

Chem 12B Midterm 3

Instructor: Richmond Sarpong

April 26th 2018

8:10–9:30 am, 100 Lewis

You have **80 minutes** to complete this exam. Please write your answers clearly only on the pages indicated *and be as detailed as possible*. Nothing written outside the numbered pages will be graded. There should be 9 total pages in this exam.

Name: _____

UID: _____

GSI Name: _____

Question

Score

1 _____ (18 points)

2 _____ (12 points)

3 _____ (12 points)

4 _____ (15 points)

5 _____ (22 points)

6 _____ (9 points)

7 _____ (12 points)

Total _____ (100)

Question 1 (18 points total):

(a) Classify the following transformations as either cycloadditions, electrocyclizations, cheletropic reactions, or sigmatropic rearrangements. (1 pt each)

(b) For each pericyclic reaction, provide a descriptor (e.g., [m+n] cycloaddition, [m,n] sigmatropic rearrangement, or $n\pi$ electrocyclicization). (2 pts each)



a)

b)



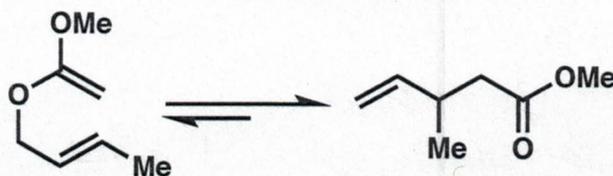
a)

b)



a)

b)



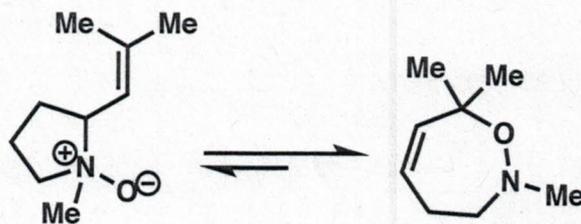
a)

b)



a)

b)

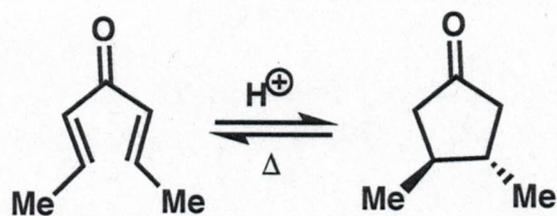


a)

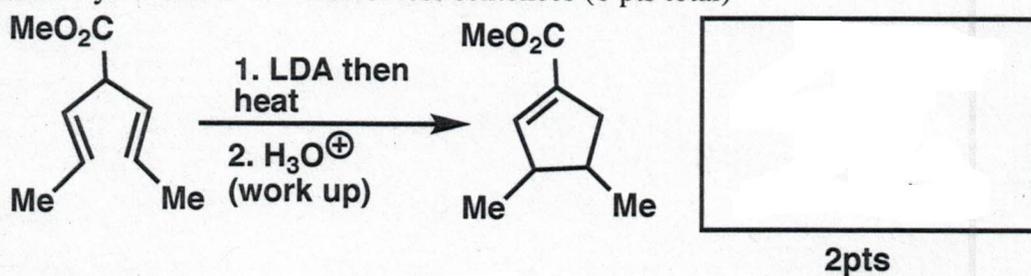
b)

Question 2 (12 points):

(a) Provide a molecular orbital picture to rationalize the observed outcome of the following Nazarov transformation (6 pts).



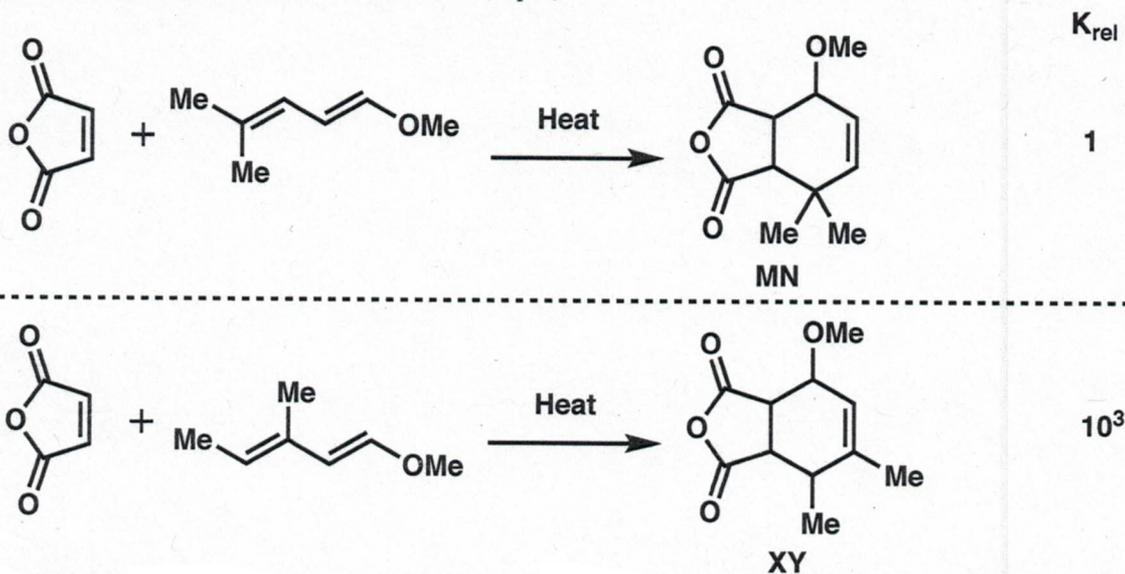
(b) Predict the stereochemistry of the following transformation (redraw in box) and provide a rationalization for your answer in three or less sentences (6 pts total)



Rationalization (4 pts)

Question 3 (12 points total):

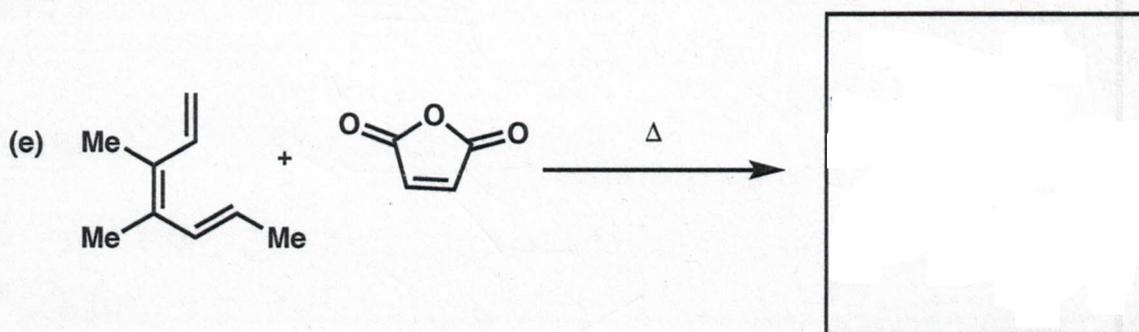
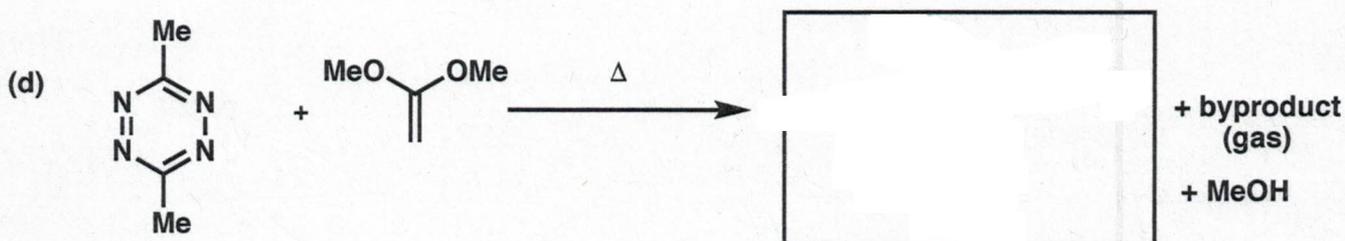
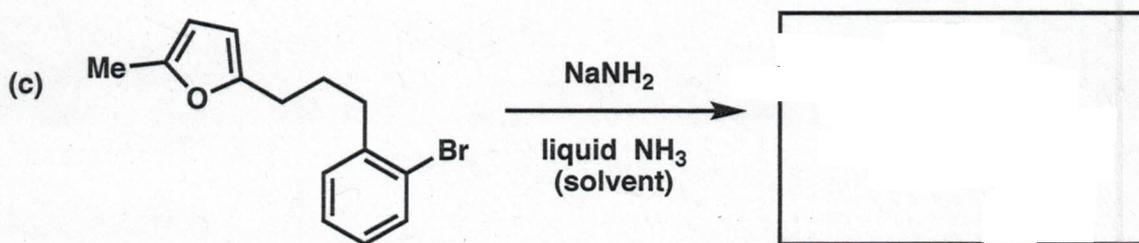
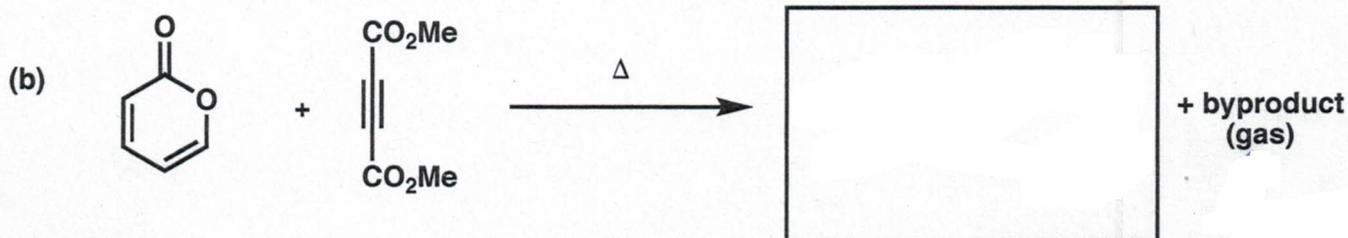
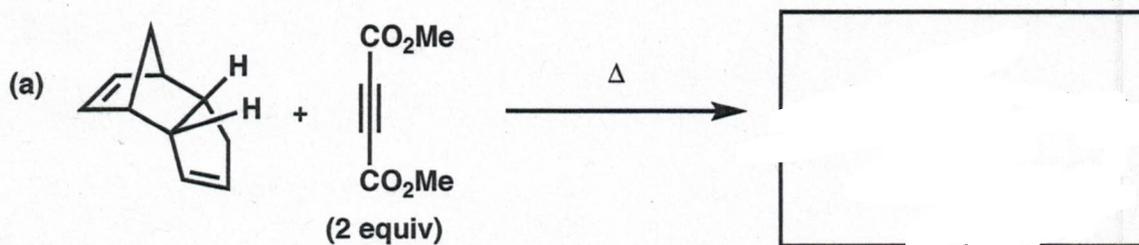
(a) Provide rationalization for the observed differences in the relative rate of reaction (K_{rel}) for the following reactions in three sentences or less. (4 pts).



(b) Knowing that the reactions above proceed through an *endo* transition state, redraw **XY** showing the relative stereochemistry of all four stereocenters (3 pts) and provide a conformational drawing of the presumed transition state to rationalize your answer (5 pts).

Question 4 (15 Points total):

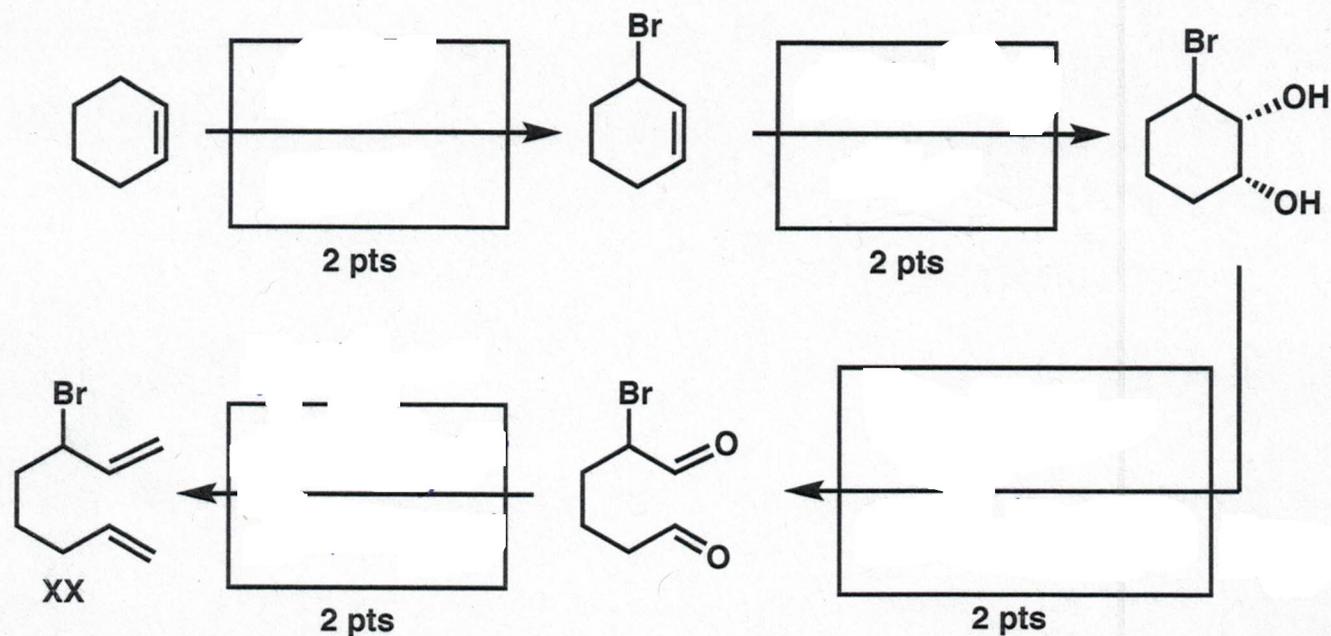
Provide the products of the following reactions knowing that they involve several steps including a Diels-Alder cycloaddition. Unless indicated, each reactant is 1 equiv (3 pts each).



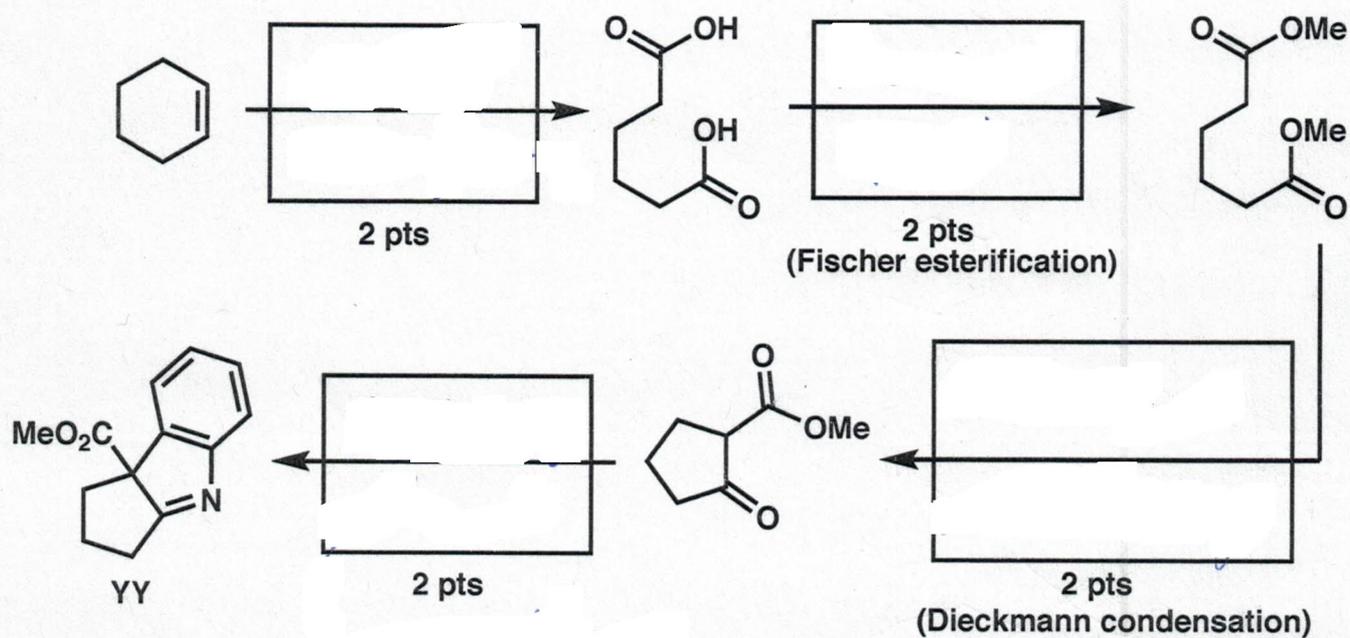
Hint: Product contains a 2.2.2 bicycle

Question 5 (22 points):

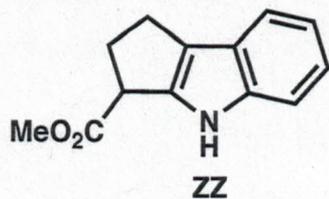
(a) Fill in the following boxes for the transformation of cyclohexene to bromodiene **XX**.



(b) Provide conditions that lead to **YY** from cyclohexene (2 pts each).



(c) **ZZ** forms as the minor product of the Fischer indolization type reaction that leads to **YY** in 5(b). Provide a mechanism for the formation of **ZZ** from the β -ketoester precursor shown in 5(b) (6 pts).



Question 6 (9 pts)

Provide a mechanism for the following conversion to **AA** knowing that it involves an aza-Cope Mannich reaction.

