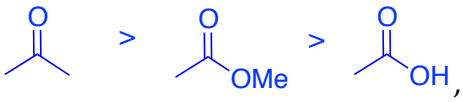
CHM2123 Problem Set #6: Reactions of Aldehydes and Ketones Under Basic Conditions

Assigned November 7th , 2013

1. Both of the reactions studied in this experiment rely on the formation of an enolate anion *via* base catalysis, whereby the enolate can react as a nucleophile.

   a) Place the following compounds in order of decreasing enolate stability, and justify your answer. (**2 points**)



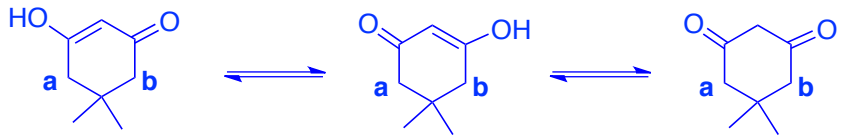
, where the enolates formed are stabilized by resonance. Acetone forms the most stable enolate. The stability of the enolate is directly proportional to the pKa of the alpha-hydrogen. The alpha-hydrogens of acetone have a pKa of ~20, whereas those of esters and carboxylic acids are roughly 25.

The enolate of acetone has two resonance contributors, while the enolates of methyl acetate and acetic acid each have three resonance contributors, but the electron donating properties of their functional groups increase the negative charge on the carbon and thus destabilize the enolates.

In the presence of one eq. base, the carboxylic acid will be deprotonated at the O-H. The formation of a carboxylate enolate is possible with lithium diisopropylamine, but the resulting enolate is considerably more basic and reactive (ie. the least stable) relative to ketone enolates.

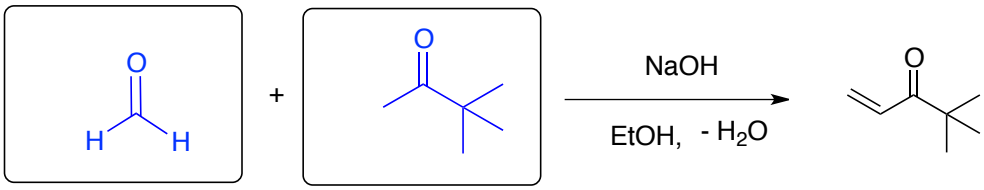
*(**1 point** for the correct order, **0.5 points** if 2/3, **1 point** for justification in terms of acidity of alpha-carbon, resonance)*

   b) Characterization of carbonyl compounds prone to formation of enolates by ^{1}H NMR can produce interesting results. The ^{1}H NMR spectrum of the following molecule indicates that the protons of carbons **a** and **b** give one single signal. Explain this observation. (**1 point**)



*One single signal (a singlet) is observed for the four hydrogens on carbons **a** and **b** under **acid/base** conditions. These hydrogens are all considered **equivalent** due to the **keto-enol tautomerization. (0.5 points** tautomer, resonance, **0.5 points** acid/base environment)*

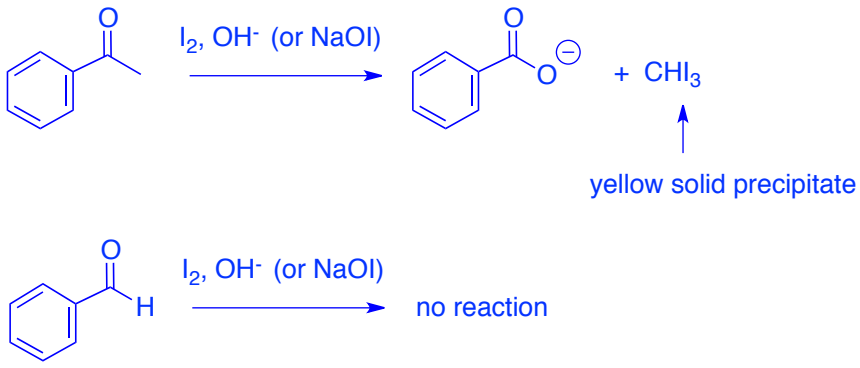
2. Provide the starting materials for the following Aldol condensation reaction. (**2 points**)



***1 point** each*

3. Robert Nadon, one of our technicians in undergrad chem lab, found two jugs of reagents containing acetophenone and benzaldehyde on the shelf for exp. 6, but the labels have peeled off. Using your knowledge of enolate chemistry, *briefly* describe a single chemical test (with a chemical equation) to help Bob identify which bottle is which without the use of spectroscopy or chromatography. (**2 points**)

Haloform reaction:

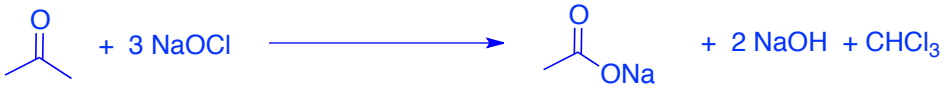


*(**1 point** Haloform reaction, **1 point** for test by formation of yellow solid)*

- *Tollens silver mirror test, while this would identify the aldehyde, does not use enolate chemistry as asked. (**0 points**)*
- *Use of NaOCl will not form a yellow solid precipitate*

4. The haloform reaction is executed in this experiment to synthesize benzoic acid from a methyl ketone, acetophenone. Provide an explanation for the following steps in the procedure.

a) Why is acetone added at the end of the reaction? Explain with a balanced chemical equation. (**2 points**)



Acetone is added to quench any unreacted hypochlorite via another Haloform reaction.

*(**1 point** equation, **1 point** destroy excess bleach)*

b) Why do you add HCl in step 5? (**1 point**)

To protonate the carboxylate product of the Haloform reaction, and isolate benzoic acid from solution.

*(**0.5 points** protonate, **0.5 points** precipitate final product)*