Massachusetts Institute of Technology
Organic Chemistry 5.13

Monday, December 18, 2006 Prof. Timothy F. Jamison, Dr. Kimberly Berkowski

Final Exam

Name _____

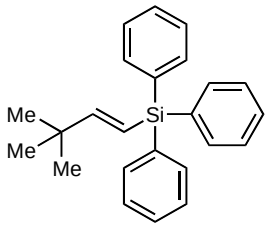
(please both **print** and **sign** your name)

Official Recitation Instructor _____

Directions: *Closed book exam, no books, notebooks, notes, etc. allowed. Calculators are* ***not*** *permitted for this exam. However, rulers and molecular model sets* ***are*** *permitted.* ***Show all of your work if you wish to receive partial credit.*** You should have **22** pages total: **18** exam pages including this page and **4** blank pages for scratchwork.

Question:		**Grader:**
1. _____/	**20 points**	_____
2. _____/	**15 points**	_____
3. _____/	**10 points**	_____
4. _____/	**10 points**	_____
5. _____/	**20 points**	_____
6. _____/	**6 points**	_____
7. _____/	**8 points**	_____
8. _____/	**12 points**	_____
9. _____/	**5 points**	_____
10. _____/	**5 points**	_____
11. _____/	**5 points**	_____
12. _____/	**6 points**	_____
13. _____/	**6 points**	_____
14. _____/	**6 points**	_____
15. _____/	**16 points**	_____
Extra Credit: _____/	**5 points**	_____
Total: _____/	**150 points**	_____

1. 20 points total) A research team led by Prof. Tomooka at the Tokyo Institute of Technology observed an unexpected product during an attempted ozonolysis. Rather than cleavage of the double bond to give two aldehydes, a single product was isolated having an elemental analysis that was consistent with a product derived from one molecule of alkene and one molecule of ozone. The reaction conditions and ^{1}H NMR data of the unexpected compound (**A**) are provided below:



1. O_3
2. Me_2S

A

^{1}H NMR of **A** (ppm):

9.72, d (*J* = 2.4), 1H
7.55 - 7.35, m, 15H
4.06, d, (*J* = 2.4), 1H
0.94, s, 9H

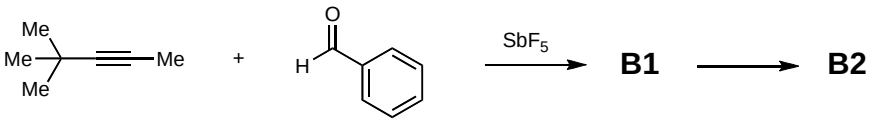
a. (**10 points**) First, write the **expected** (but not observed in this case) **ozonolysis products** (plural), **circle each one**, and write an **arrow-pushing mechanism** for their formation.

b. (**5 points**) Determine the structure of the **unexpected, observed product** (**A**) and **write the structure** below. **Circle your final answer**.

(**1.**, continued):

c. (**5 points**) Write an **arrow-pushing mechanism** for the formation of **A** in the reaction.

2. **(15 points total**) Treatment of the alkyne and aldehyde shown below with a strong Lewis acid (SbF_5) afforded, by way of a [2+2] cycloaddition, intermediate **B1**, which then isomerized to product **B2** having the NMR data provided.

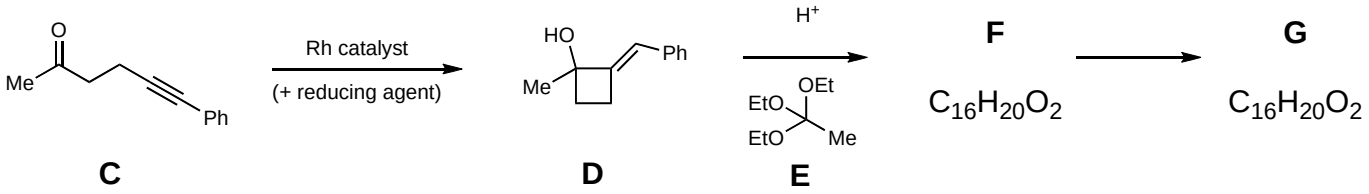


^{1}H NMR of **B2** (ppm):	^{13}C NMR of **B2** (ppm):
7.60 - 7.33, m, 5H	212.8, 137.1, 136.0,
7.25, s, 1H	135.2, 128.6, 128.5,
2.43, s, 3H	127.9, 44.0, 27.9, 1.4.
1.25, s, 9H	

a. (**10 points**) **Write the structures** of **B1** and **B2**. **Circle your final answer for each.**

b. (**5 points**) **Write an arrow-pushing mechanism** for the formation of **B2** by way of **B1**.

3. (10 points total) Prof. Murakami and his coworkers at Kyoto University recently developed a catalytic reaction to convert ynone **C** to the strained allylic alcohol **D**. Treatment of **D** with triethylorthoacetate (**E**) and an acid catalyst caused a **Johnson orthoester Claisen rearrangement** to occur, giving product **G**, by way of intermediate **F**. Product **G** contains both an **ethyl ester** and **an alkene**, in which (as in standard Claisen rearrangements) the C=O of the ester and the C=C double bond are connected by 2 carbon atoms, and both **F** and **G** have MF $C_{16}H_{20}O_2$.

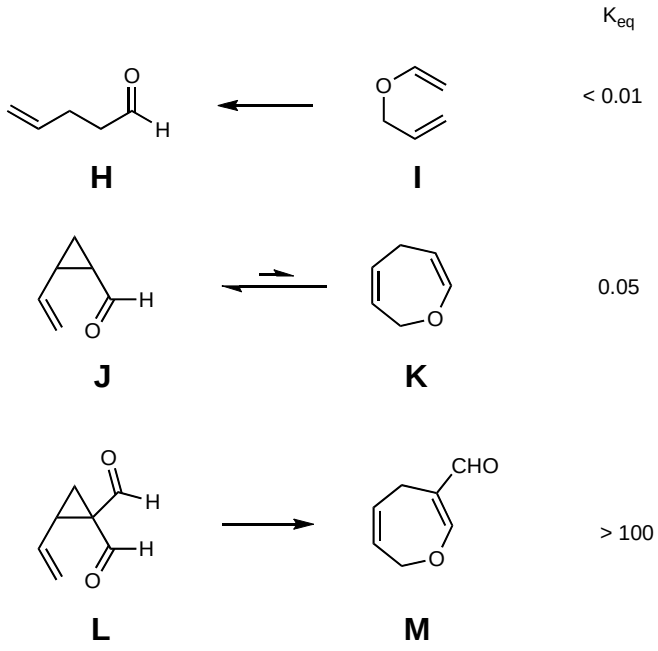


C **D** **E**

a. (**5 points**) **Write the structure** of **F** below (not the element fluorine…). **Circle your final answer.**

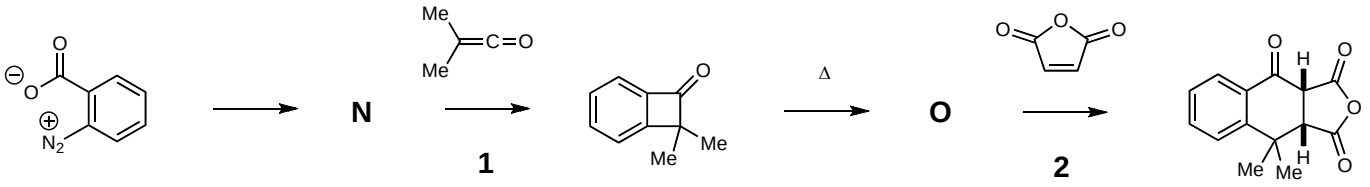
b. (**5 points**) **Write the structure** of **G** below. **Circle your final answer.**

4. (10 points) Explain the **position of equilibrium** or **direction of the reaction** in the **3** reactions below. You may refer to each compound by the letter provided under each structure. Approximate equilibrium constants (K_{eq}) for each reaction are provided.



(Write your answer in the space below.)

5. (20 points, 5 points each) Answer the questions below based on the information provided in the reactions shown.



a. **Draw the structure** of compound **N** (not the element nitrogen…) below (circle your answer) **and write an arrow-pushing mechanism** for its formation.

b. **Draw the structure** of compound **O** (not the element oxygen…) below (circle your answer) **and write an arrow-pushing mechanism** for its formation.

c. **What type of pericyclic reaction** occurs in step **1**? **What type of pericyclic reaction** occurs in step **2**? Write (and circle) your answers to these questions below.

d. For each of the pericyclic reactions **1** and **2**, do **one** (and one **only**) of the following:

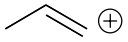
i. If the reaction is an **electrocyclization**, **write** in the space below whether it is **conrotatory** or **disrotatory. Circle** your answer.

ii. If the reaction is a **cycloaddition**, **write** in the space below its **Woodward-Hoffmann classification** (e.g., π4a + π6s). **Circle** your answer.

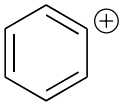
iii. If the reaction is a **sigmatropic rearrangement**, write in the space below its **Woodward-Hoffmann classification** (i.e., [s,s] or [s,a]). **Circle** your answer.

6. (6 pts) Provide a detailed explanation for the following observations.

a) Molecule **A** is more stable than molecule **B**

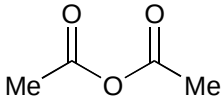


A

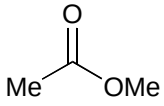


B

b) Molecule **A** is more electrophilc than molecule **B**

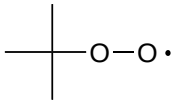


A

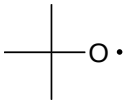


B

c) Molecule **A** is more stable than molecule **B**



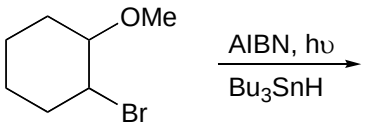
A



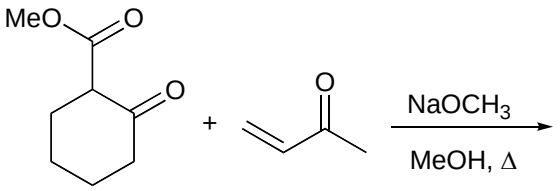
B

7. (8 pts) Provide the product of each reaction.

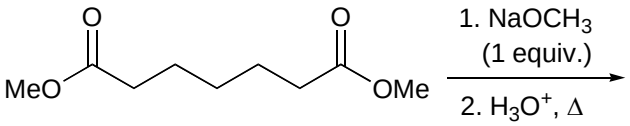
a)



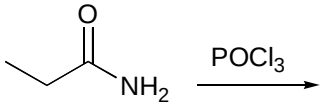
b)



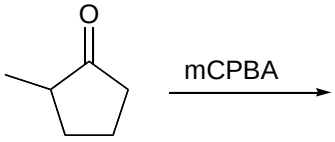
c)



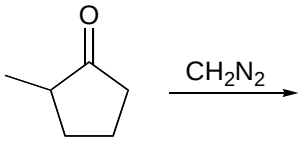
d)



e)

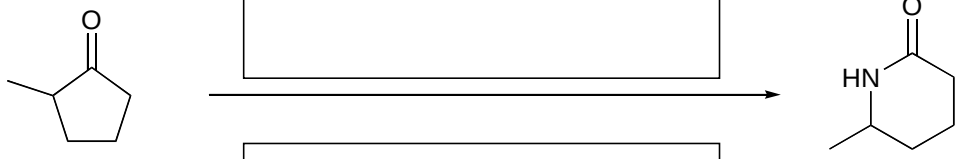


f)

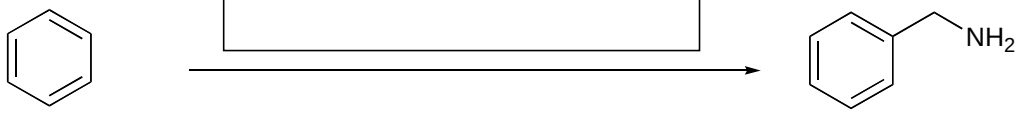


8. (12 pts) Provide the necessary reagent(s) for each transformation.

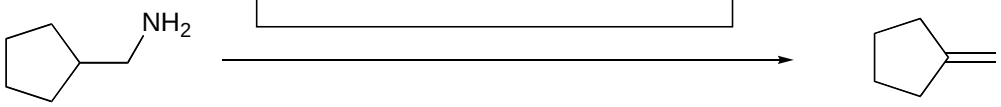
a)



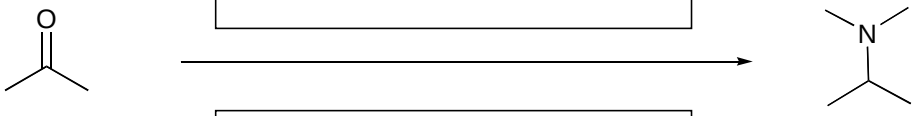
b)



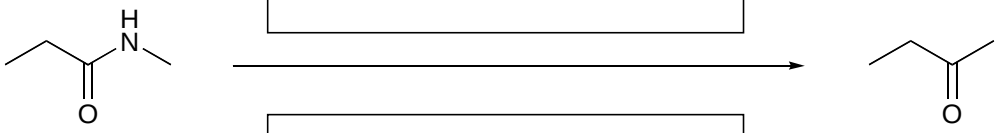
c)



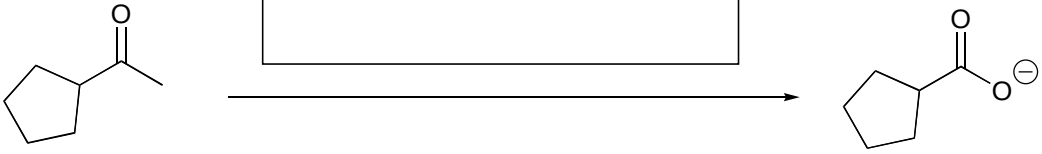
d)



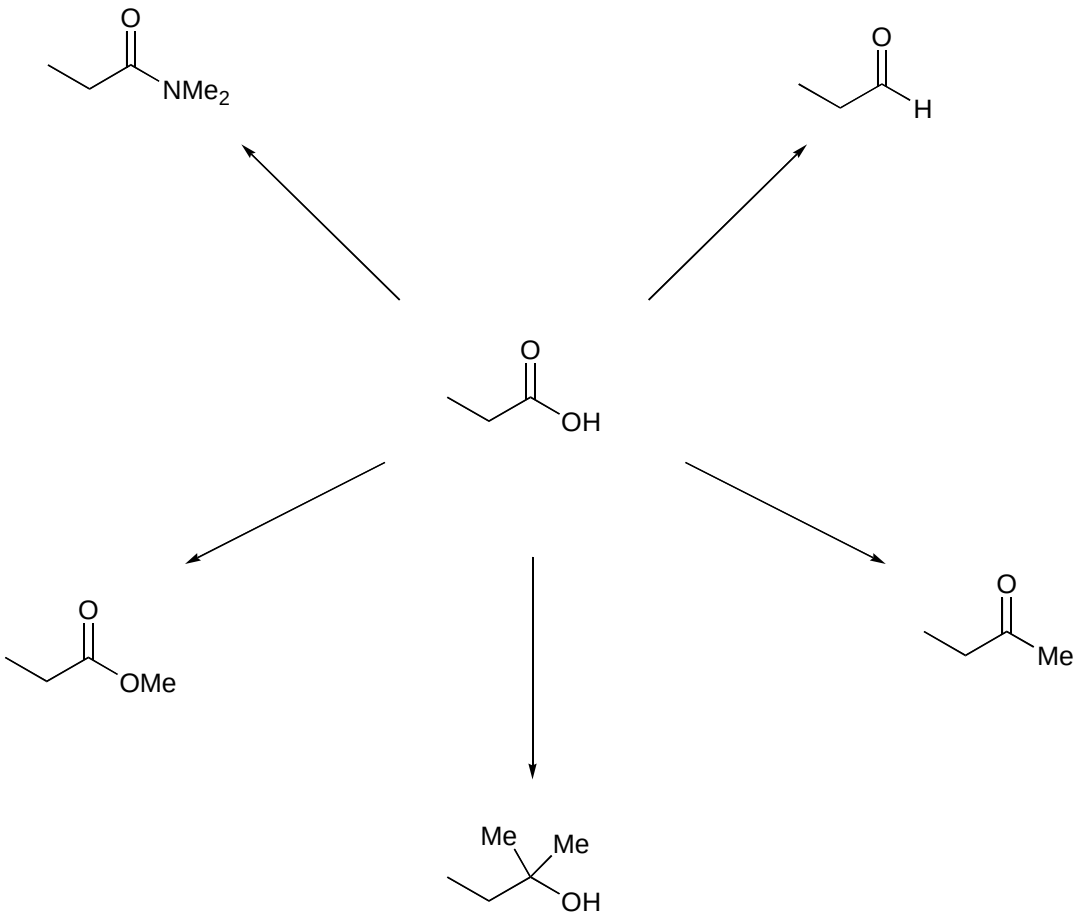
e)



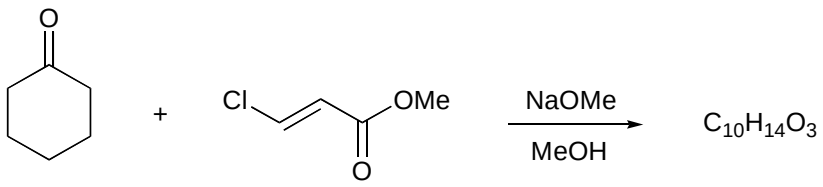
f)



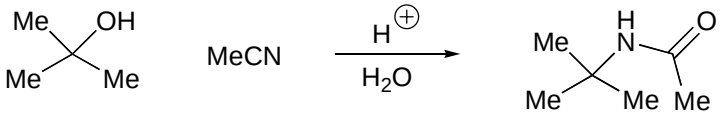
9. (5 pts) Provide the appropriate reagents to transform the carboxylic acid into the given functional groups.



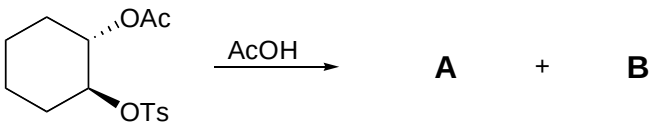
10. (5 pts) Provide a mechanism and product for the following reaction.



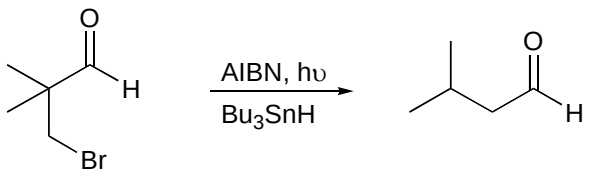
11. (5 pts) Provide a reasonable mechanism for the following reaction.



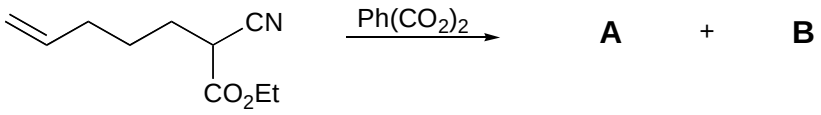
12. (6 pts) Provide the mechanism and products for the following reaction.



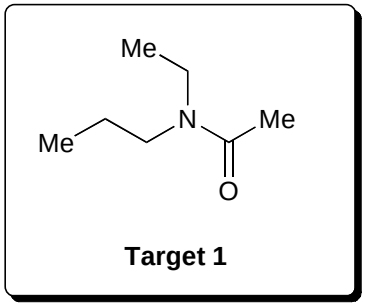
13. (6 pts) Provide a reasonable mechanism for the following reaction.



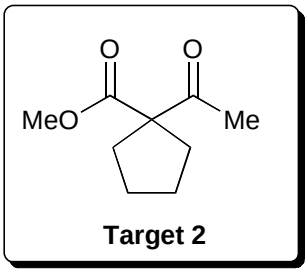
14. (6 pts) Provide the structures of **A** and **B** and propose a reasonable mechanism for each product.



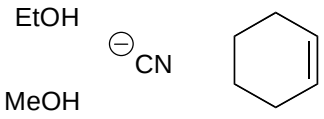
15. (16 pts) Synthesize the following target compounds from the given starting materials only.



Target 1



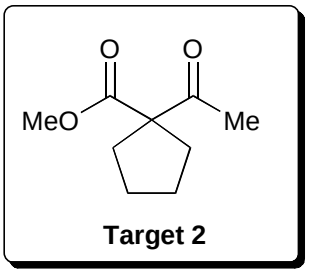
Target 2



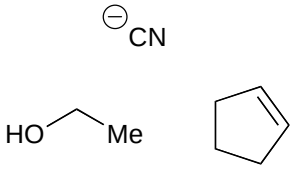
starting materials

SYNTHESIS OF TARGET 1:

SYNTHESIS OF TARGET 2:



Target 2



starting materials

Extra Credit: (5 pts) Provide a synthesis of Alternariol from the 14-carbon polyketide. Credit will be awarded for a retrosynthesis.