Chem 2062 Spring 2006
Quiz 4 (Take-home)
Due Tue, May 9 at noon

1. Each of the following compounds can be produced by one of the α-carbon substitution reactions we discussed.

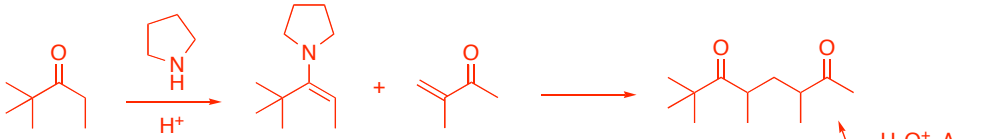
   Perform retrosynthetic analysis on the compounds below, showing the C-C bond(s) that are formed, and construct a forward reaction showing both the enolate formation as well as the substitution reaction. For full credit, the products must be able to be produced in good yield with minimal side-products, so choose your disconnection carefully.

   State the name of the reaction in each case. No mechanisms are necessary.

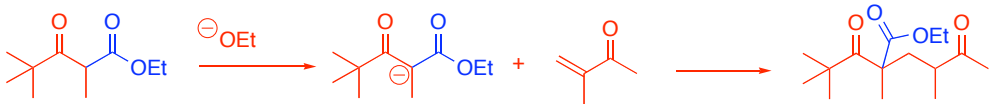
   Excellent performance on this question can earn you up to 5 extra points toward Exam 4.

a.

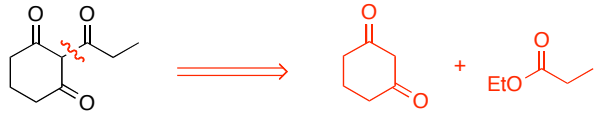
Use an enamine since both the reactants have α hydrogens. Michael reaction will proceed cleanly.

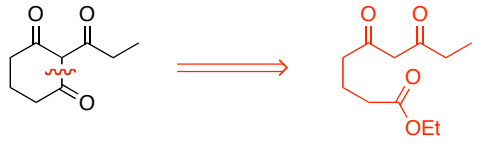


Or use a temporary ester group (similar to malonic ester synthesis).
Only one enolate will form from the ß-dicarbonyl compound.

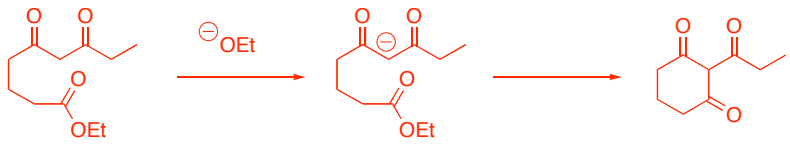


b.

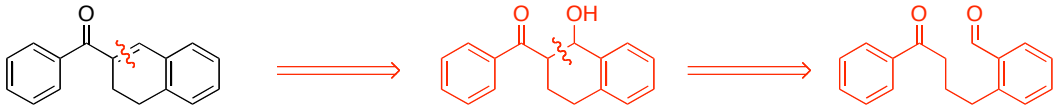




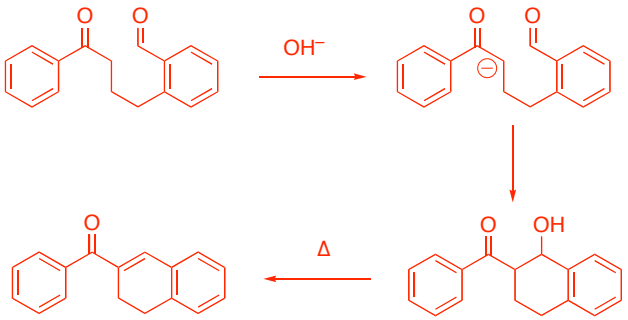
Either of these Claisen disconnections will proceed cleanly for the most part, since the hydrogen between the 2 carbonyls is more acidic than any other α hydrogen. The bottom reaction is slightly preferable because the ring formation is intramolecular - less chance of side-products.



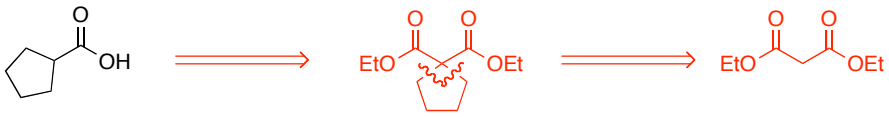
c.



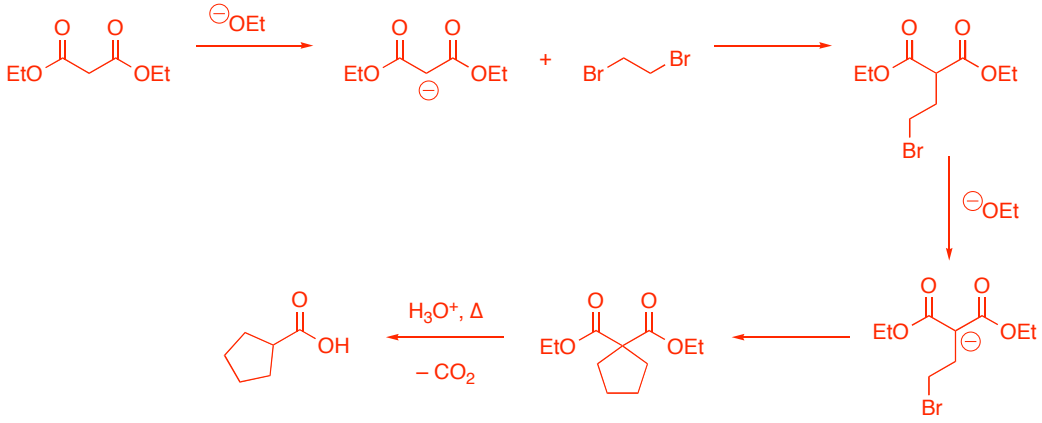
An intramolecular aldol condensation and dehydration. Like the above problem, this reaction will be very clean due to the fact that the bond-forming reaction is intramolecular. Also, this compound only has one type of α hydrogen. Even though hydroxide is not strong enough to fully deprotonate the ketone, the reaction will be driven to completion by the loss of water



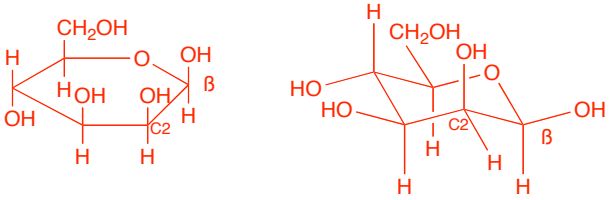
d.



In this malonic ester synthesis, the malonic ester must be alkylated twice by the same compound to make the ring.

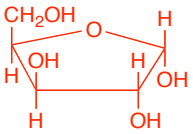


2. Draw Haworth projections *and* chairs for the following compounds:
   a. ß-D-mannopyranose (C2 epimer of glucose) -
   What is the name of its anomer? You don't need to draw its structure.

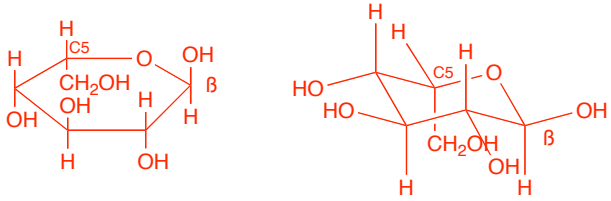


Its anomer is a-D-mannopyranose, which would have the opposite configuration at C1, the hemiacetal carbon.

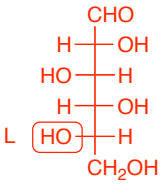
   b. α-D-xylofuranose (C3 epimer of ribose) - draw the Haworth projection only.



   c. ß-L-idopyranose (C5 epimer of glucose) - why is it L?



It is L because the bottom hydroxyl in the open chain's Fischer projection is pointed to the left.



3. An imaginary disacaccharide contains a D-glucopyranose joined with a D-mannopyranose (like in 2a) by a ß-1,4' linkage. Draw this disaccharide as chairs.