

## Enol and Enolate Chemistry

March 2, 2020

- Acidity and keto-enol tautomerism.
- Racemization pathways for chiral aldehydes and ketones
- The haloform and HVZ reactions.
- Lithium enolates and their alkylation.
  - A useful pKa trick for predicting acid-base equilibria.

**110b Teaching Fellows:** Felipe Becerril, Christina Beck, Isabelle Cheng, Junha Gu, Nathalie Hong, Shy Lavasani, Allison Liu, Casey Morrison, Jerusalem Nerayo, Eric Tang, Baili Zhong, Martín Acosta Parra.

**O'Leary office hours:** T/Th 9:30-10:00 am, SN 208.

**Chemistry Seminar!** Dr. Levi Moore, US Air Force Research Lab. "Next-Generation Propulsion Materials using Thiol-ene Click Chemistry: Research in the Applied Materials Group at the Air Force Research Laboratory," 11:00 AM Tuesday, March 3, SN Aud.

**O'Leary's evening review session:** Wednesdays 7:00 PM, SN Aud. **Course website:** <http://pages.pomona.edu/~djo04747/110/>

**Suggested Problems for Exam 3.** 10E/11E Chapter 18 problems: 15, 16, 20, 21, 26, 27, 29, 30, 32, 34.

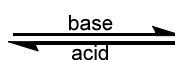
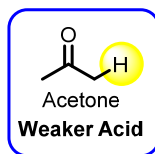
## Tautomerism, Enols, and Enolates

### Bond Energy Keto

105 kcal/mol (C-H)

172 kcal/mol (C=O)

277 kcal/mol



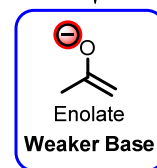
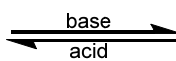
**pK<sub>a</sub> Keto**  
19 – 20

### Bond Energy Enol

120 kcal/mol (O-H)

148 kcal/mol (C=C)

268 kcal/mol



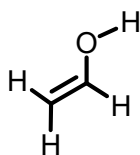
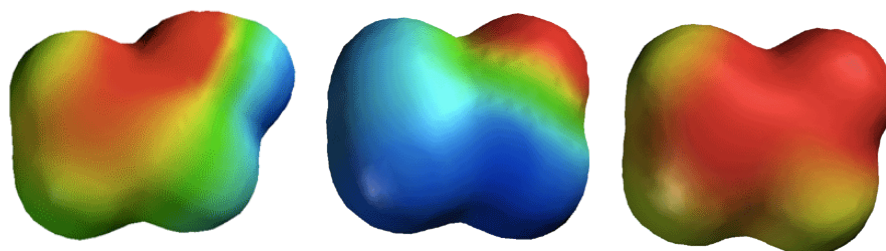
**pK<sub>a</sub> Enol**  
10

Tautomerism

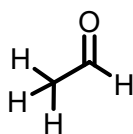
Resonance

**Tautomerism:** The equilibrated formation of enols from acyl groups through proton exchange. In most cases the equilibrium will favor the keto form over the enol form.

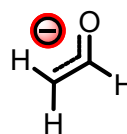
## Tautomerism, Enols, and Enolates



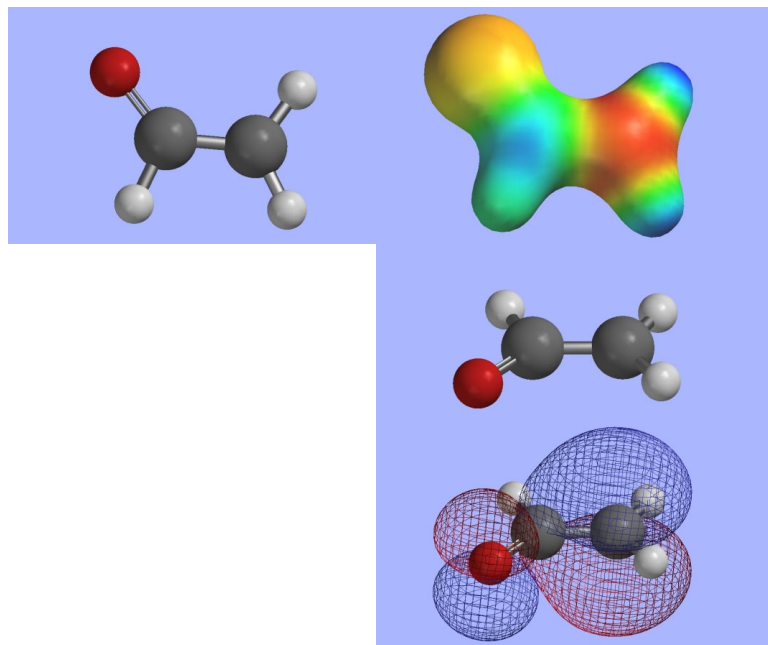
Acetaldehyde  
enol form



Acetaldehyde  
keto form

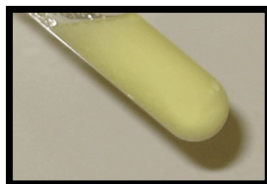
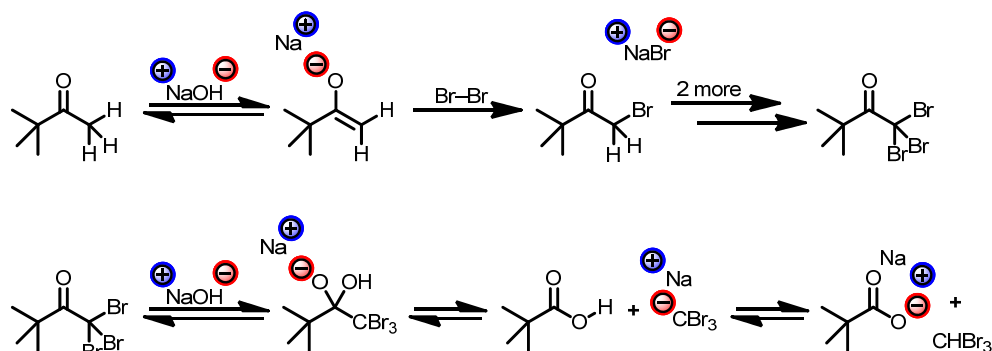


Acetaldehyde  
enolate anion



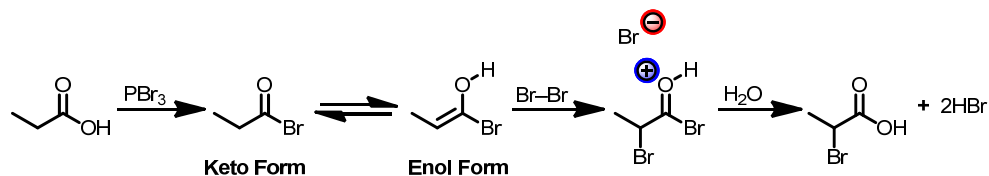
acetaldehyde enolate

## Haloform Reaction



The **iodoform test** is an analytical reaction used to test for methyl ketones (before NMR). A positive test produces iodoform (CHI<sub>3</sub>), a heavy, pale yellow solid that is insoluble in water. The test will also give a positive result in the presence of acetaldehyde and ethanol.

## Hell-Volhard-Zelinsky (HVZ) Reaction



The **Hell-Volhard-Zelinsky reaction** effects the synthesis of α-halogenated carboxylic acids. These are useful synthetic intermediates that easily lead to α-amino and α-hydroxy acids through nucleophilic displacement.

