

Massachusetts Institute of Technology  
Organic Chemistry 5.13

Wednesday, October 26, 2005

Prof. Timothy F. Jamison

Hour Exam #2

Name SOLUTIONS  
(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.

Please read through the entire exam before beginning, in order to make sure that you have all the pages and in order to gauge the relative difficulty of each question. Budget your time accordingly.

**Show all of your work if you wish to receive partial credit.** You should have 7 pages total: 5 exam pages including this page and 2 blank pages for scratchwork.

Question:

Grader:

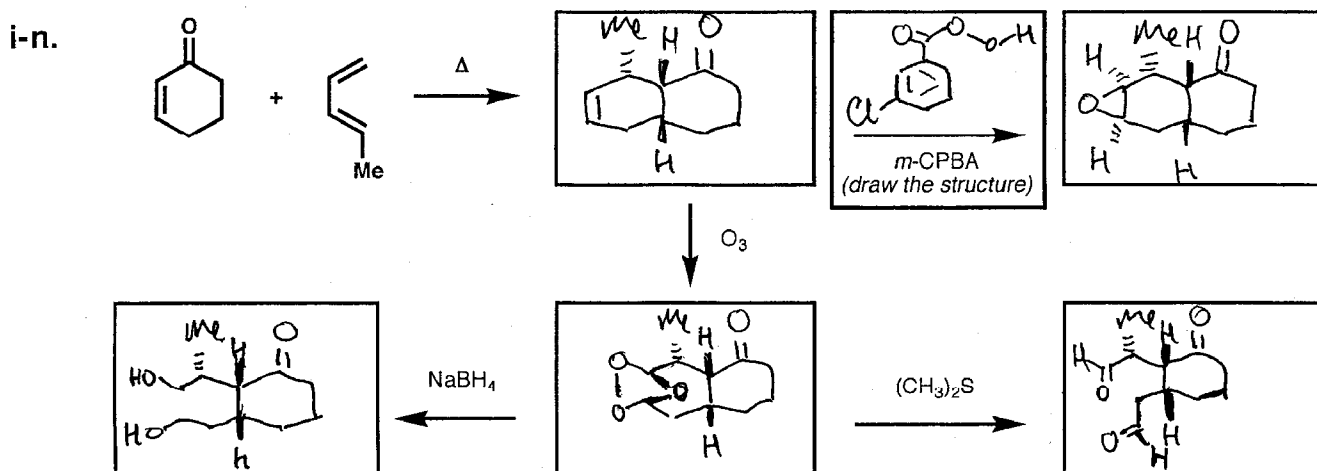
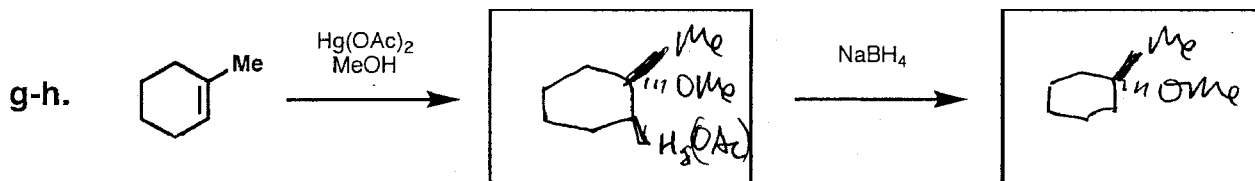
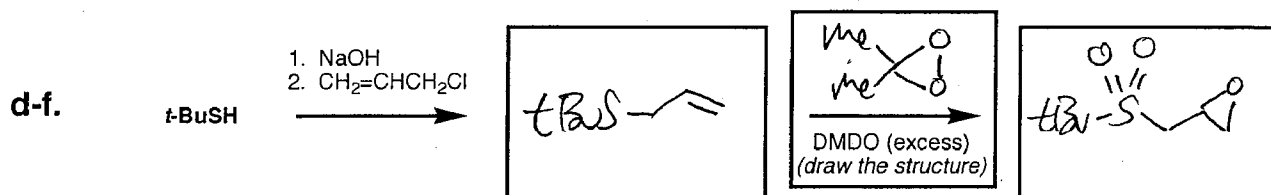
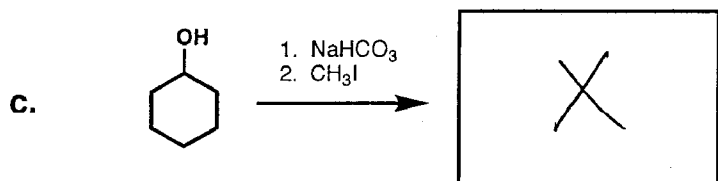
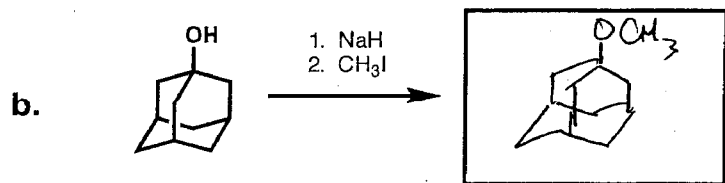
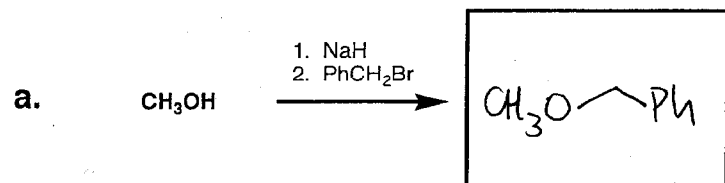
1. \_\_\_\_\_ / 42 points (page 2) \_\_\_\_\_

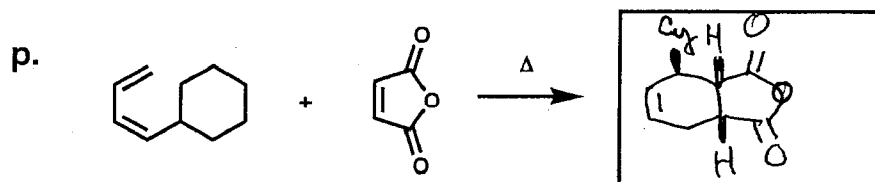
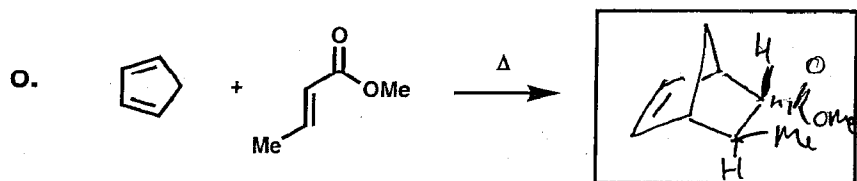
1. \_\_\_\_\_ / 30 points (page 3) \_\_\_\_\_

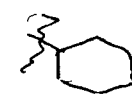
2. \_\_\_\_\_ / 28 points \_\_\_\_\_

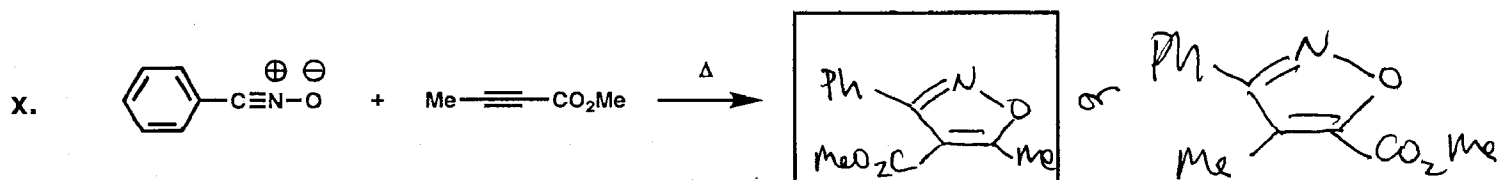
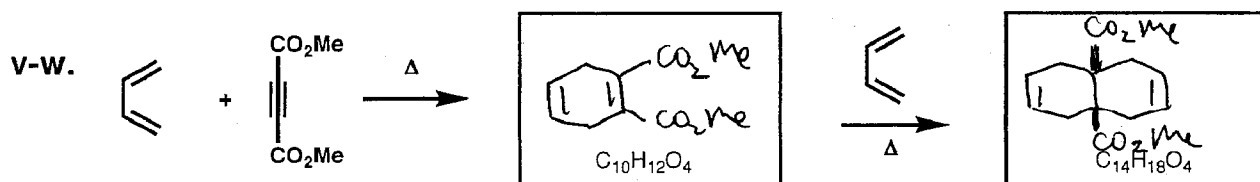
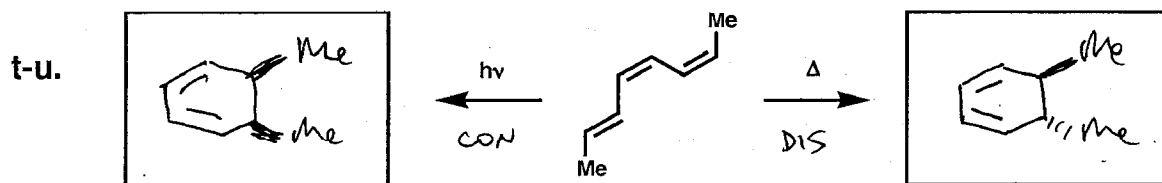
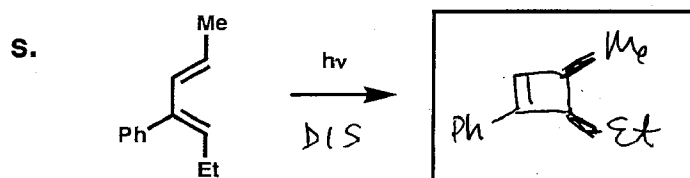
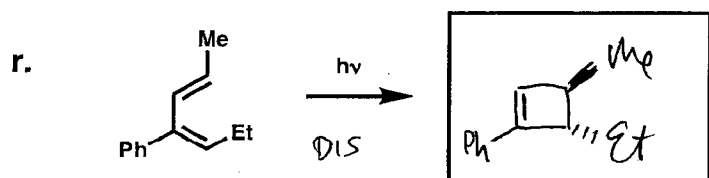
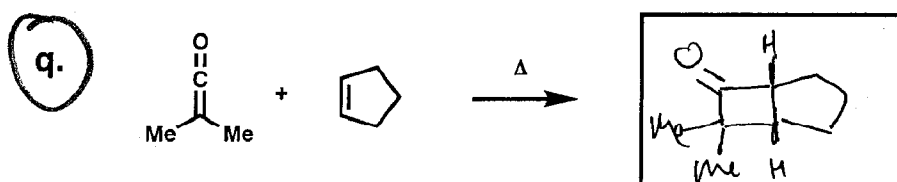
Total: \_\_\_\_\_ / 100 points \_\_\_\_\_

1. (72 points total, 3 points per box) In each box below, draw the structure of the **reagent** or **major product** of the reaction, where appropriate. If **no reaction** occurs, put a large **X** in the box. Clearly indicate the **double bond geometry** and **relative stereochemistry** of the major product, where appropriate.

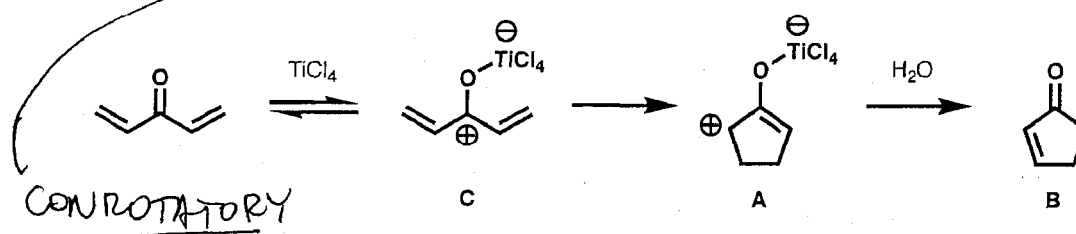




Cy = cyclohexyl = 



2. (28 points total) In a **Nazarov Cyclization** (below), treatment of a dienone with a strong Lewis acid effects a thermal  $4\pi$  electrocyclic ring closure, giving intermediate **A**, and an aqueous workup affords the final product (**B**), the thermodynamically most stable cyclopentenone.



- In the diagram below, **draw the  $\pi$  atomic orbitals** (by shading the lobes appropriately) that represent the  $\pi$  system of **C** (the precursor to **A**) in the reaction above (2 points each).
- Write the **number of nodes** in the box to the left of each orbital array (1 point each).
- For the ground state of **C**, draw the **electron population** for each orbital on the line to the right of each orbital array. Clearly indicate whether each electron is "spin up" or "spin down". If there are no electrons in a given orbital, leave the line blank (1 point each).

| # of nodes | orbitals | electron population  |
|------------|----------|----------------------|
| 4          |          | _____                |
| 3          |          | _____                |
| 2          |          | _____                |
| 1          |          | $\uparrow\downarrow$ |
| 0          |          | $\uparrow\downarrow$ |

$E \uparrow$

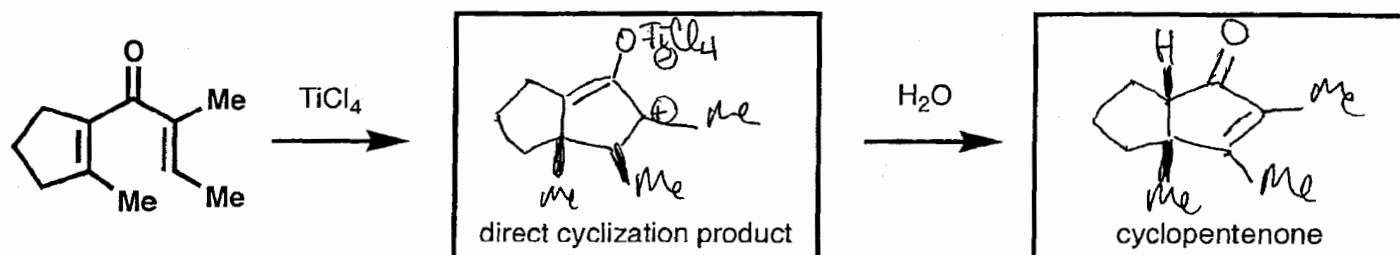
1 point per box

2 points per orbital array

1 point each

4. (continued)

- d. (4 points each) For the example of the Nazarov cyclization below, in the indicated boxes draw the direct product of the **electrocyclic ring closure** and the **cyclopentenone** final product after the aqueous workup. In both cases, clearly indicate stereochemistry and double bond geometry, as appropriate.



LESS STABLE CYCLOPENTENONES (2 pts PARTIAL CREDIT):

