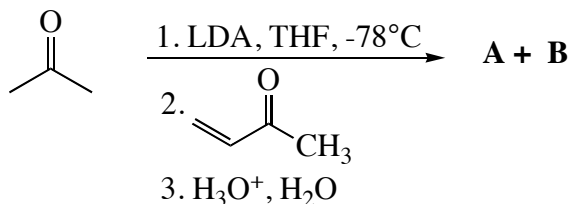


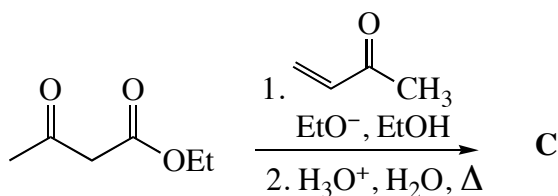
51C Practice Problems 9
Spring, 2019

1. In a Michael reaction, an enolate adds 1,4 to an α,β -unsaturated carbonyl. Unstabilized enolates do not work well in the Michael reaction, because 1,2 addition strongly competes (will get a mixture of 1,2 and 1,4 addition.)
- a. Show the two products that you would isolate if the enolate of acetone reacts with methyl vinyl ketone (MVK).

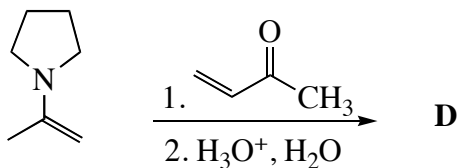


To make this reaction give only 1,4 addition, you can use an acetoacetic ester, which gives a stabilized enolate, or you can use the enamine of acetone. When an enamine is used as a nucleophile in a Michael reaction, the reaction is called a *Stork enamine reaction*. The Stork enamine reaction gives exclusive 1,4-addition.

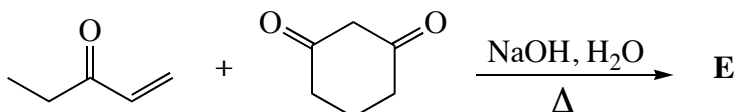
- b. Predict the product in the following Michael reaction:



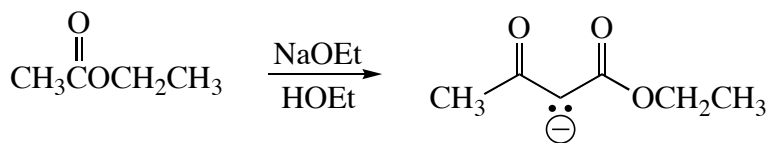
- c. Predict the product of the following *Stork enamine reaction*:



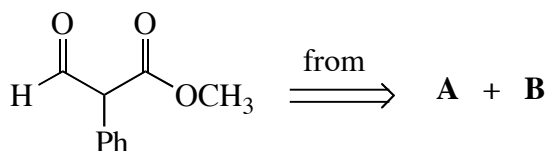
- d. When the product of a Michael reaction is treated with NaOH, H₂O, and heat, a Robinson Annulation occurs. Draw the product of the following Robinson Annulation and provide a mechanism for its formation:



2. a. Provide a mechanism for the following Claisen condensation:



- b. Ethoxide ion is used as the base in the condensation above to avoid some unwanted reactions. Show what side reactions would occur if the following bases were used: NaOCH_3 or NaOH
- c. Esters with only one α -hydrogen generally give poor yields in the Claisen Condensation. Why?
3. Show the two organic starting materials that would be used to synthesize the following β -keto ester by a Crossed-Claisen Condensation. Give conditions for this synthesis.



4. Provide reagents and major product for each of the following reactions. For reagents, if more than one step is required, number each step.

