

Today

Chap 17 Reactions at the α -C of a Carbonyl

Sections 17.2, 17.3: Keto-Enol
Tautomerization

Section 17.1 The Acidity of α -Hs

Next Class

Alkylation of the α -C of a Carbonyl
Section 17.6, 17.7

Second Class from Today

Benzene and Aromaticity 8.1, 8.2, 8.16 - 8.18

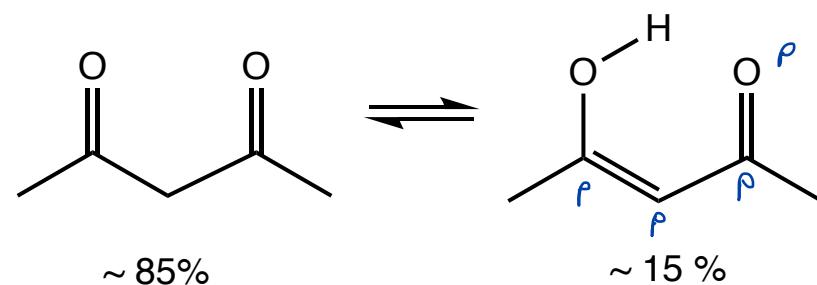
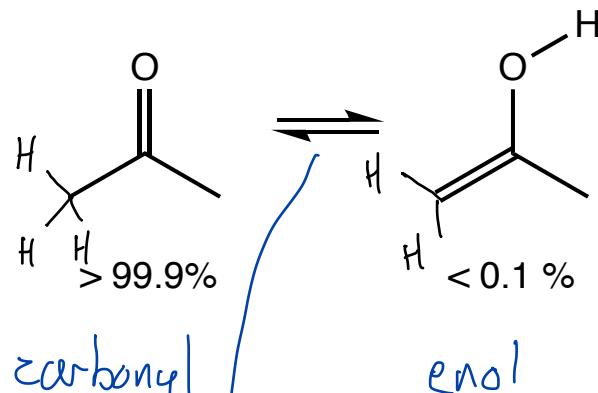
Third Class from Today

Electrophilic Aromatic Substitution
8.16 - 8.21, 18.1 - 18.8

On a separate piece of paper rework test 2 and end in on Friday, April 14

Keto-Enol Tautomerization

Section 17.2, 17.3



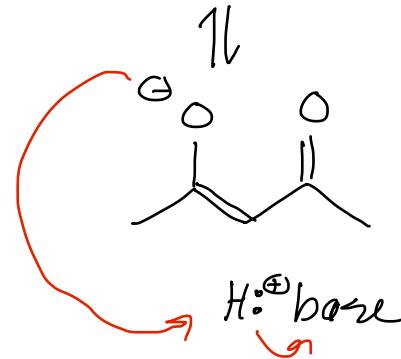
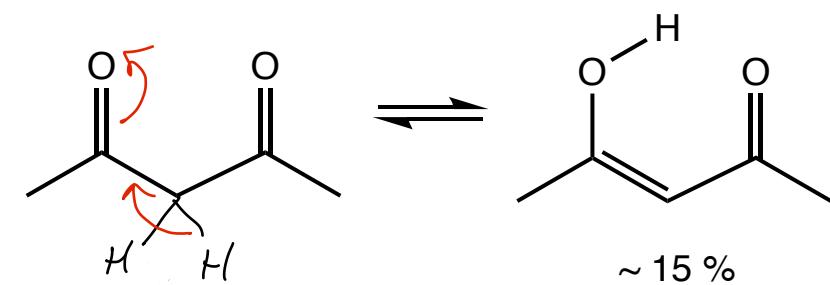
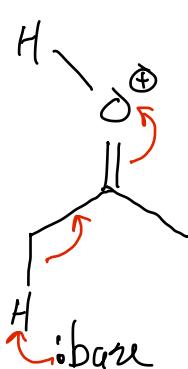
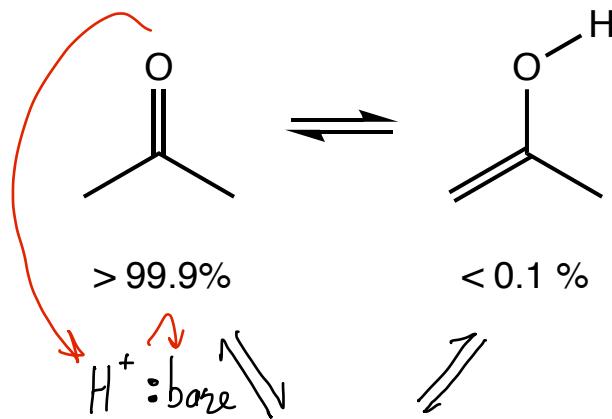
not resonance contributors... the structure has changed. There is a new O to H σ Bond

Typically, the $\text{C}=\text{O}$ version is more stable. The stability of the enol form can be increased by e^- delocalization

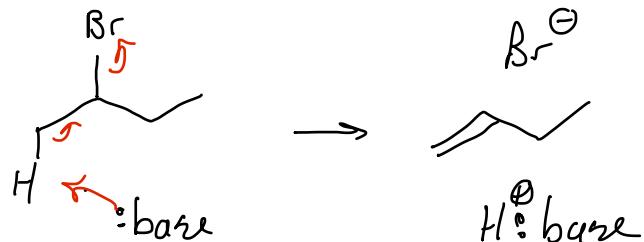
more enol form (as compared to acetone)
because $\text{C}=\text{C}$ π bond is part of an extended π system

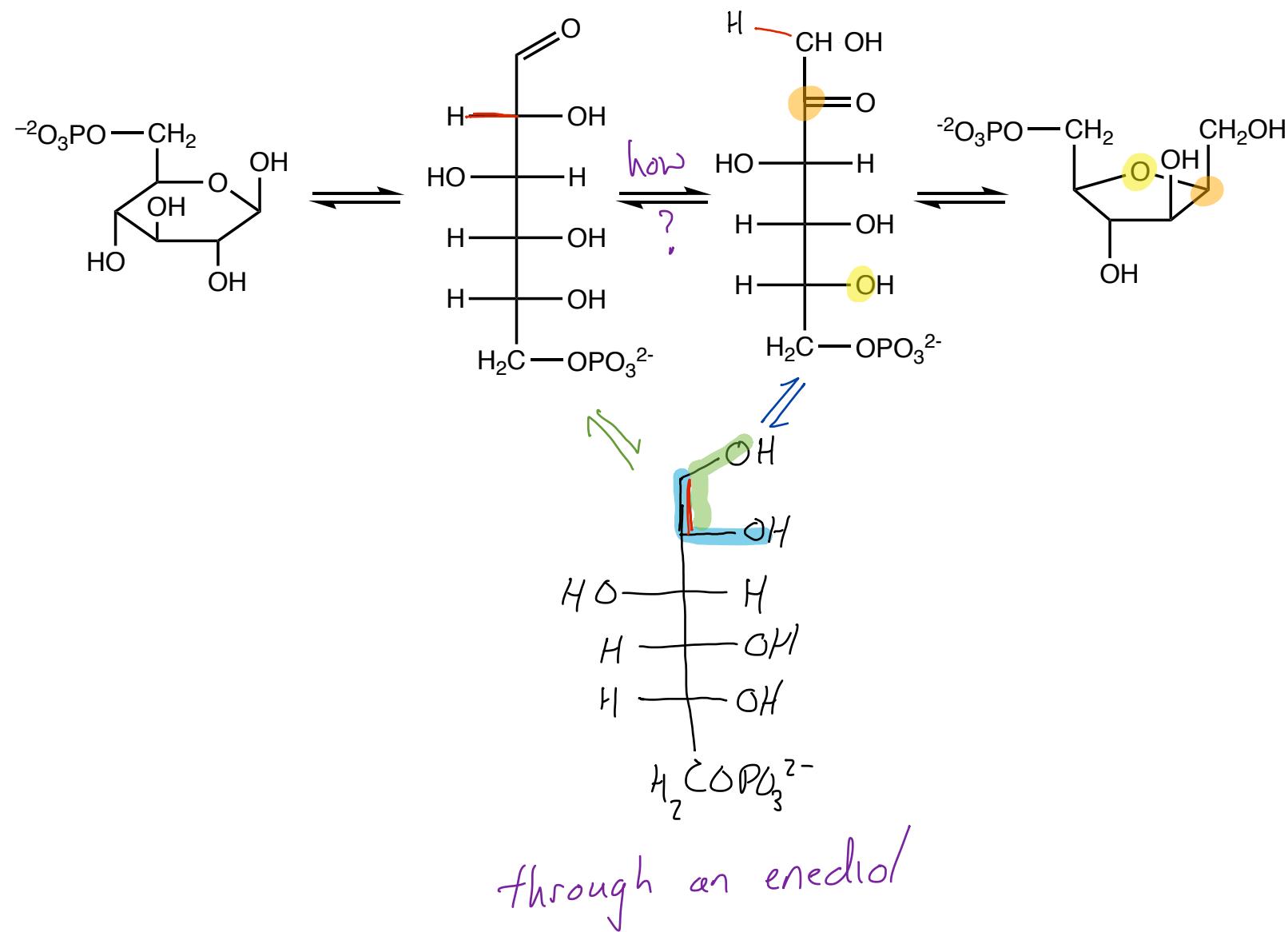
Keto-Enol Tautomerization

Section 17.2, 17.3



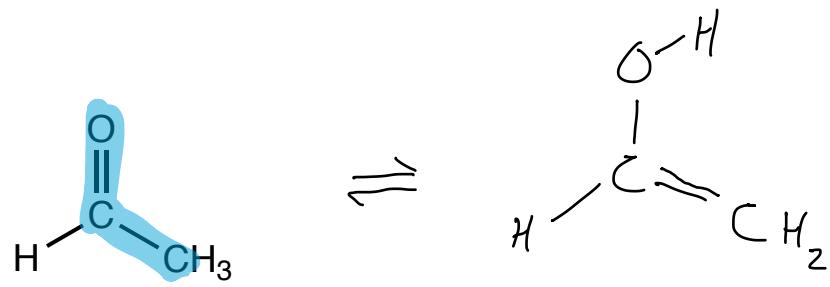
The C has been activated,
but we haven't added a
nucleophile ...





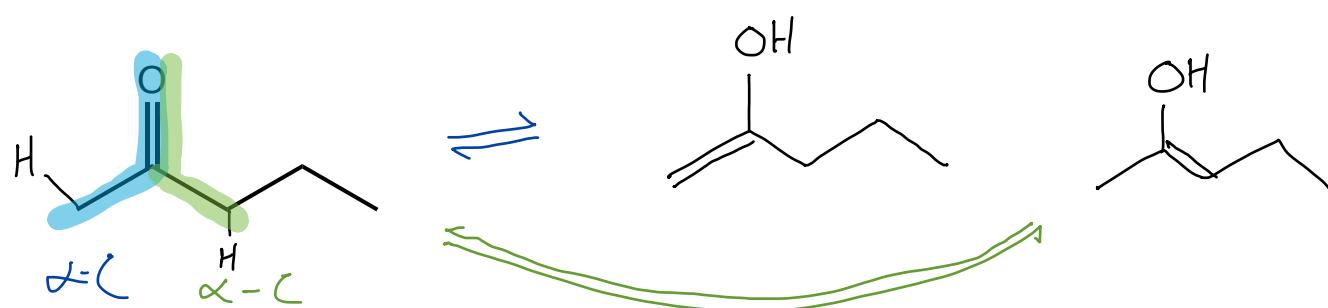
Keto-Enol Tautomerization: Draw Some Enols

Practice

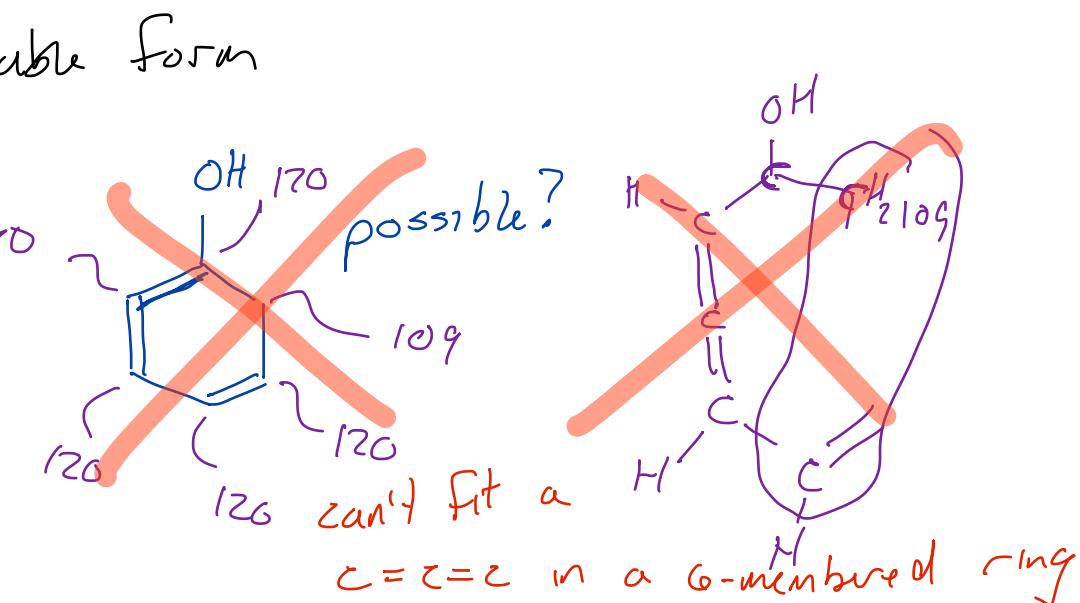
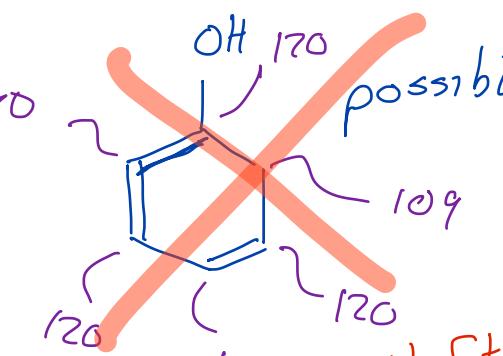
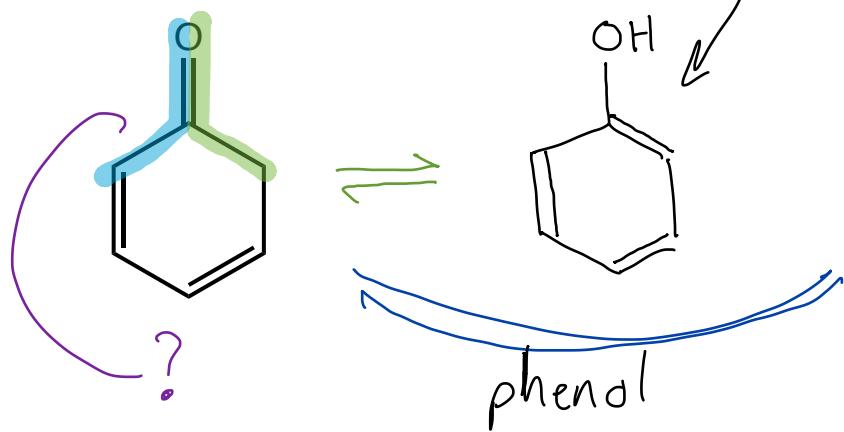


drawing the end version.

1. Find Carbonyl
2. find α -C that has an H on it
3. Move that H to the O and draw $\text{C}=\text{O}$ as $-\text{O}-\text{H}$
4. draw db from $\text{C}=\text{O}$ C to α -C



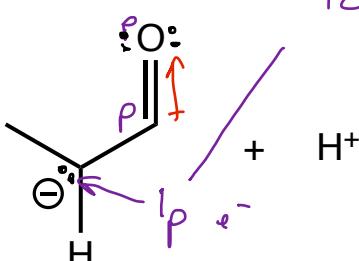
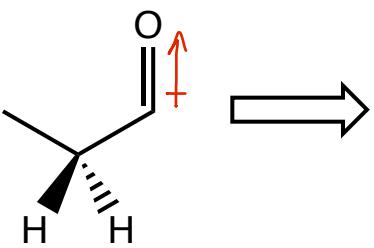
this is the more stable form



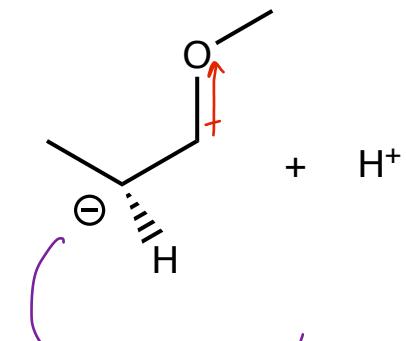
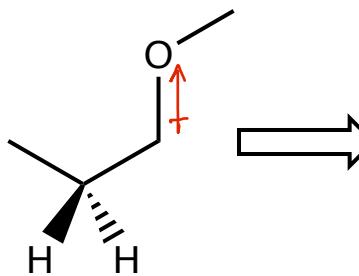
Acidic α -Hydrogens

Isn't it hard to make carbanions?

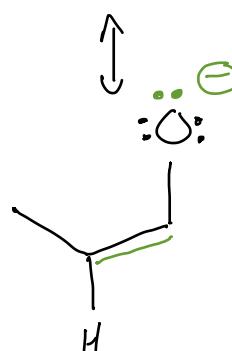
Section 17.1

lone pair e^- 's adjacent
to π bond... H^+

vs

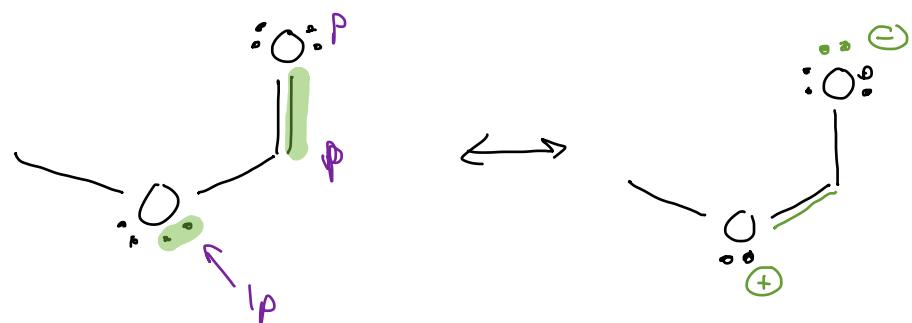
 H^+

generate resonance contributor by switching position of $lp e^-$'s + π bond



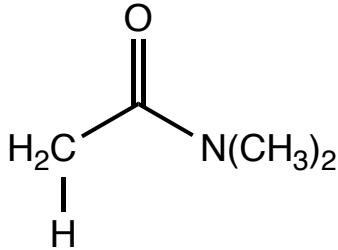
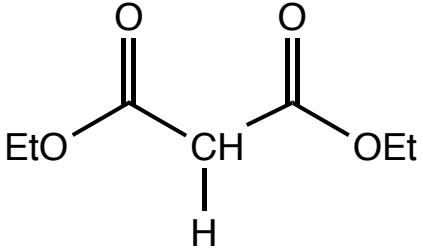
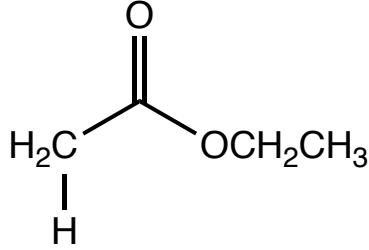
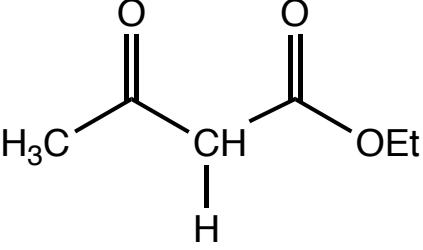
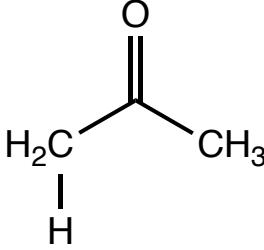
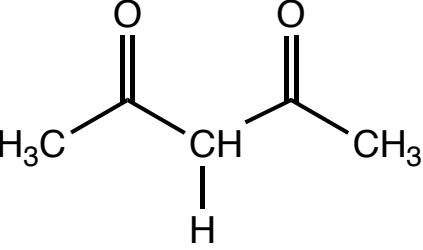
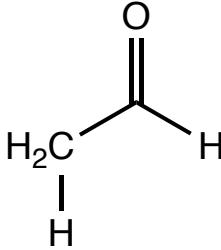
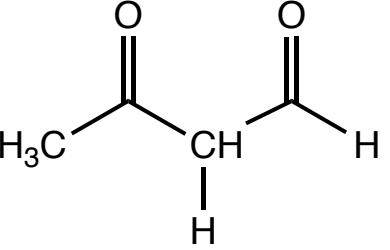
\ominus charge is spread out over the $C + O$ by e^- delocalization much easier to do

negative charge confined to \approx atom... hard to do

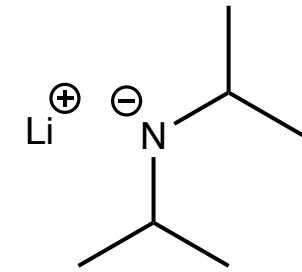


Acidic α -Hydrogens

Section 17.1

	pK_a		pK_a
	30		13.3
	25		10.7
	20		8.9
	17		5.9

- $\text{CH}_3\text{CH}_2\text{-H}$ $pK_a = 50$
 $\text{CH}_3\text{CH}_2\text{O-H}$ $pK_a = 16$
 $\text{CH}_3\text{C(O)O-H}$ $pK_a = 4.75$



LDA
lithium diisopropylamide

$$pK_a \text{ LDAH}^+ = 35$$