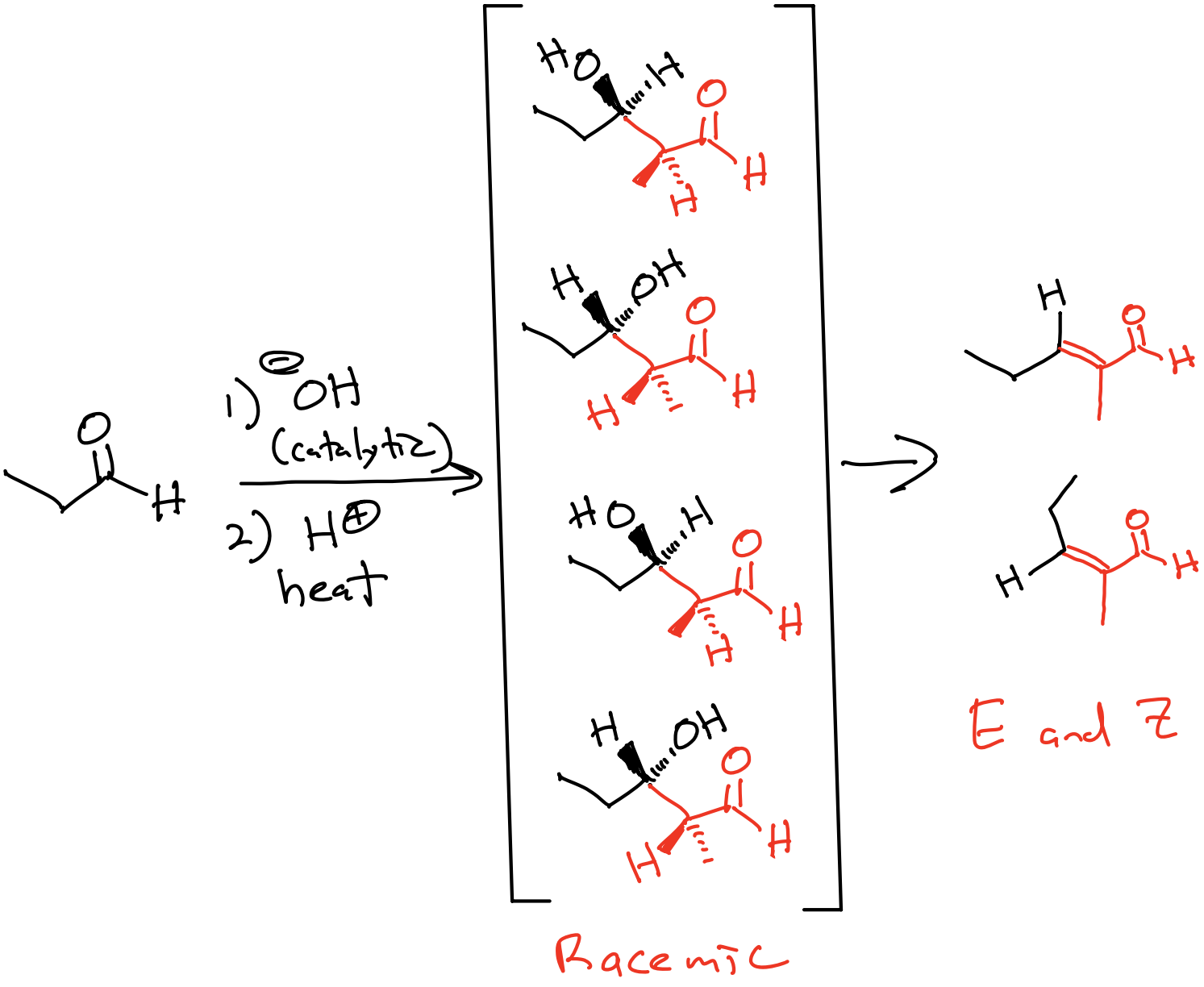


Dehydration




⊖OH
catalytic
Racemic


1) NaOEt
(0.5 equivalents)
2) H3O⊕
mild
Racemic


1) ⊖OH
(catalytic)
2) H⊕
heat
Racemic
E and Z