

Organic Chemistry c3444y

3rd Hour Exam

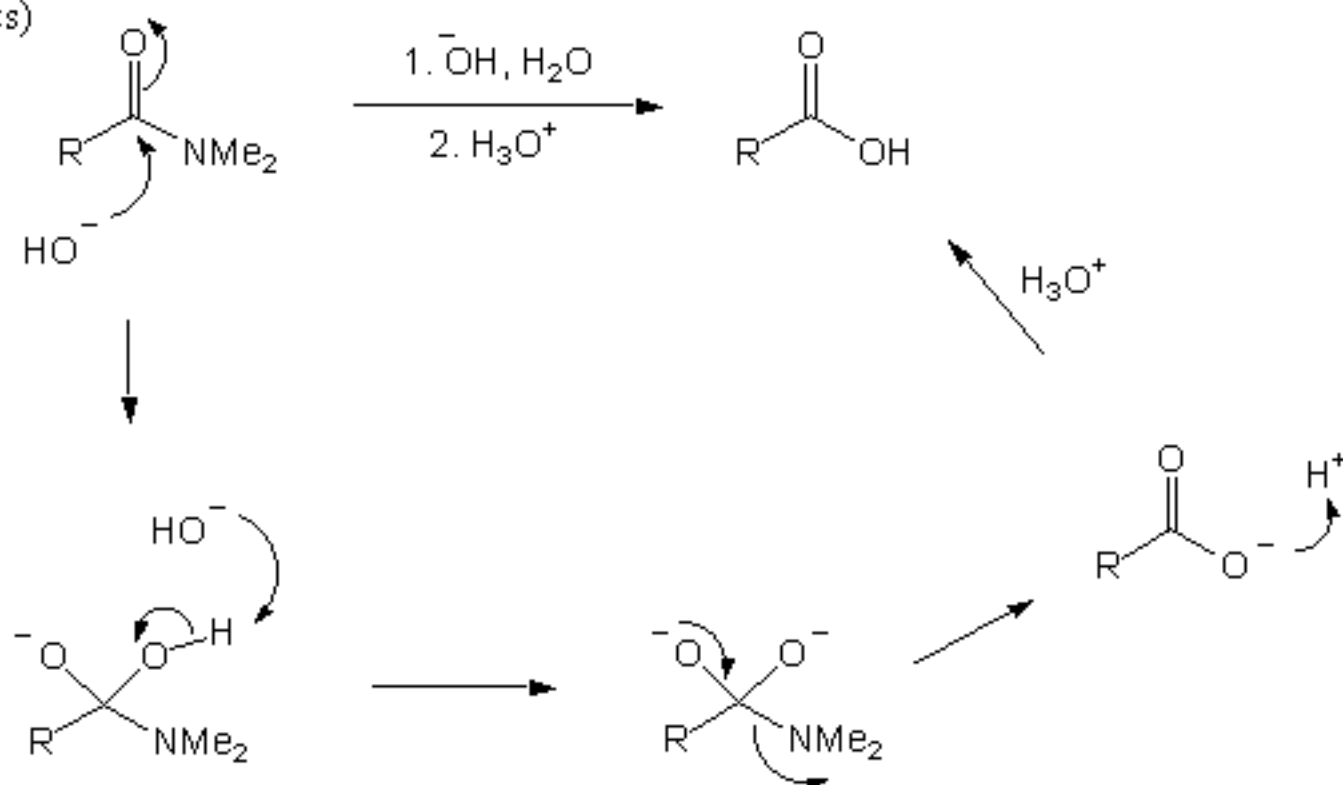
Monday, March 27, 2000

Prof. Leighton

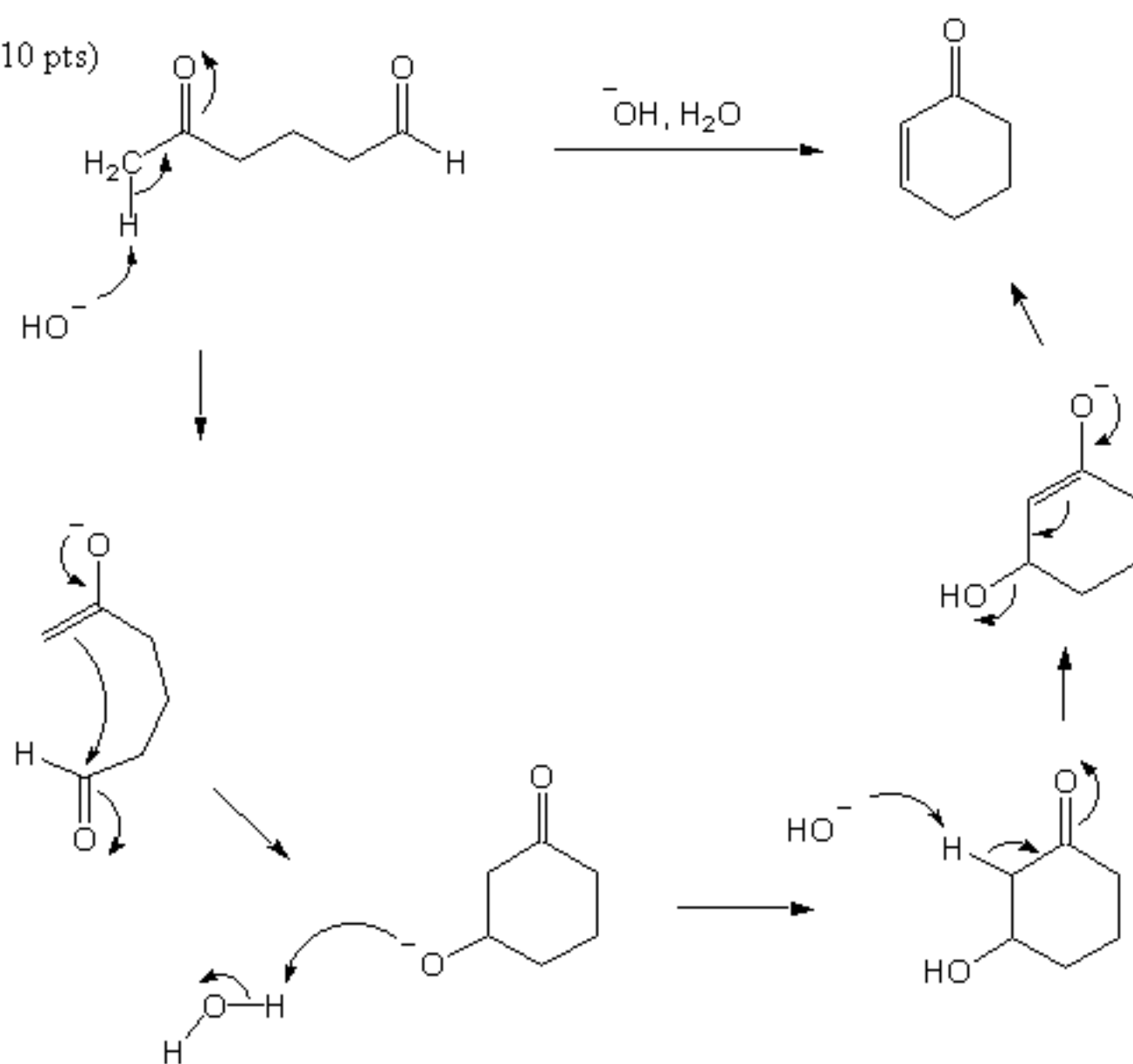
Answer Key

1. Provide detailed mechanisms for the following transformations:

a. (10 pts)

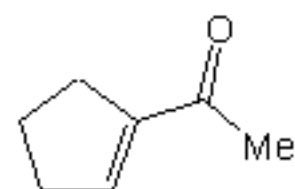
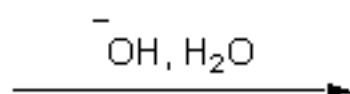
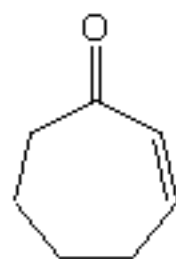


b. (10 pts)

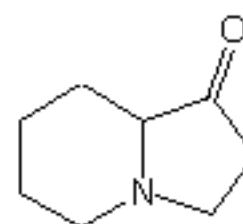
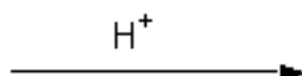
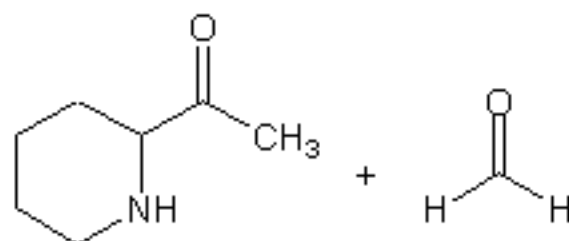


2. Predict the major product of the following reactions:

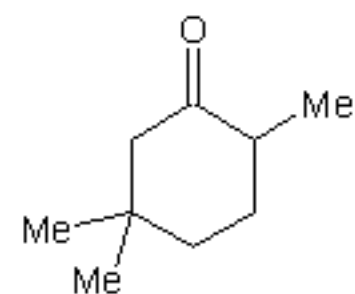
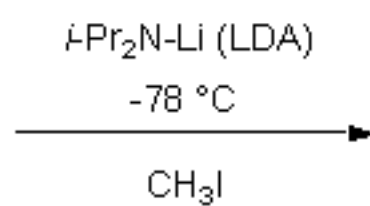
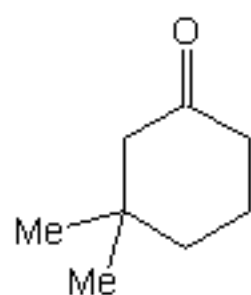
a. (10 pts)



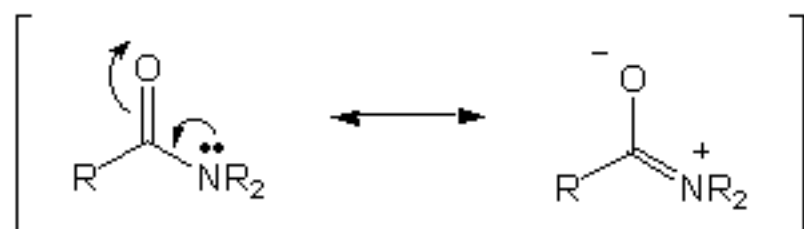
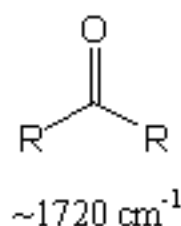
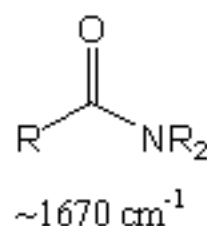
b. (10 pts)



c. (5 pts)

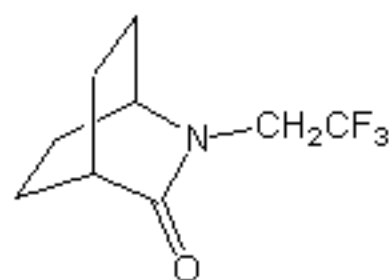


3. a. (5 pts) Using resonance structures, provide a *brief* explanation for the observation that amides typically display a lower C=O stretching frequency in the IR spectra relative to ketones:



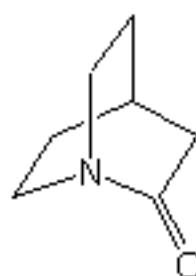
For amides, this resonance structure is a strong contributor. Thus, amide carbonyls have more single bond character than our reference ketones. The C=O bonds are therefore longer and "looser" leading to a lower frequency stretch in the IR spectra.

- b. (10 pts) Rank the three compounds shown below from lowest frequency to highest frequency for the C=O stretch in the IR spectra. Please clearly write one letter in each box.



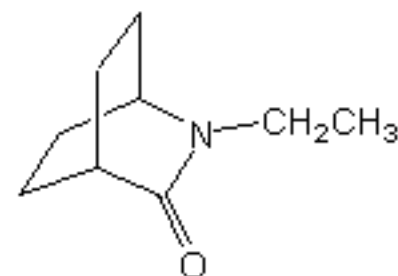
A

Normal amide, however, relative to C, N is less strongly donating because of the CF₃ group. Thus the effect is weaker than in C, and we would expect a higher frequency C=O stretch than C.



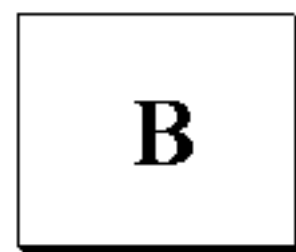
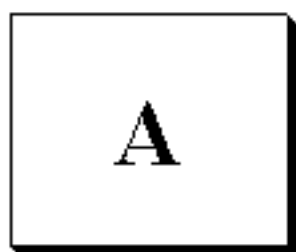
B

*No Resonance!
Just a C=O attached to a Nitrogen. Should have the highest frequency C=O stretch, in that there is no significant resonance structure with a C-O single bond.*



C

Normal Amide.

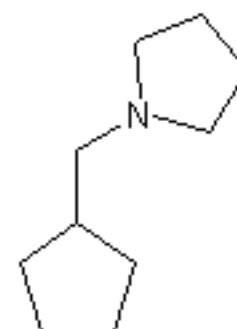
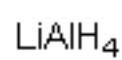
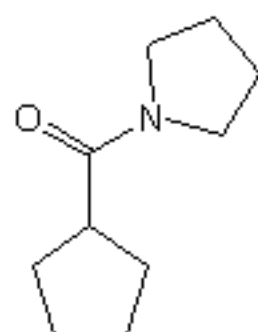
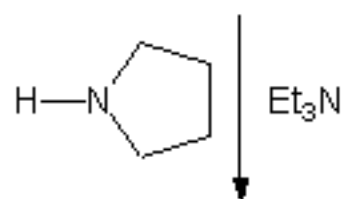
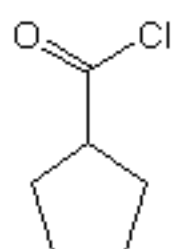
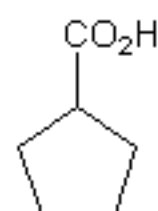
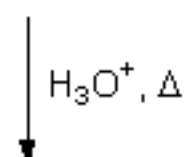
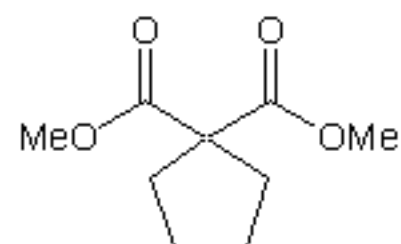
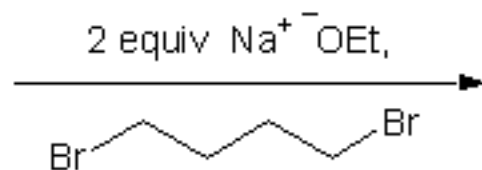
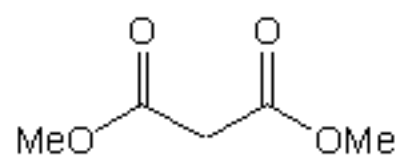


Lowest
Frequency

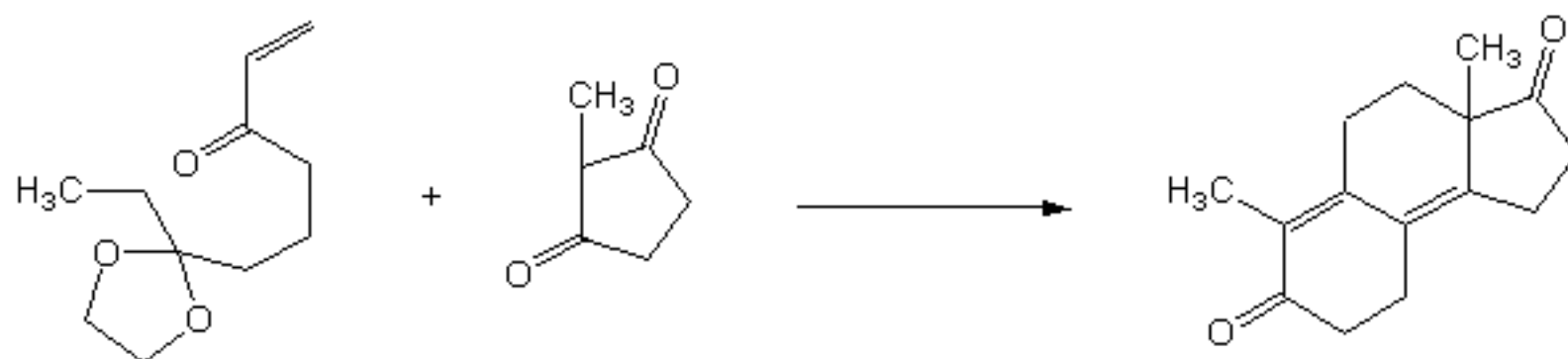


Highest
Frequency

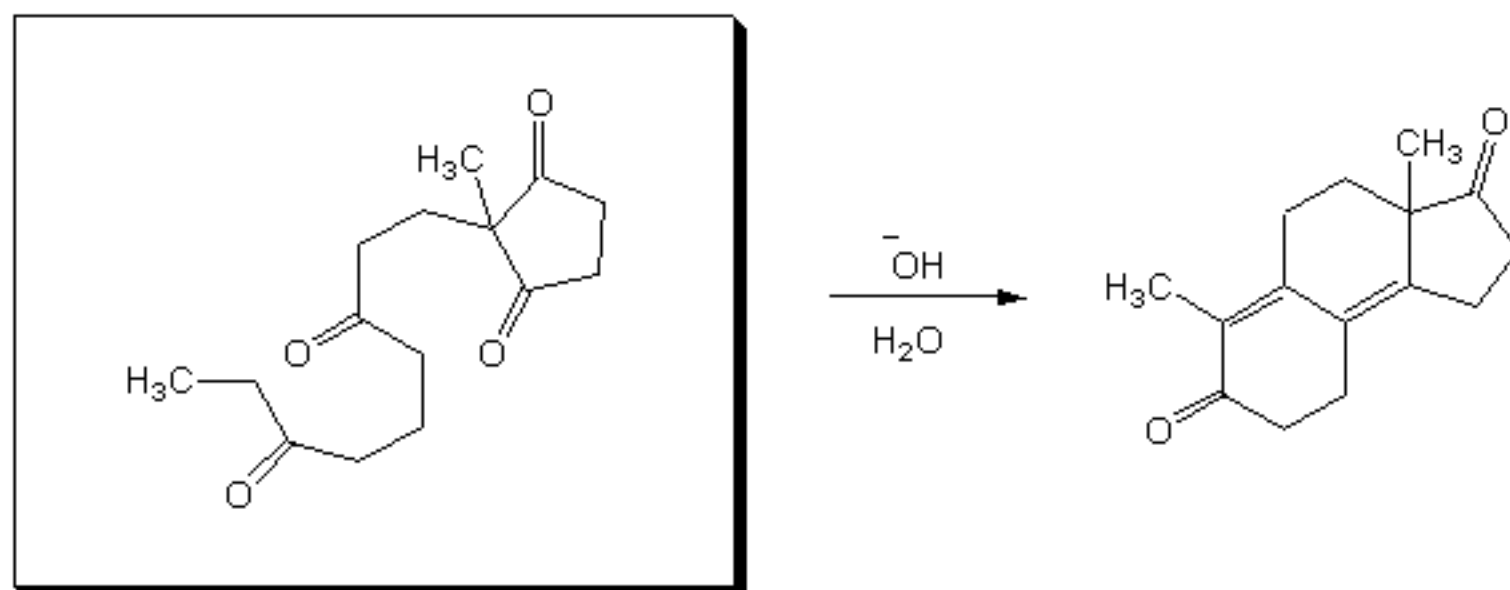
4. (20pts) Provide the missing products of the following sequence of reactions:



5. The illustrated tricyclic compound may be synthesized in only a few steps from the illustrated starting materials. If you understand the Robinson Annulation, then you can understand this modified version of it.



- a. (10 pts) The last step involves *two* aldol condensations, one after the other. The starting material for this double aldol condensation is a tetraketone. Thinking "backwards" from the product, provide the structure of this tetraketone:



- b. (10 pts) Show how you might synthesize the tetraketone you have just identified in two steps from the starting materials provided above.

