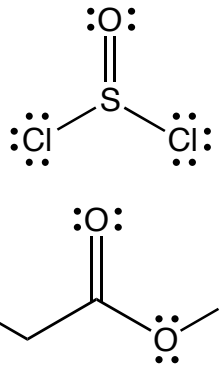
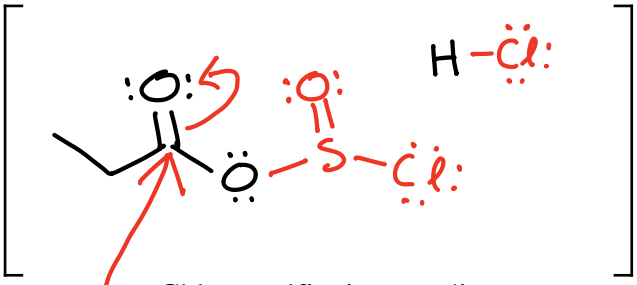
Reaction with Thionyl Chloride



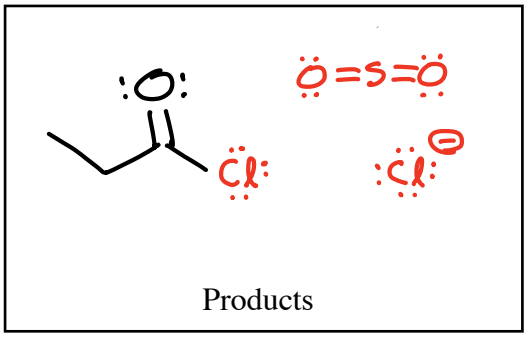
Several Steps



Chlrorosulfite intermediate

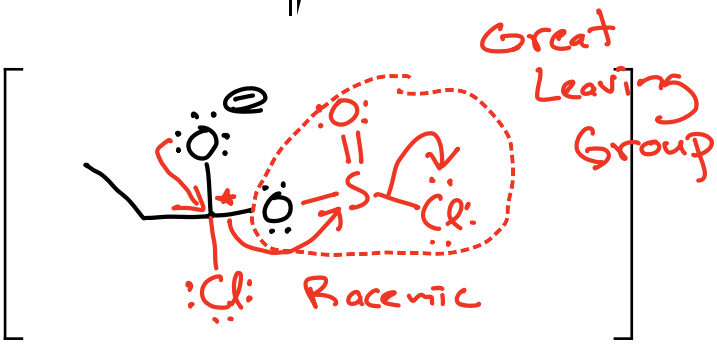
KRE → An acid chloride

Make a bond



Products

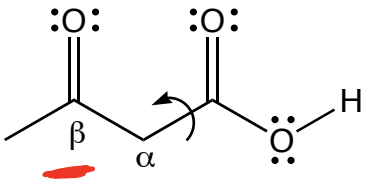
Break a Bond



Great Leaving Group

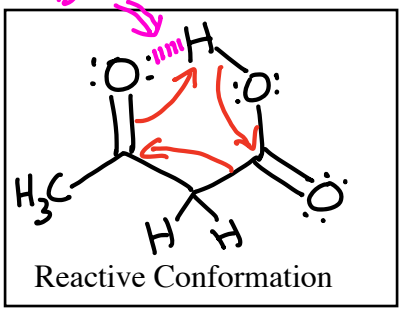
Racemic

Decarboxylation of a β-Keto Acid

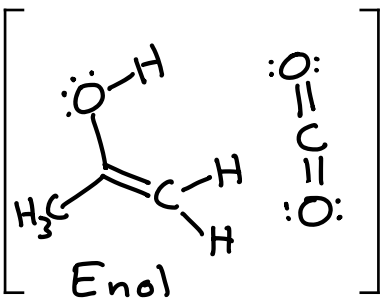


Bond rotates to give a more stable conformation

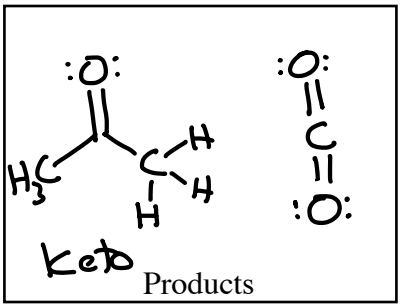
Hydrogen Bond



Reactive Conformation



Enol



Keto Products

6-Membered Ring
6 "Pi" Electrons
} VERY STABLE

"Aromatic"

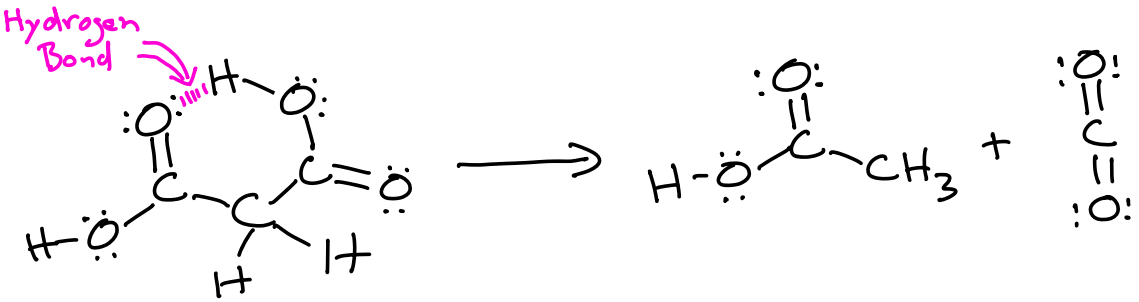
C-C Bond Breaks!

KRE → Ketone and CO_2

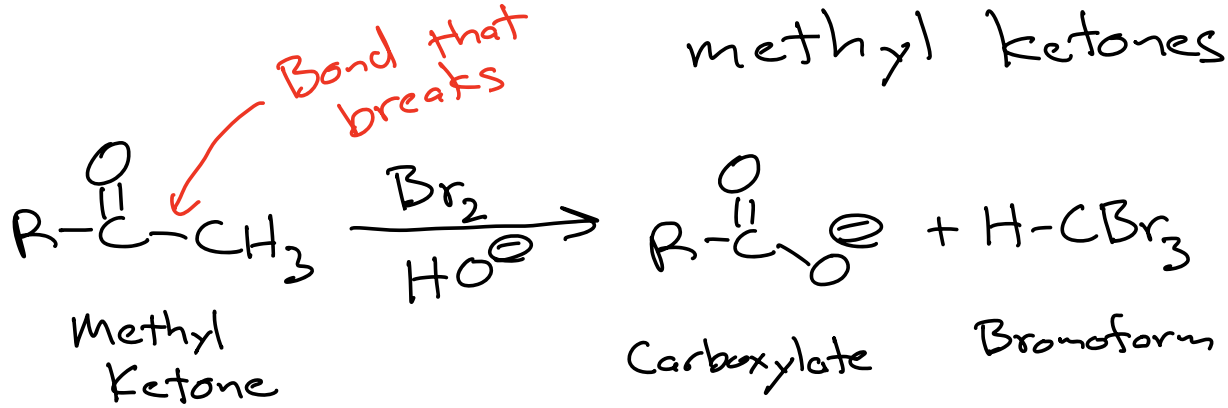
Broke a C-C Bond!

Time capsule: Important for products of Claisen reaction!

This also works with β-diacids



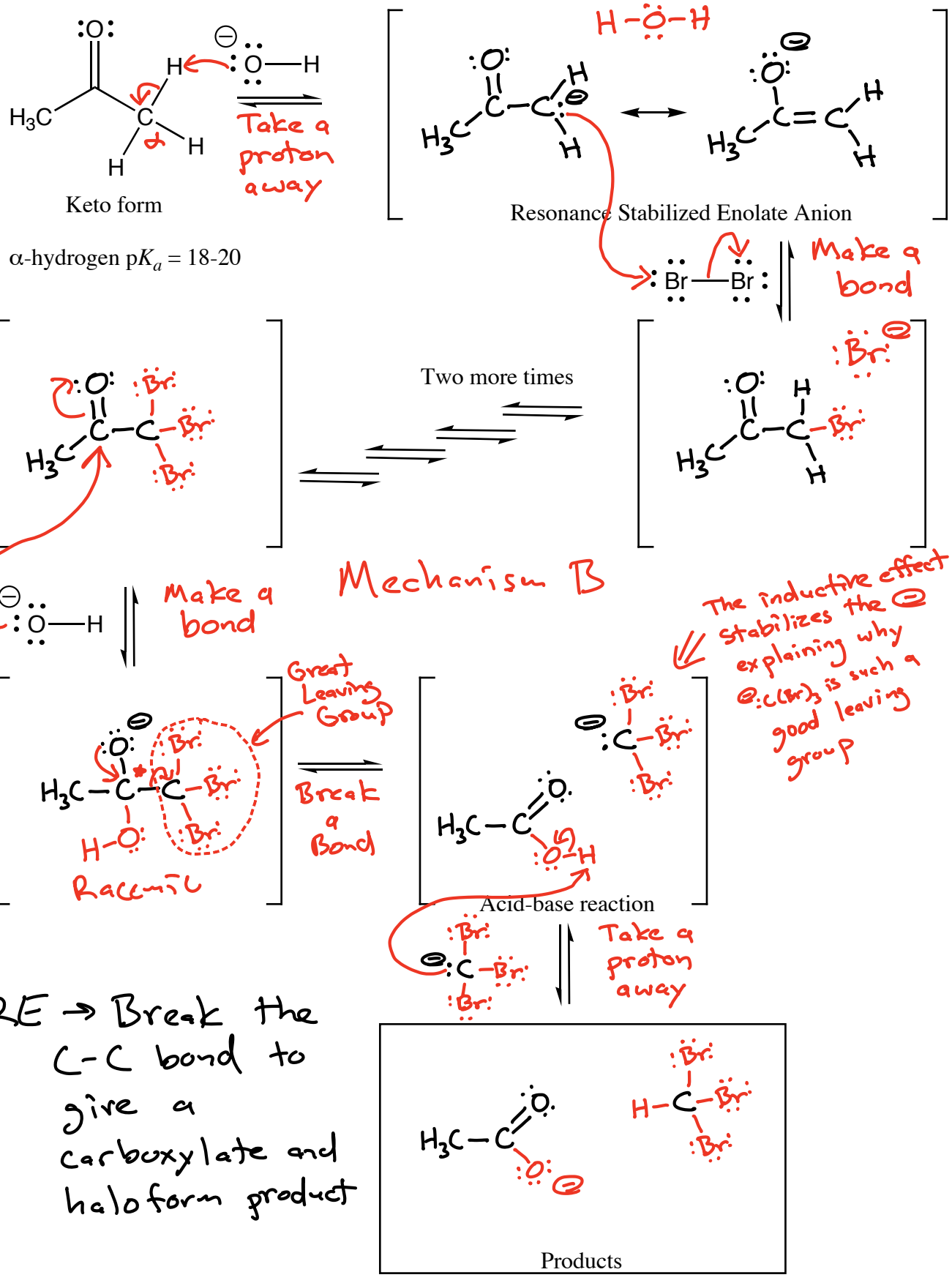
The haloform reaction → uses methyl ketones



Not that useful for synthesis, however the mechanism contains three elements that are important to second semester organic chemistry

acidity of α-hydrogen
enolate nucleophile
Mechanism B

The Haloform Reaction



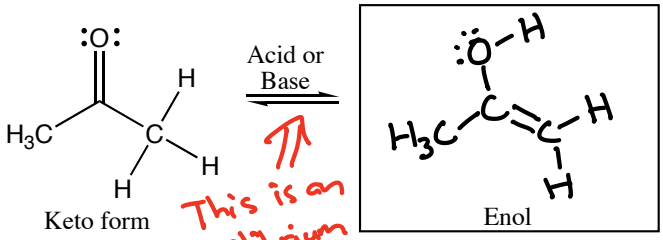
KRE → Break the C-C bond to give a carboxylate and haloform product

Be Careful!

Do not confuse the keto-enol vs. enolate contributing structures!

Keto-Enol Tautomerization vs. Enolate Resonance

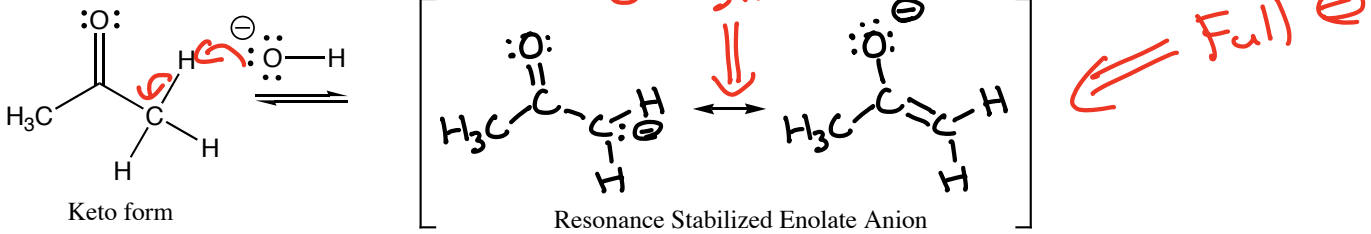
Keto-Enol Tautomerization



This is an equilibrium

Both the keto and enol molecules are Neutral!

Enolate Resonance

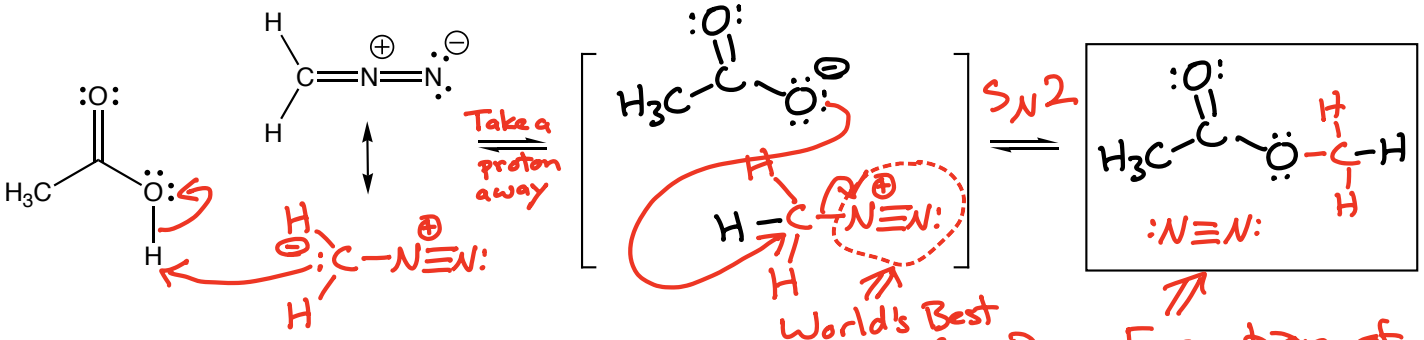


Contributing structures!

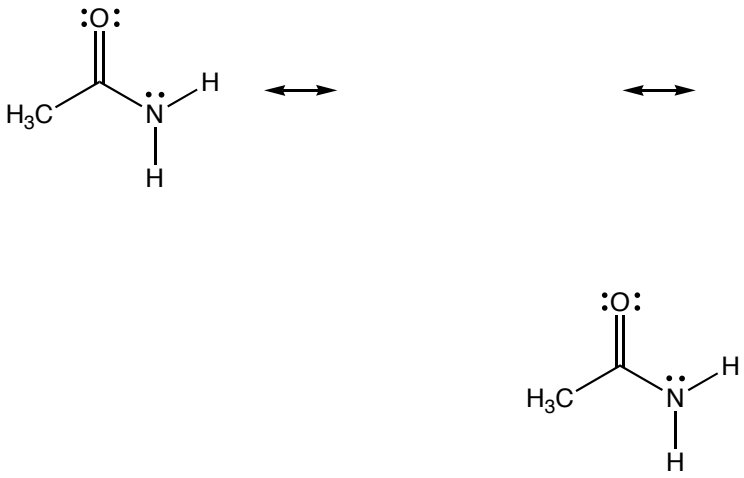
Full ⊖

α-hydrogen pK_a = 18-20

Diazomethane reaction



Amide Resonance VERY IMPORTANT!!!!!!



Summary of Carboxylic Acid Reactions → So Far...