

Organic Chemistry II (Final Exam)

Name:

Key

Signature:

Recitation Instructor:

Instructions

1. Keep the exam closed until you are instructed to begin.
2. The exam consists of 6 questions. The first thing you should do is make sure that no pages are missing. If a page is missing, notify a proctor immediately.
3. You will have 2 hours.
4. Make sure to show all of your work, and this should fit into the space provided. If you need to use the back of the paper, you must make note of it in the space provided for credit.

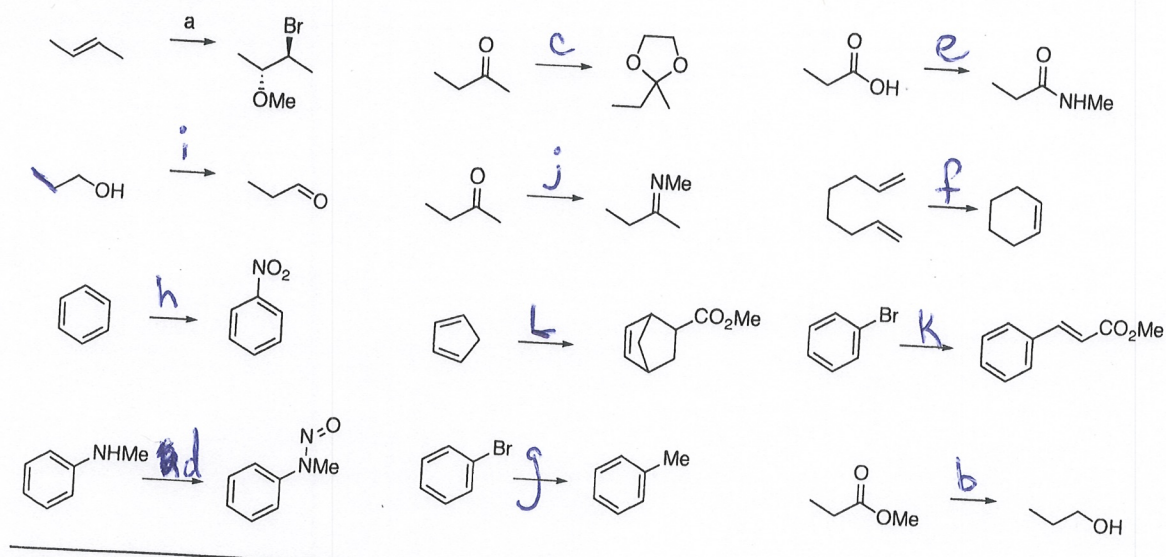
Good Luck!

1. ____ (20 points)
2. ____ (20 points)
3. ____ (25 points)
4. ____ (5 points)
5. ____ (20 points)
6. ____ (10 points)

MOOKIE WILSON, LF When I'm in a slump, I comfort myself by saying if I believe in dinosaurs, then somewhere, they must be believing in me. And if they believe in me, then I can believe in me. Then I bust out.



1. Reaction Knowledge. Chose the most consistent reagents necessary to carry out the following modifications. Show this by putting the associated letter above the reaction arrow, as is done with reaction 'a'. Note: there are more reagents than reactions, and so not all letters will be used (20 points, 2 points each, chose only 10 out of the 11).



- a. Br_2, MeOH
- b. LiAlH_4
- c. $\text{H}_2\text{SO}_4, \text{HOCH}_2\text{CH}_2\text{OH}$
- d. $\text{NaNO}_2, \text{H}_2\text{SO}_4$

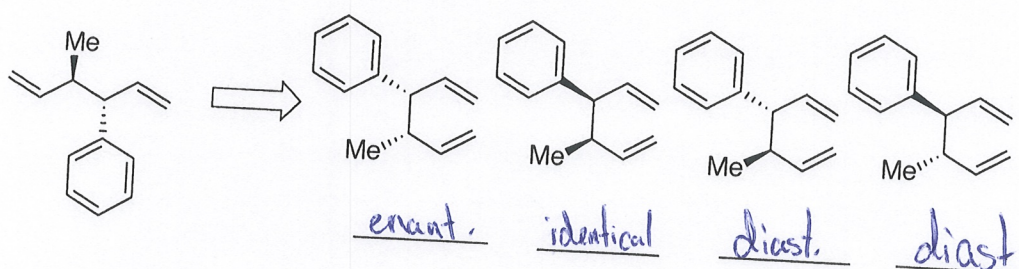
- e. $\text{DCC}, \text{NH}_2\text{Me}$
- f. Grubbs Catalysis 'Ru='
- g. $\text{Pd}(0), \text{Me}_4\text{Sn}$
- h. $\text{H}_2\text{SO}_4, \text{HNO}_3$

- i. PCC
- j. $\text{H}_2\text{SO}_4, \text{NH}_2\text{Me}$
- k. $\text{Pd}(0), \text{Et}_3\text{N}, \text{CH}_2=\text{CHCO}_2\text{Me}$
- l. heat, $\text{CH}_2=\text{CHCO}_2\text{Me}$

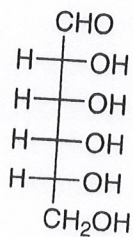
- m. $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$
- n. NaNHMe
- o. Argon, heat
- p. $\text{H}_2\text{NNH}_2, \text{AcOH}$

2. Conformational Perception. (20 points total)

2a. Assign each of the 4 syn periplanar dienes as either enantiomers, diastereomers or identical to the linear diene. (8 points)

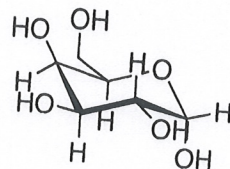
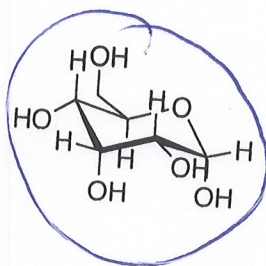
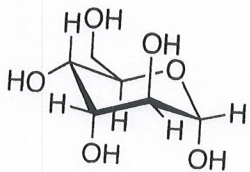


2b. Which one of the following chair conformations are most closely associated with the fisher projection shown (5 points)

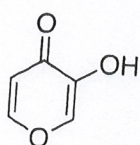


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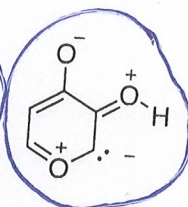
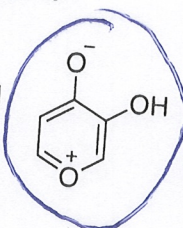
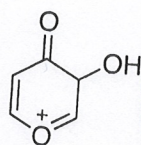
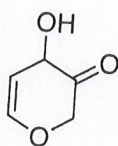
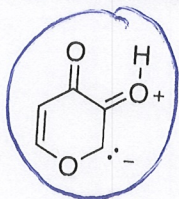


2c. Circle all the molecules that are resonance forms of the molecule shown, and is this molecule aromatic, non-aromatic or neither (5 points)



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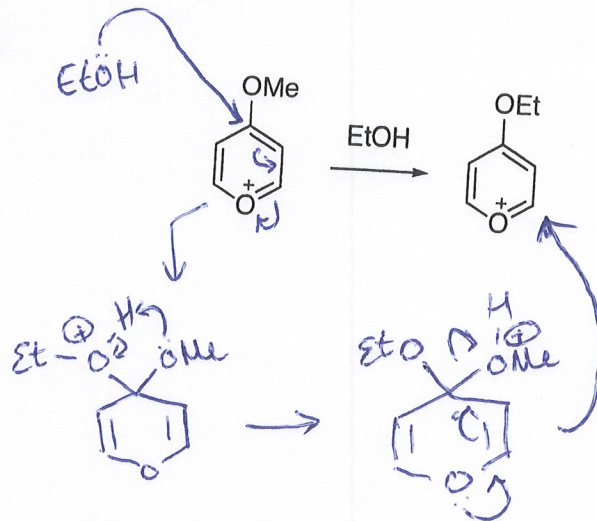


2d. Is the molecule shown in 2c aromatic, antiaromatic or non aromatic. (2 points)

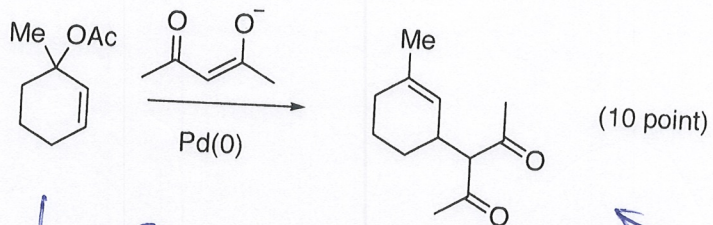
Answer: aromatic

3. **Mechanisms.** Use electron arrow pushing to show mechanisms for the following reactions

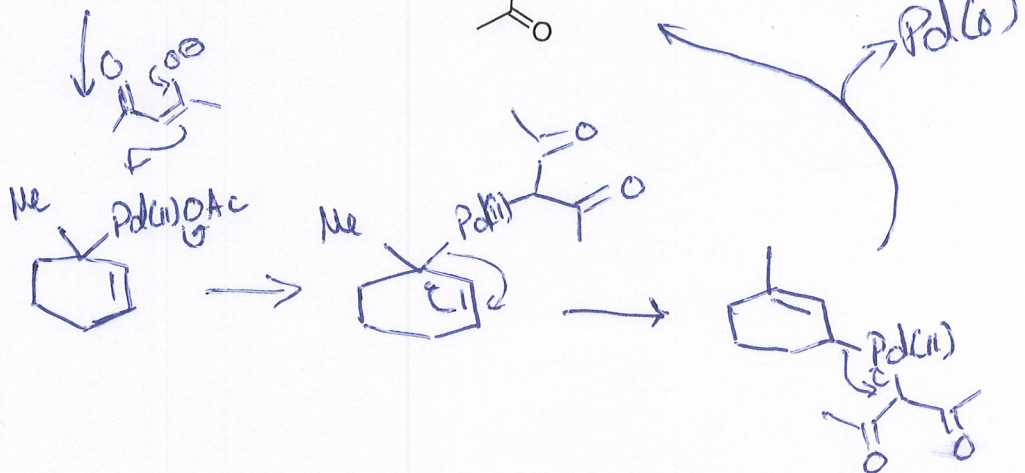
3a. (5 points)



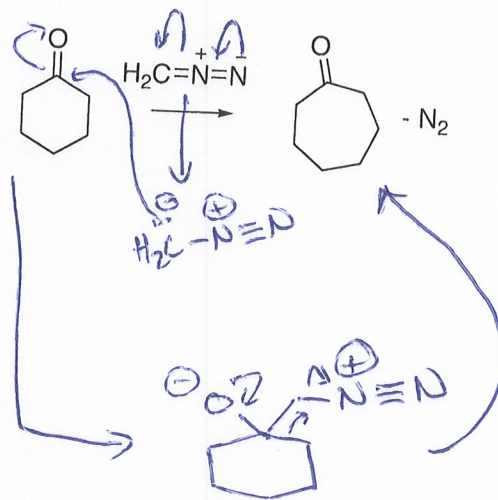
3b. (10 points)



one answer of many

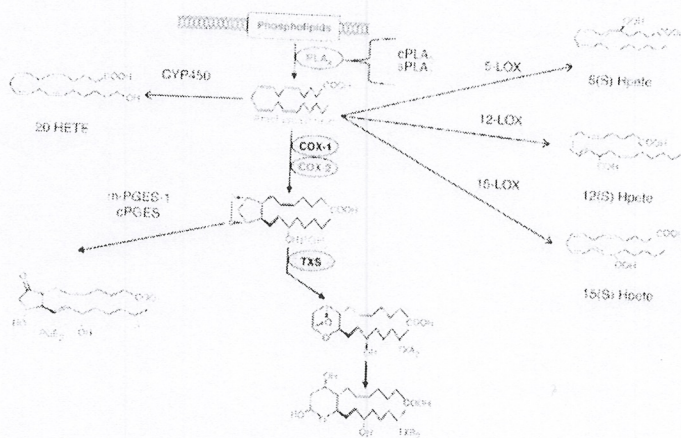


3c. (10 points)



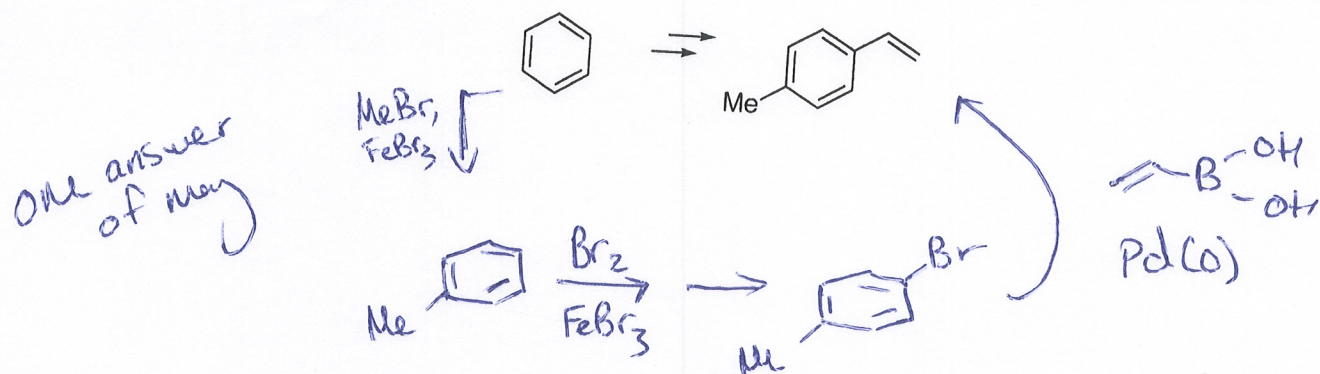
4. Those 5 points from my discussion on the latter chapters I promised. In our overview of lipids, polymers, and sugars, I mentioned how phospholipids can be hydrolyzed by PLA2 to generate arachidonic acid, which can be converted to a variety of molecules called eicosanoids which are biologically important. In less than 5 words, why are eicosanoids, such as prostaglandins, relevant to human health.

I was looking for inflammation, as mentioned (5 points)
in class, but I took many answers.

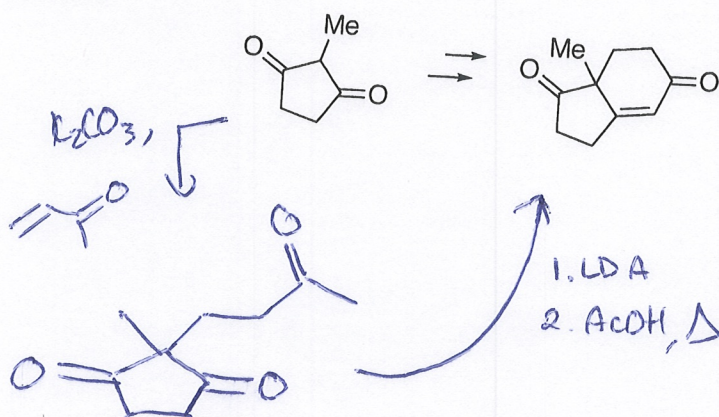


5. **Synthesis.** Propose a sequence of reactants and reagents necessary to carry out the following syntheses. Make sure to show all intermediate products (compounds resulting from each reaction) for full credit. (20 points)

5a. (10 points)

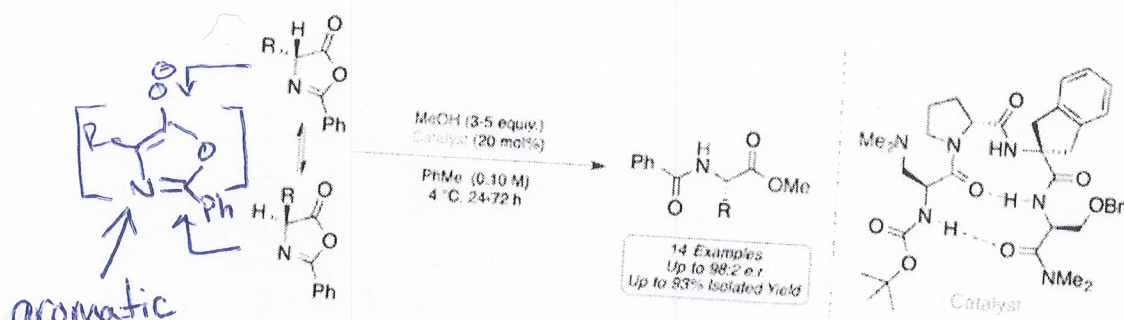


5b (10 points)



6. Concept Questions. (10 points)

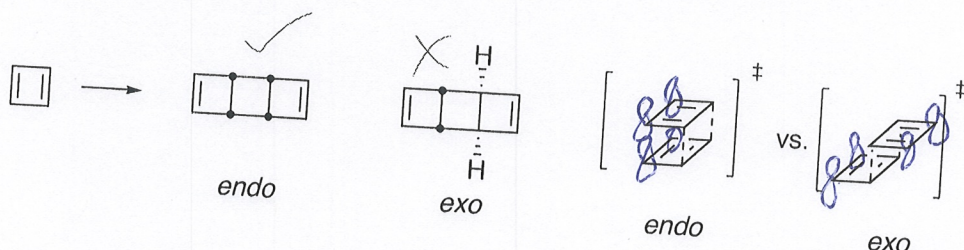
6a. The following is a reaction developed recently in the lab of our most recent Friedman Lecturer, Scott Miller of Yale. The reaction relies upon the rapid interconversion of the two enantiomers of the starting materials, of which one is selectively methanolized by a chiral peptide to provide a single enantiomer of protected amino acids. **In less than 10 words**, using what you have learned this semester, explain why the starting material more readily racemizes and the product does not? (5 points)



aromatic

answer deprotonation and enolization both lead to aromatic intermediate.

6b. Cyclobutadiene undergoes rapid dimerization to form SELECTIVELY the endo product, and not the exo product, as is often observed in Diels-Alder reactions. In class we went beyond simply 'endo rule' and explained the hypothesized molecular basis for endo selectivity based upon the transition state from one reaction to the other (shown on right). **In less than 10 words**, what are the interactions present in the transition state to endo that are absent in the interactions to exo that is believed to provide this selectivity. Make sure to illustrate these interactions to help explain your answer. (10 points)



answer: π - π stacking of non-C-C bond forming π bonds