The Chemistry of Enolates and Enols

April 29, 2013

- Acidity and keto-enol tautomerism.
- The haloform and HVZ reactions.
- The acid- and base-catalyzed aldol reactions.

Announcements

Suggested Problems for Chapter 22: 22.50, 22.55, 22.59, 22.61, 22.62, 22.66, 22.69, 22.70(a), 22.71, 22.73(a,c,d,f), 22.75(a,e,j), 22.76, 22.80(a,f), 22.81(a,j), 22.83(a), 22.84(d), 22.85(a).

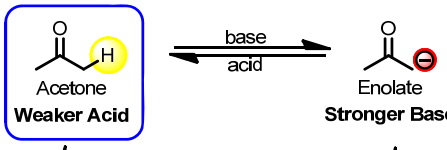
TA Office Hours: Mon 7-8 pm: Rob Craig - 302 Schlinger (x4056); Tue 3-4 pm: Kelly Kim - 302 Schlinger (x4047); Tue 7-8 pm: Corey Reeves - 302 Schlinger (x4056); Wed 5-6 pm: Adam Boynton - 139 Noyes (x3202); Wed 8-9 pm: Ben Suslick (UTA) - Lloyd Lounge; Thu 8-9 pm: Evan Zhao (UTA) - Fleming Lounge ; Thu 9-10 pm: Crystal Chu - 202 Schlinger (x3634); Sun 3-4 pm: Chung Wan Lee - 302 Schlinger (x4056).

Midterm exam review session: Friday evening, May 3, 153 Noyes.

Miderm examination: Monday, May 6, 9:00-9:55 AM, 153 Noyes.

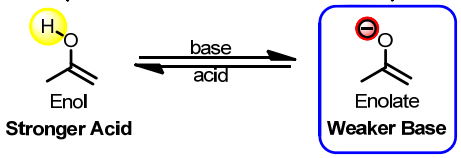
Tautomerism, Enols, and Enolates

Bond Energy Keto
440 kJ/mol, 105 kcal/mol (C–H)
720 kJ/mol, 172 kcal/mol (C=O)
1160 kJ/mol, 277 kcal/mol



pK_a Keto
19 – 20

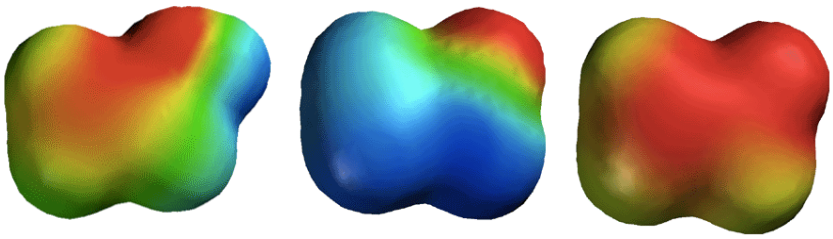
Bond Energy Enol
500 kJ/mol, 120 kcal/mol (O–H)
620 kJ/mol, 148 kcal/mol (C=C)
1120 kJ/mol, 268 kcal/mol

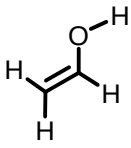


pK_a Enol
10

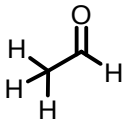
Tautomerism: The equilibrated formation of enols from acyl groups through proton exchange. In most cases the equilibrium will favor the keto form over the enol form.

Tautomerism, Enols, and Enolates

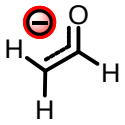




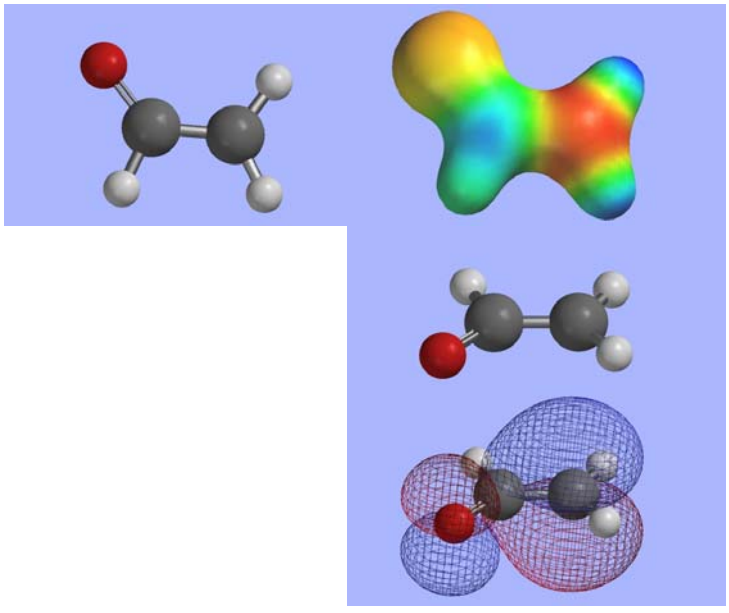
Acetaldehyde
enol form



Acetaldehyde
keto form

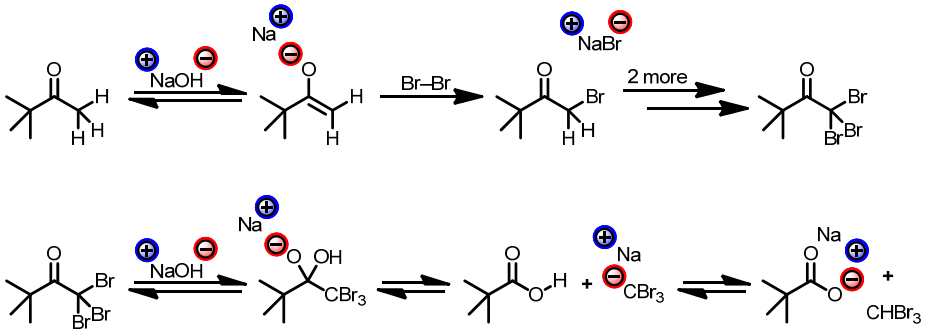


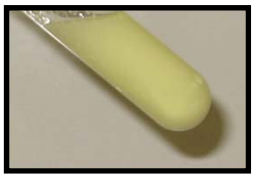
Acetaldehyde
enolate anion



acetaldehyde enolate

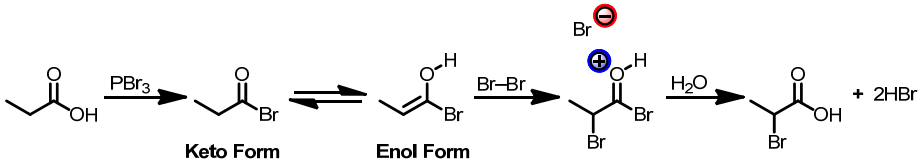
Haloform Reaction



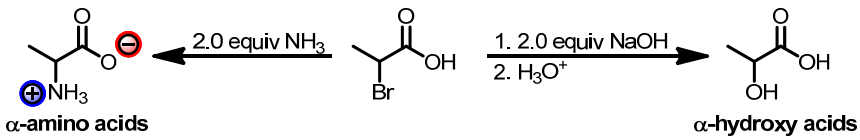


The **iodoform test** is an analytical reaction used to test for methyl ketones (before NMR). A positive test produces iodoform (CHI_3), a heavy, pale yellow solid that is insoluble in water. The test will also give a positive result in the presence of acetaldehyde and ethanol.

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.



Alexander Borodin
1833-1887

Organic Chemist
Co-discoverer, the aldol reaction

A "Sunday Composer"
Member of "The Five"
Most recognized piece:

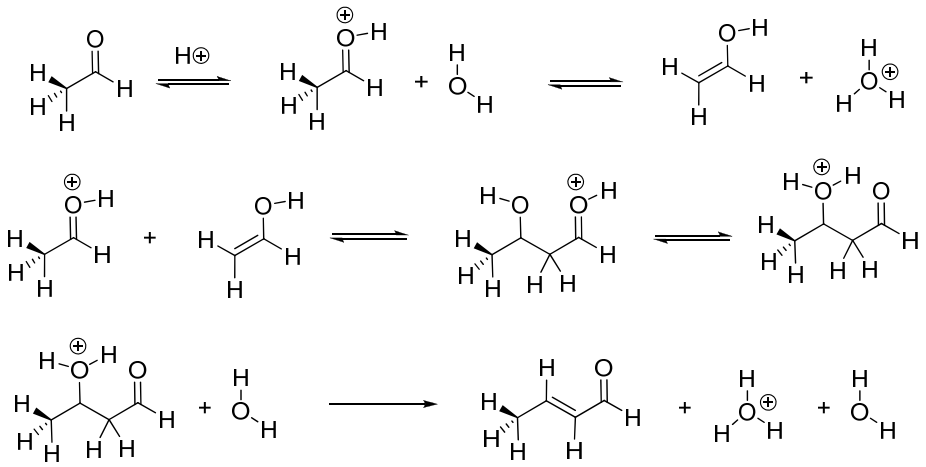
Prince Igor

"my heart ached to see how a great genius wasted his time on such [scientific] matters and could not accomplish his real work."

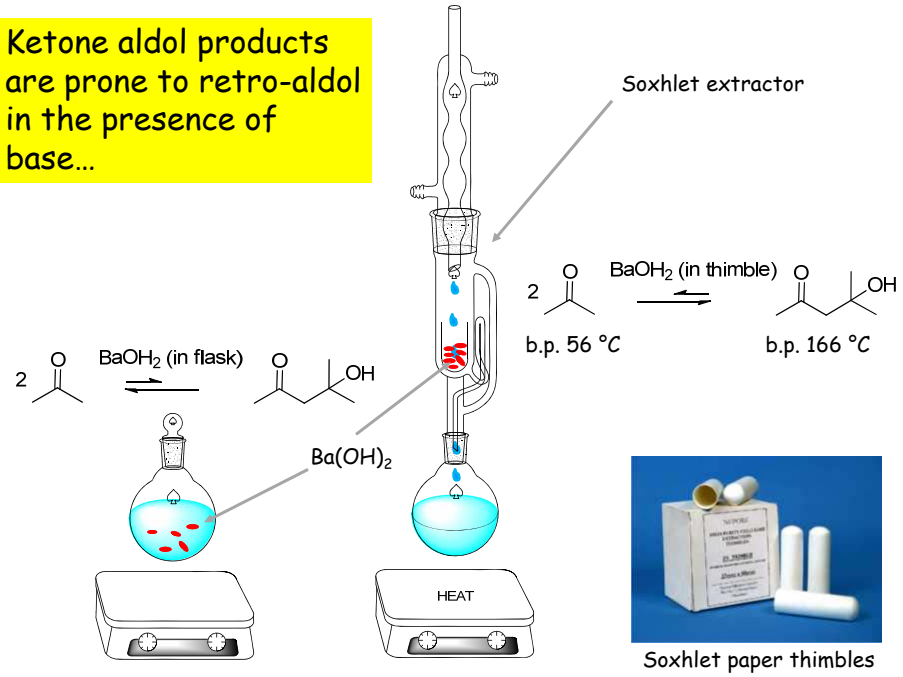
-Rimski-Korsakov

http://www.youtube.com/watch?v=t8C8frqCKKg

Acid-Catalyzed Aldol Condensation



Ketone aldol products are prone to retro-aldol in the presence of base…

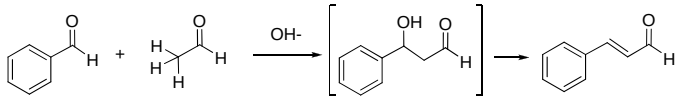


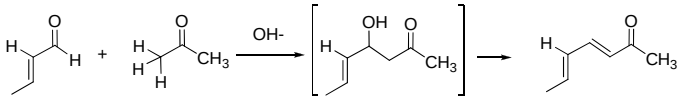
Soxhlet paper thimbles

Crossed Aldol Reactions

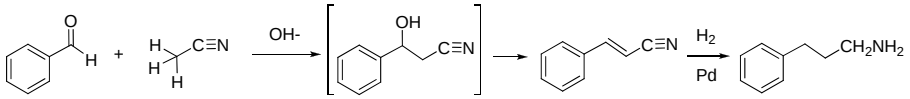
no acidic α-H

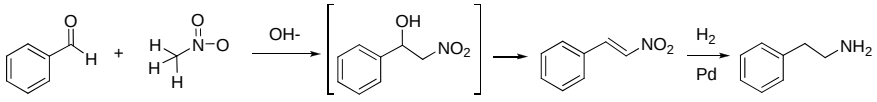
acidic α-H





Claisen-Schmidt reaction

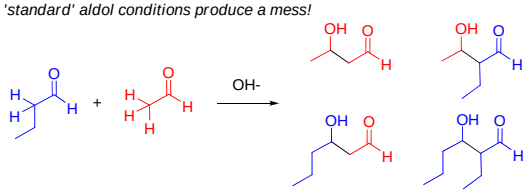


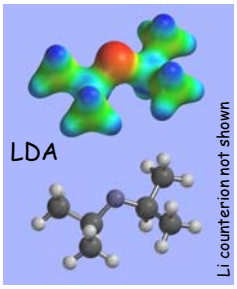


Henry reaction

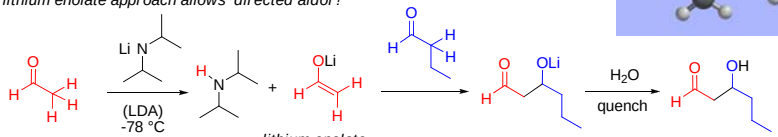
Lithium Enolates Allow Directed Aldol Reactions

'standard' aldol conditions produce a mess!

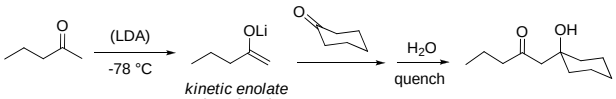




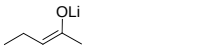
lithium enolate approach allows 'directed aldol'!



lithium enolate (pre-form)



kinetic enolate (pre-form)



thermodynamic enolate (not formed under these conditions)