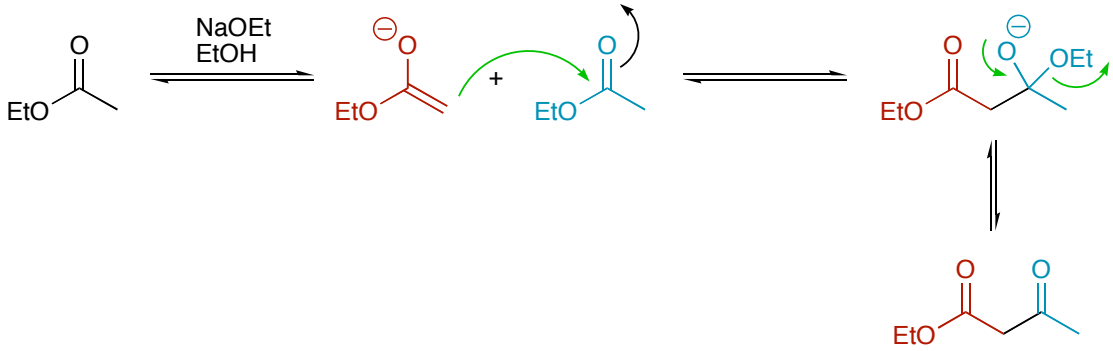
Chapter 22 - Carboxylic Alpha-Substitution Reactions

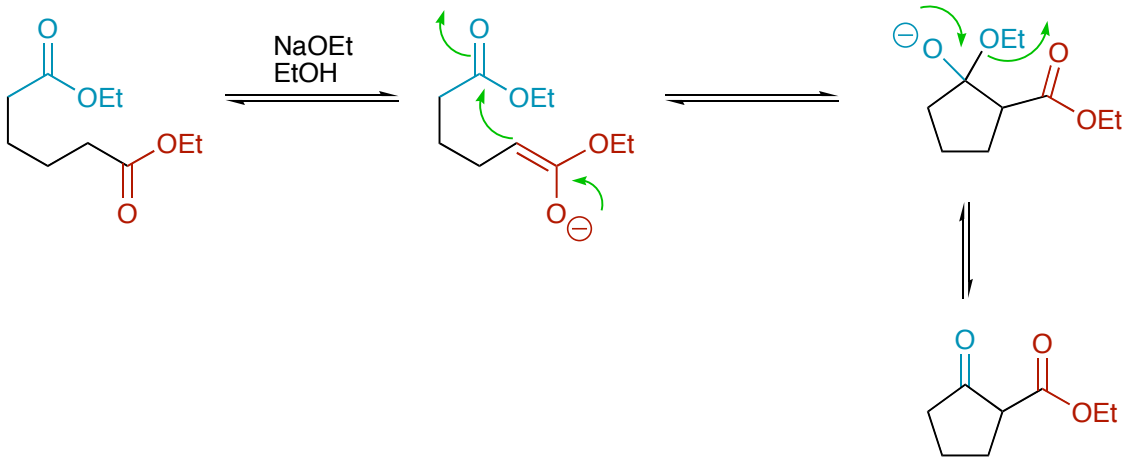
Claisen Condensation

The Claisen Condensation is very similar to an aldol reaction, except it is carried out with esters rather than aldehydes or ketones. This allows for the formation of a ketoester product as the intermediate loses ethoxide as a leaving group. A full equivalent of base is required for the Claisen condensation due to the product being more acidic than the starting ester.



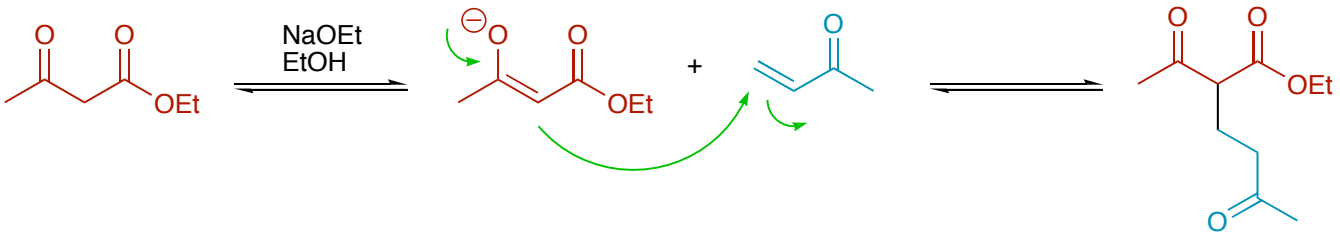
Dieckmann Cyclization

The Dieckmann Cyclization is just intramolecular version of the Claisen Condensation.



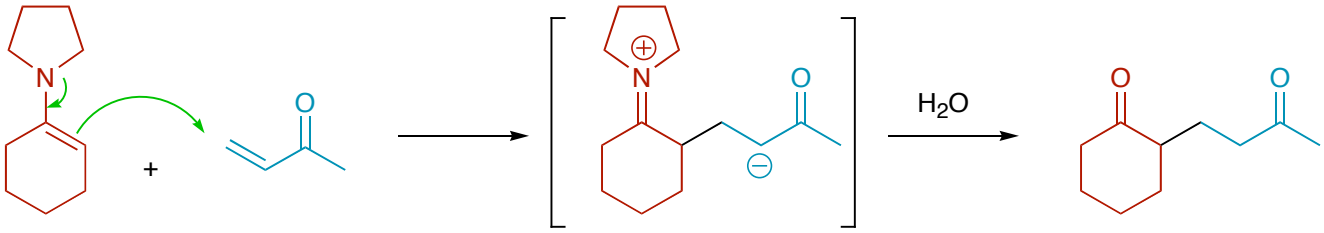
Michael Reaction

Like amines and Gilman reagents, enolates will react with unsaturated carbonyls at the beta carbon.



Stork Enamine Reactions

Enamines also participate in Michael reactions quite readily. This offers some advantages over using enolates as there are no strong bases used. Note that the intermediates are not isolated, but the imine is hydrolyzed at the end to afford the ketone.



Robinson Annulation

Rings can be made from two different molecules (an annulation reaction) by combining the Michael Reaction and the Aldol Condensation. There are many systems which have been designed to proceed with multiple steps all in one reaction pot.