## Lecture outline

Ch 20 - Rxns a to $\alpha$ carbonyl group -
enols and enolates, aldol and Claisen condensations
Carbonyl compounds exist in equilibrium with enol tautomers -


Compound
enol
amount of enol at equilibrium

$6 \times 10^{-5} \%$

$6 \times 10^{-7} \%$

$1.4 \times 10^{-2} \%$

$9.1 \%$


80 \%

Draw the enol tautomer of each compound above and explain the variation in the position of the equilibria, reflected in the enol \%s. Think about the relative stabilities of the carbonyl compound and enol and how this varies from case to case. Why is enolization so favorable for the $\beta$-dicarbonyl compound?

Enolization mechanisms (review, eh?) Fill in the details.
a. Acid-catalyzed


b. Base-catalyzed



Resonance stabilization makes Hs a to a carbonyl group moderately acidic

Cmpd

aldehyde or ketone

(ester)

(nitrile)

$\beta$-dicarbonyl cmpd

On the number line below, put a simple carbonyl cmpd, a $\beta$-dicarbonyl cmpd, an alcohol, $\mathrm{H}_{2}$, and $\mathrm{NH}_{3}$ above the $\mathrm{pK}_{\mathrm{a}}$ ranges, and then put the conjugate base of each one below the $\mathrm{pK}_{\mathrm{a}}$ ranges for their conjugate acids.

conj.
base:
What's the point of this? A base can completely deprotonate any acid to the left/right (pick one).

What bases can quantitatively deprotonate a ketone?
... and which ones can deprotonate a ketone to a small extent?

What bases can quantitatively deprotonate a $\beta$-dicarbonyl compound?

Reactions of enols and enolate ions

1. H-D exchange

write the mechanisms
2. Stereoisomerization
write the mechanisms


or


$$
\mathrm{H}^{+}, \mathrm{H}_{2} \mathrm{O}
$$

