



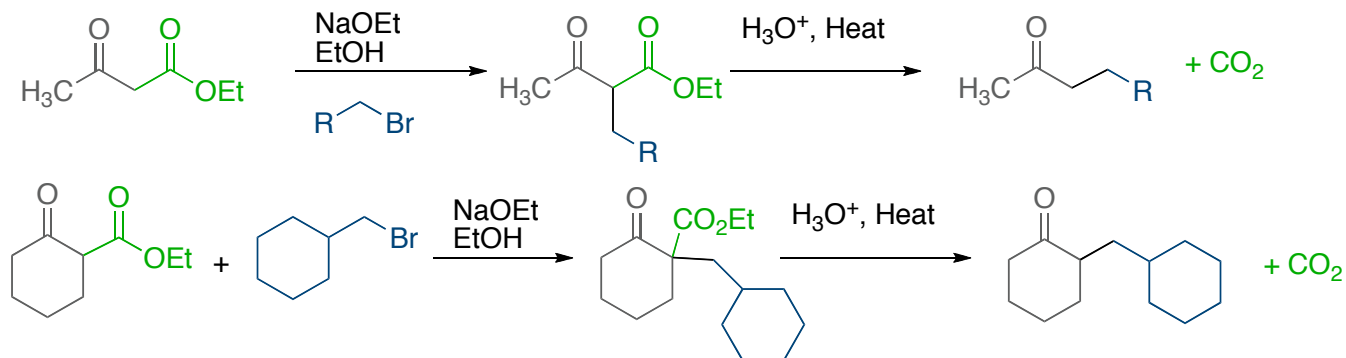
# Chem 342 • Organic Chemistry II

Lecture Summary 30 - 27 Apr 2009

## Chapter 22 - Carboxylic Alpha-Substitution Reactions

### Acetoacetic Ester Synthesis

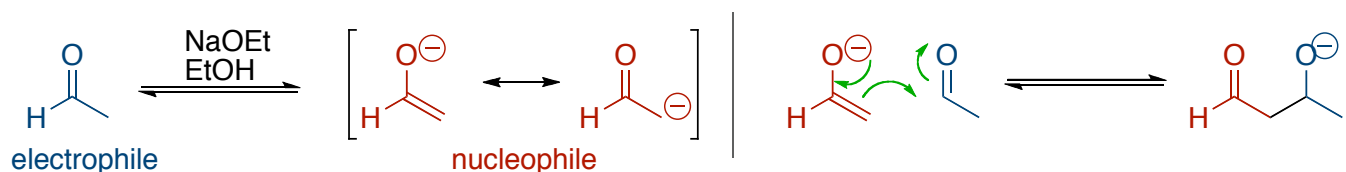
Identical to the malonic ester synthesis, if one of the carbonyls is a ketone instead of an ester, you can add the equivalent of acetone to an alkyl halide. Note that only the Carboxylic Acid part cleaves off in the end, not the Ketone part.



## Chapter 23 - Carbonyl Condensation Reactions

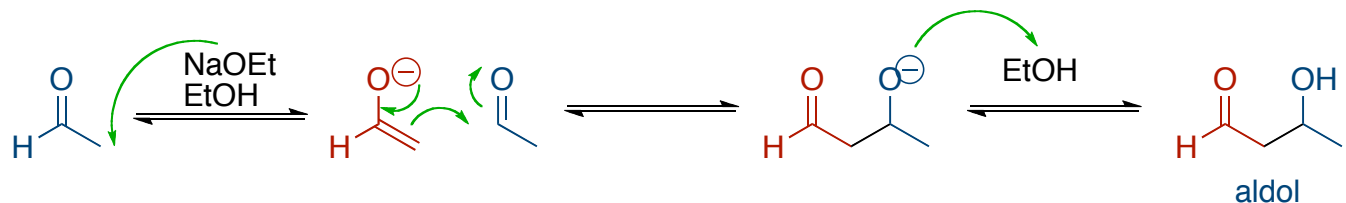
### Carbonyls and Enolates

Carbonyl compounds generally react as an electrophile. That is, nucleophiles readily add to the carbonyl carbon. However, when deprotonated, an enolate is a nucleophile. Thus, when ketones and aldehydes are treated with bases that result in equilibrium between the carbonyl and the enolate (eg. alcoxides), they can react with each other. This we call a carbonyl condensation reaction.

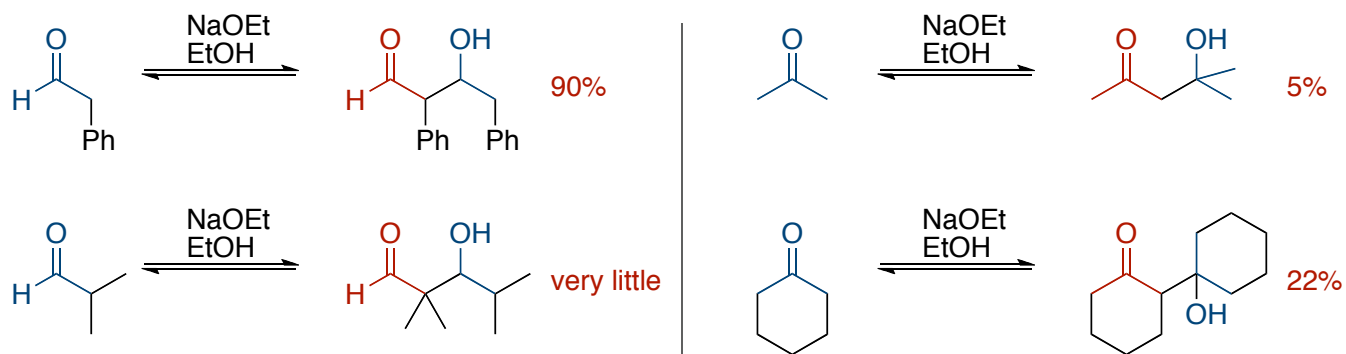


### Aldol Reaction

The product of the reaction of an enolate with an aldehyde contains aldehyde and alcohol functional groups. Thus, this is referred to as an aldol. The mechanism for the aldol reaction is base catalyzed. It is also readily reversible.

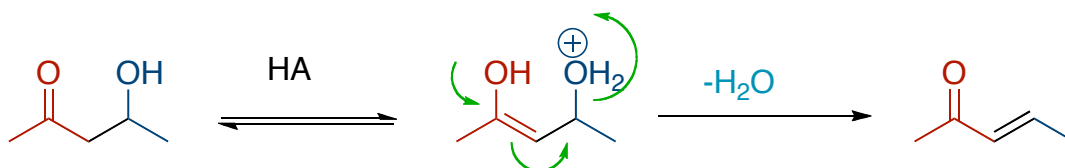
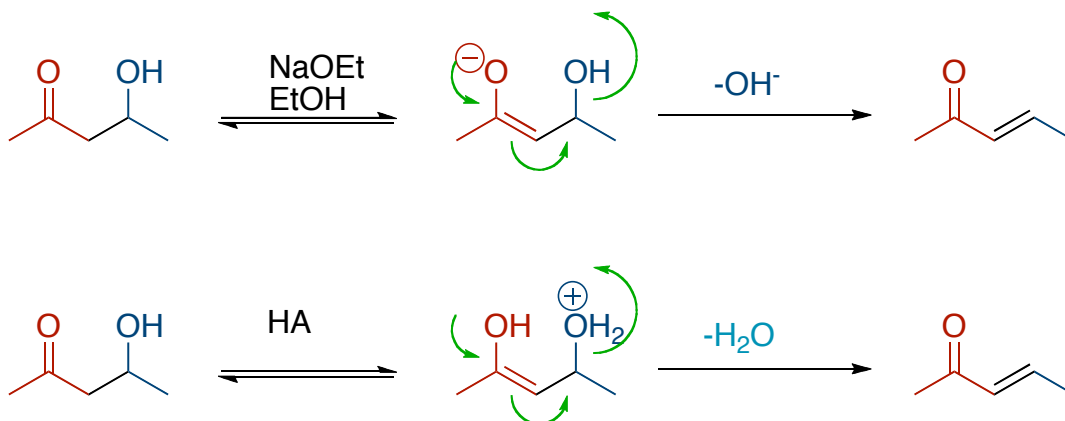
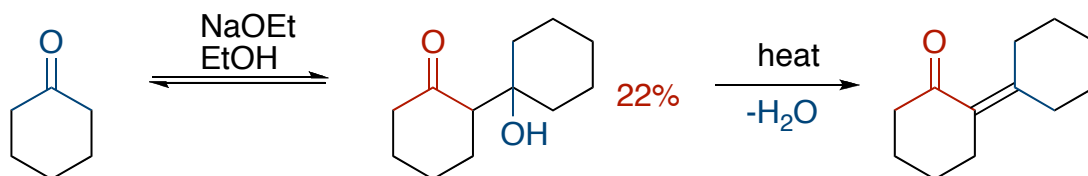


Since the reaction is reversible, the success of the reaction depends on the steric nature of the product. The more crowded it is, the more the equilibrium will shift to the starting materials. In general,  $\alpha$ -branched aldehydes are poorer, as are ketones.



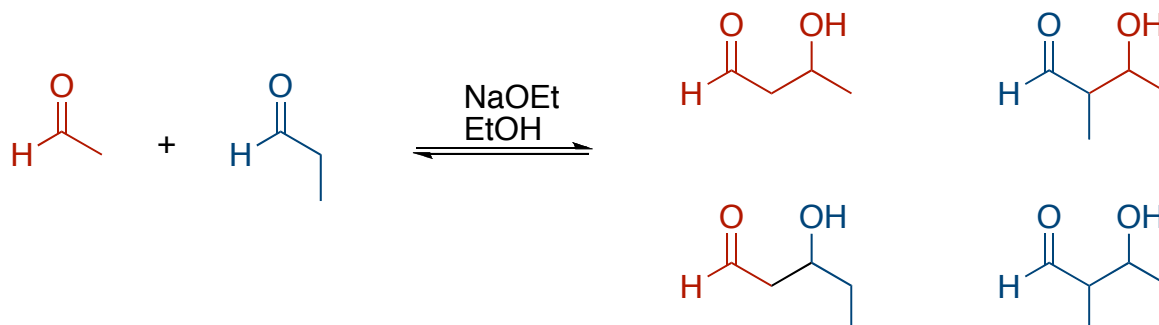
## Dehydration of Aldol Products

Beta-hydroxy carbonyl compounds, the products of an aldol reaction, readily undergo dehydration to afford a conjugated alkene. Usually this requires little more than the application of a little more heat to the reaction. The process is base or acid catalyzed. Thus, if the aldol products are isolated and treated with acid, they can also undergo dehydration readily.

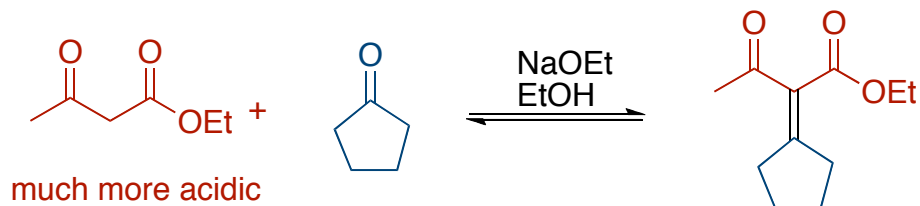
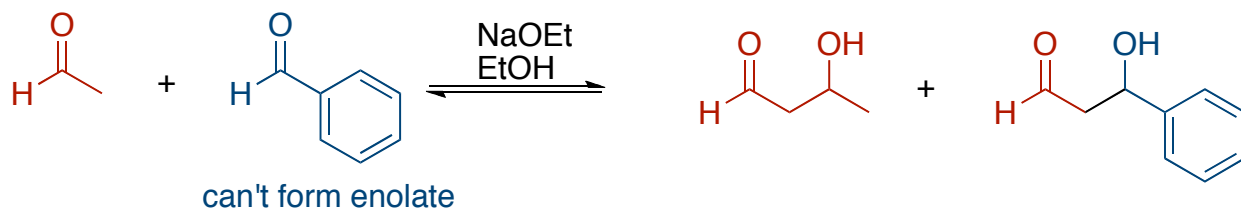


## Mixed Aldols

Aldol reactions between two different enolizable carbonyls is difficult to do without forming a mixture of products. These come from self-condensation and from cross-condensations.



Some of the possibilities can be reduced by utilizing one of the carbonyls that does not have enolizable alpha-protons. Another way to get more selectivity is to utilize a dicarbonyl compounds that is much more acidic than an aldehyde or ketone.

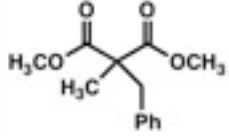
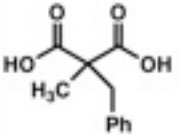
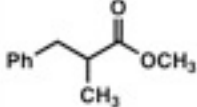


## Daily Quiz

Q: What is the product of the following sequence of reactions?

COC(=O)CC(=O)OC

 1) NaOCH<sub>3</sub>, PhCH<sub>2</sub>Br  
 2) NaOCH<sub>3</sub>, CH<sub>3</sub>I  
 3) H<sub>3</sub>O<sup>+</sup>, heat
 
→

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