Organic Chemistry c3444y

3rd Hour Exam

Monday, March 26, 2001

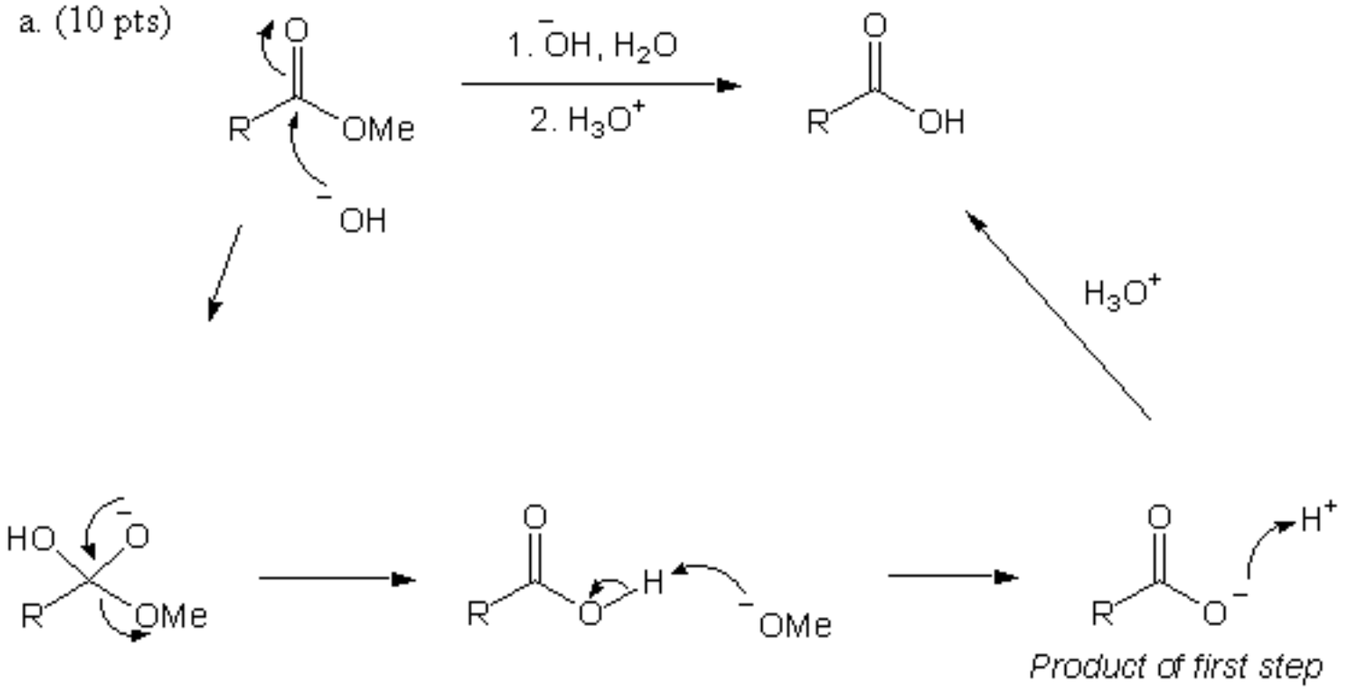
Prof. Leighton

Answer Key

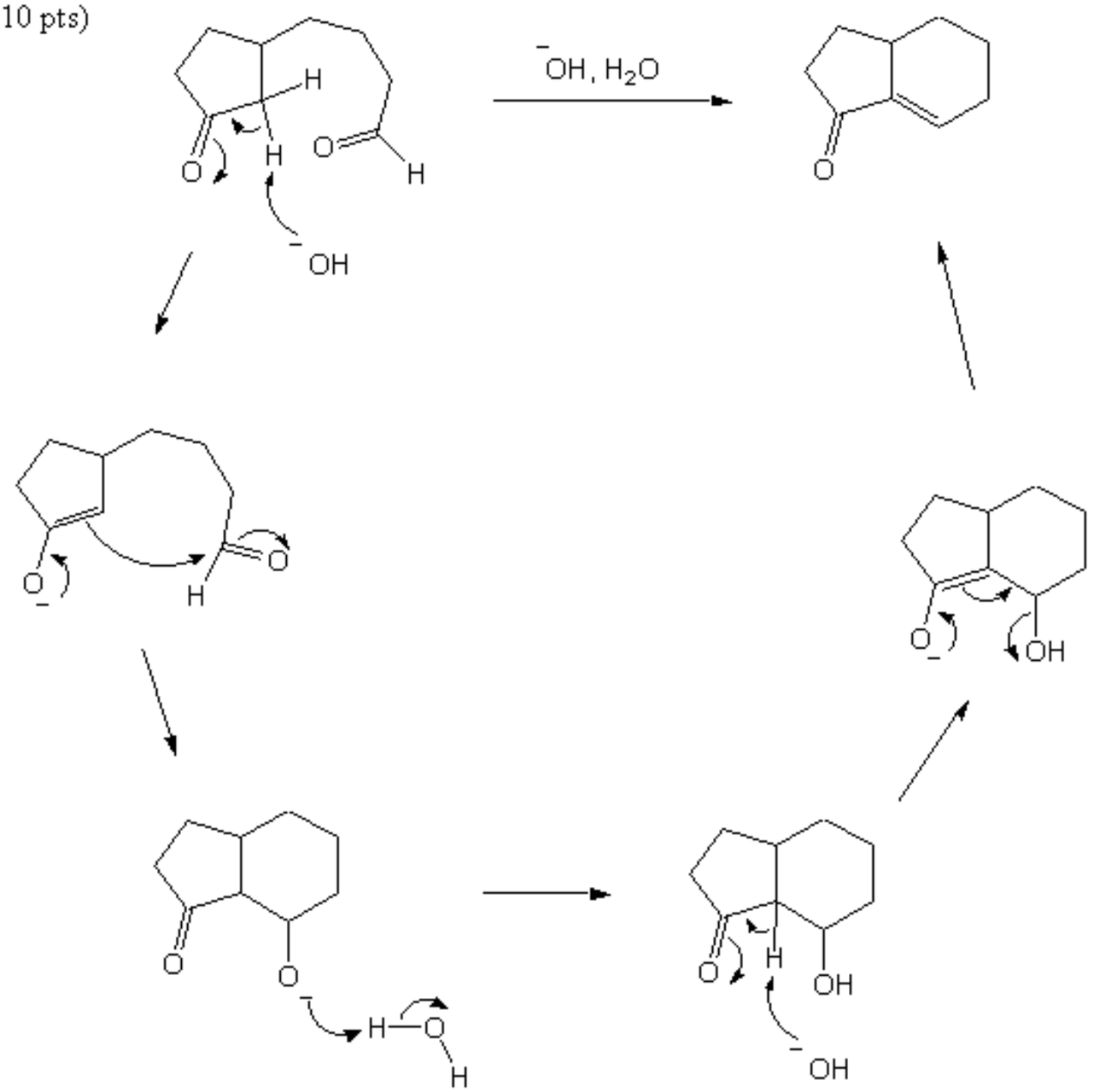
Name: _____

1. Provide detailed mechanisms for the following transformations:

a. (10 pts)



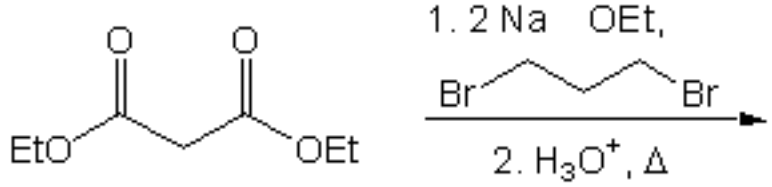
b. (10 pts)

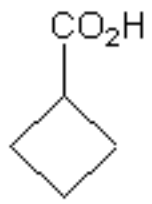


Name: _____

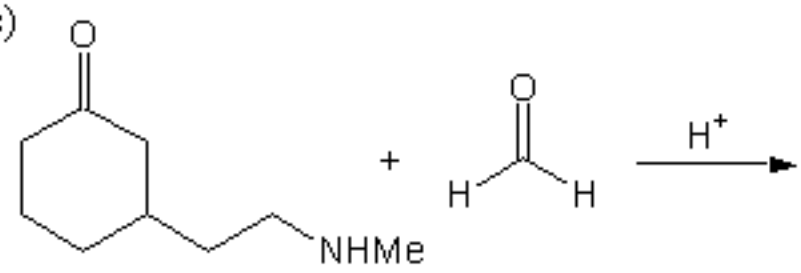
2. Predict the major product of the following reactions:

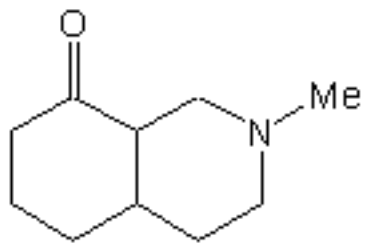
a. (9 pts)



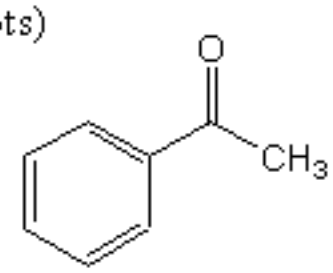


b. (8 pts)

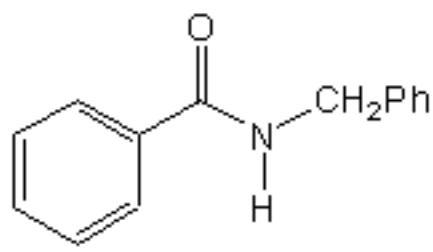




c. (8 pts)

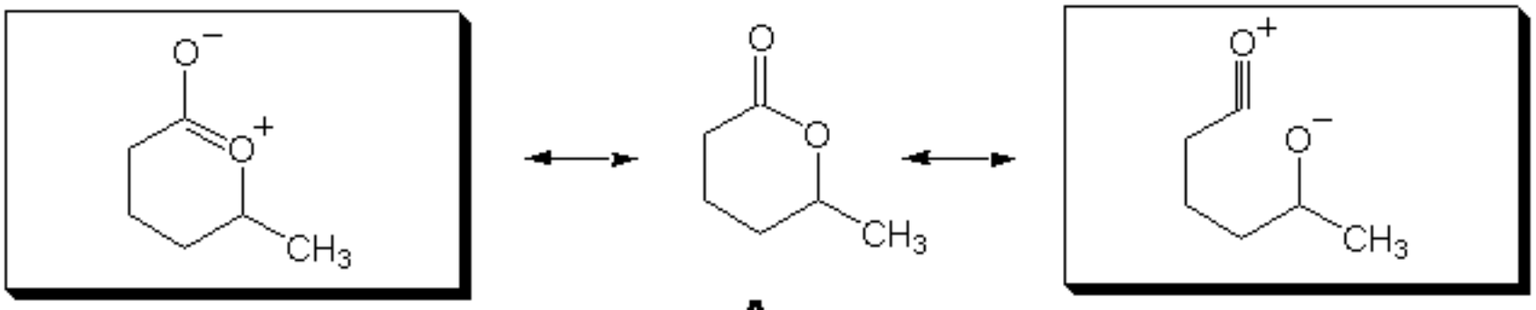


1. ^-OH, Br_2 (excess)
2. H_3O^+
3. $SOCl_2$
4. $PhCH_2NH_2$, Et_3N



Name: _____

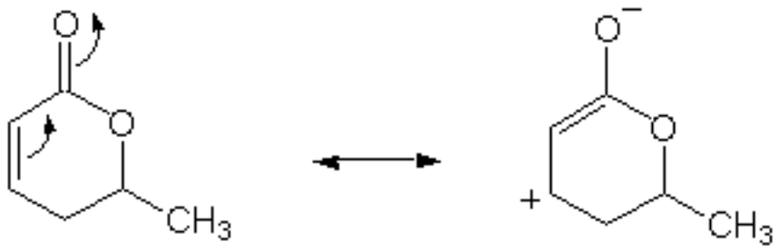
3. a. (10 pts) In class we discussed two different resonance structures for esters. First draw these resonance structures using lactone **A**. Then underneath each resonance structure predict what you think would be the effect of that resonance structure on the IR C=O stretch relative to the reference of ~1720 cm^{-1} for ketones.



Lower **A** *Higher*

b. (5 pts) Would you expect the frequency of the C=O stretch of lactone **B** to be higher or lower than that of lactone **A**? Use resonance structures to explain your *CONCISE* answer.

B

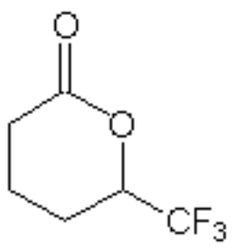


LOWER

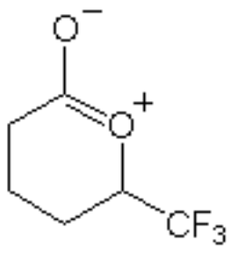
Besides the two above, we have a contribution from this resonance structure in this case. More single bond character, lower frequency C=O stretch.

c. (5 pts) Would you expect the frequency of the C=O stretch of lactone **C** to be higher or lower than that of lactone **A**? Use resonance structures to explain your *CONCISE* answer.

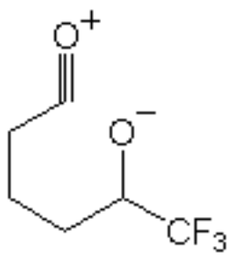
C



HIGHER



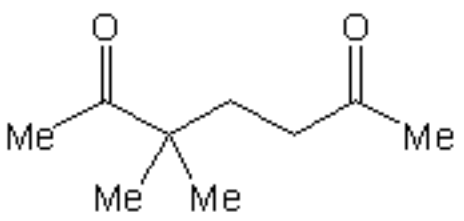
*Because of the inductive effect of the CF_3 group, this resonance structure is **less** important relative to the same structure in **A**.*

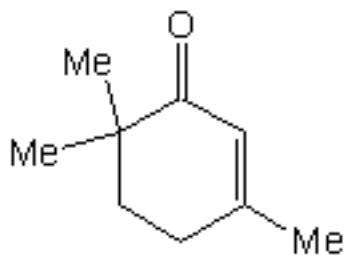


*Because of the inductive effect of the CF_3 group, this resonance structure is **more** important relative to the same structure in **A**. Therefore, more triple bond character, higher frequency C=O stretch.*

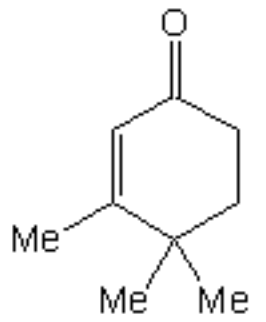
Name: _____

4. a. (6 pts) Consider the following intramolecular aldol condensation. This result is fully consistent with the two rules we use to determine the likely product of intramolecular aldol condensation reactions. State clearly and concisely these two rules.





Product

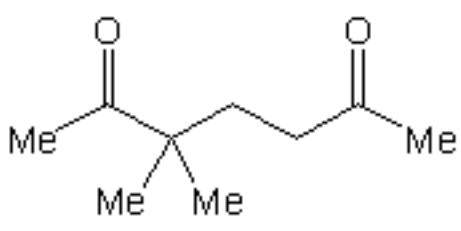


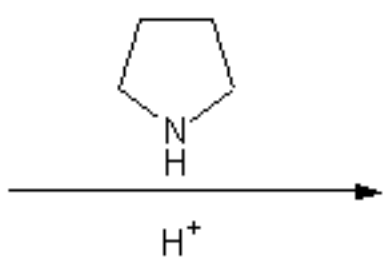
Not Formed

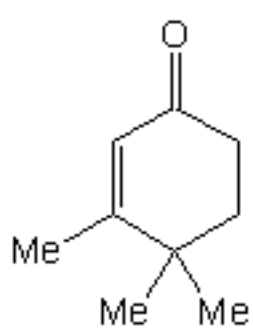
RULE 1: Only form 5 or 6 membered rings.

RULE 2: The less-hindered of the two carbonyls will serve as the electrophile.

b. (14 pts) Interestingly, if the same starting diketone is treated with an amine and some acid, the other product is formed preferentially. Your task is to describe what is happening here. You do not need to write a detailed mechanism, but you do need to show some key intermediates that demonstrate you know what is happening here, and you need to explain why this product is formed and not the same one as in the reaction above (*Hint: this is NOT a Mannich).*

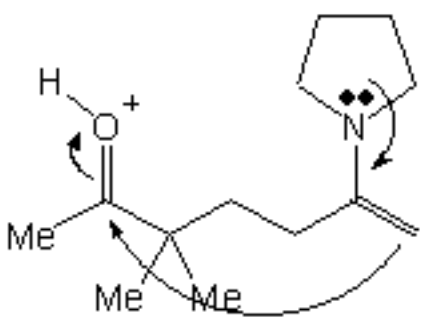






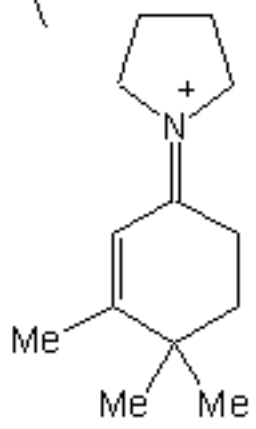
Enamine!

Enamine Formation

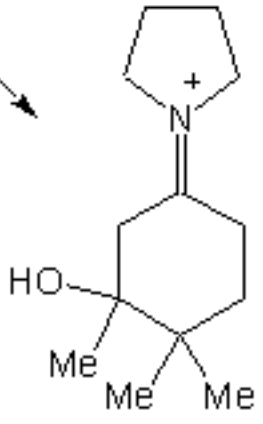


This product is formed because the enamine will form at the ***less*** hindered carbonyl. Therefore, the ***more*** hindered carbonyl will serve as the electrophile here. Thus, by either doing the standard aldol, or using the enamine chemistry, we can select for either product.

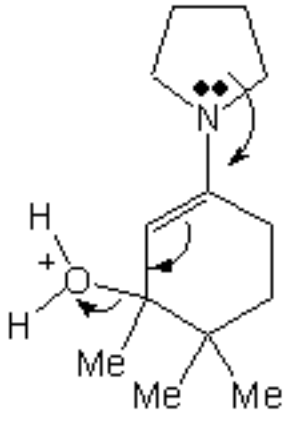
Hydrolysis



Aldol-like Addition



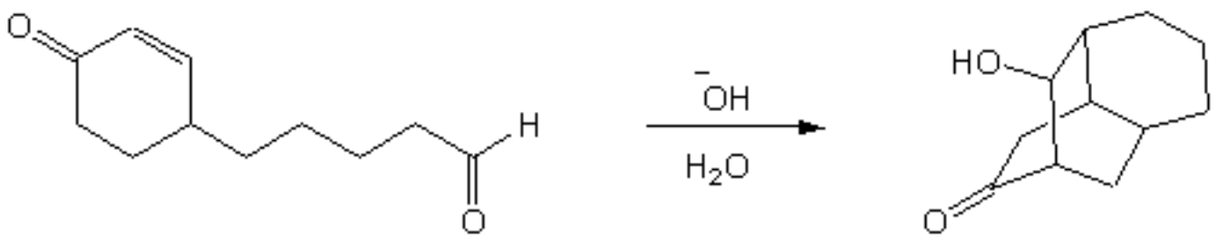
Enamine Formation and Protonation



Elimination

Name: _____

5. (15 pts) Mechanistically, the following reaction can be thought of as a modified Robinson Annulation. Provide a detailed mechanism to account for this amazing reaction:



The first sentence above was intended to be a hint that this is a Michael followed by an aldol.