Chem 332

Exam 2

April 11, 2007

Prof Fox

50 minutes

100 points

Show your work in detail

Write your name on every page

Name_____

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50 minutes

100 points

The exam is open book, open notes. Models are permitted.

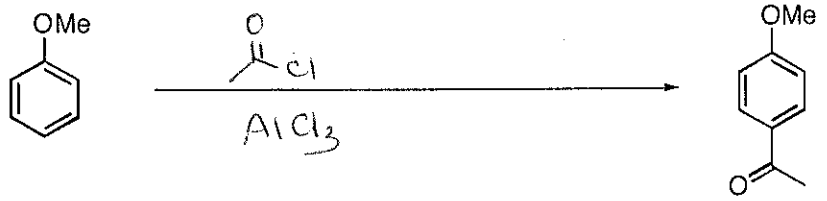
Show your work in detail

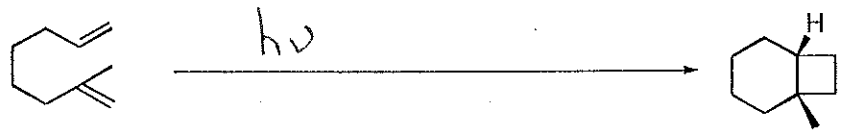
Write your name on every page .

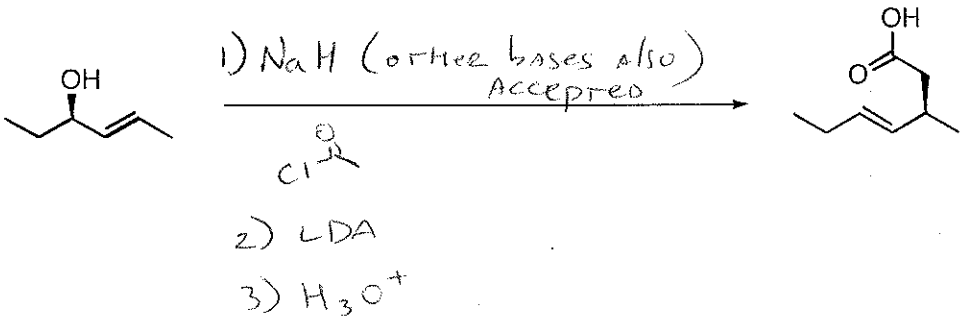
Name Key

Your Name Key

1. Provide reagents. More than one step may be required (5 points each)
Mechanisms are not needed.



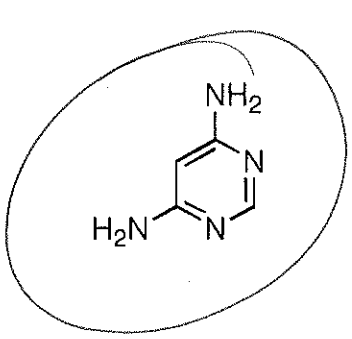


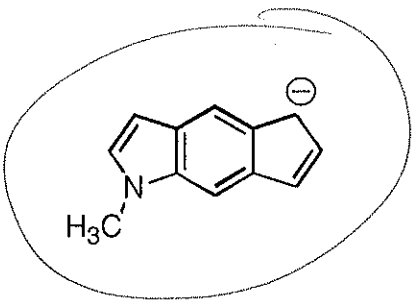


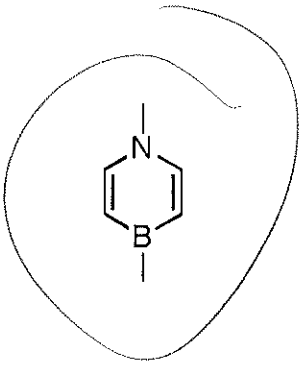
Your Name Key

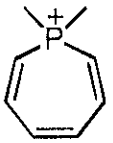
2. Circle the molecules that are aromatic. No partial credit

(4 points each)



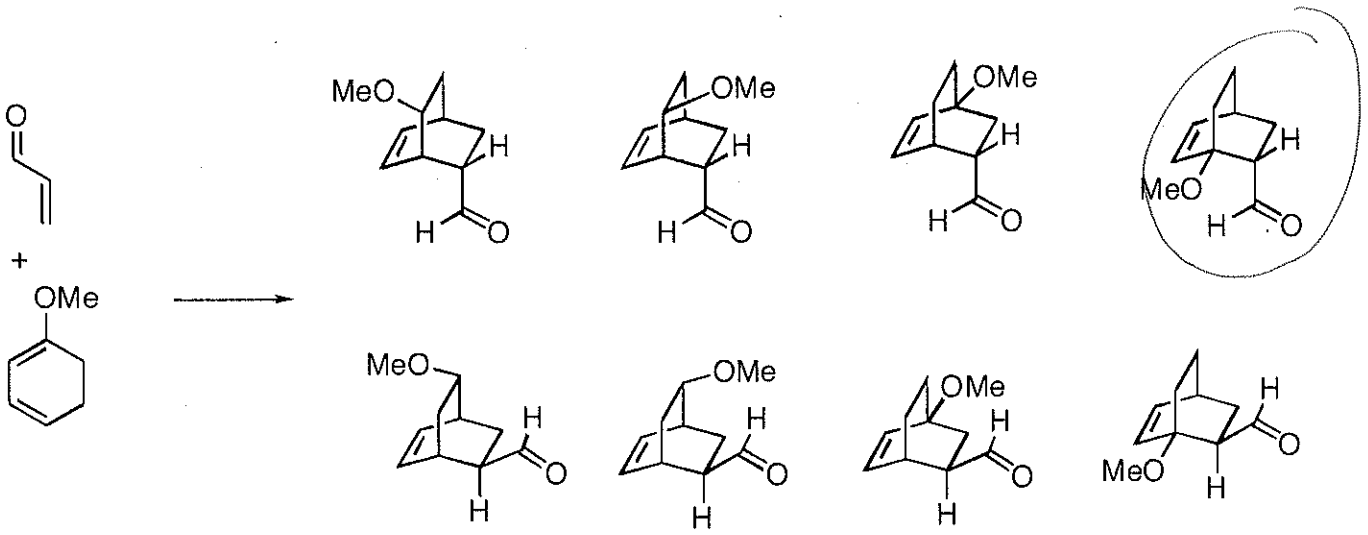






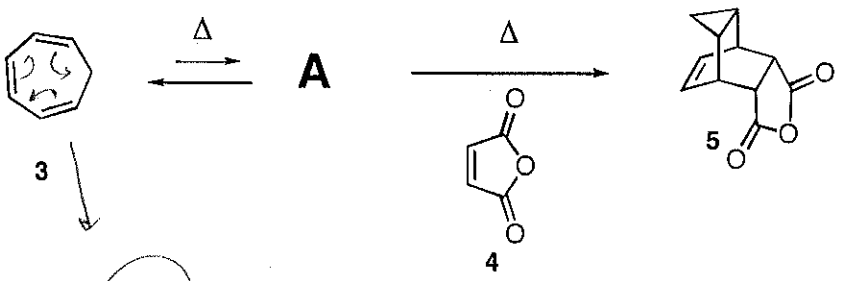
Your Name Key

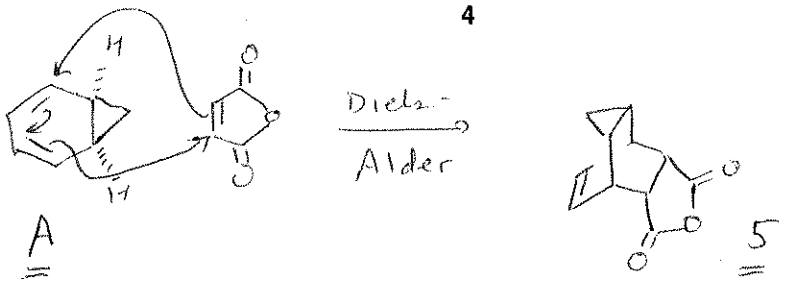
3. Circle the correct product. No partial credit. Circle only one product (10 points)



4. When heated, compound **3** equilibrates with structure **A**, which reacts with **4** to give product **5**. Provide a structure for **A**, and a mechanism for the formation of **A** and **5**.

Molecular orbital analysis is NOT required (25 points)

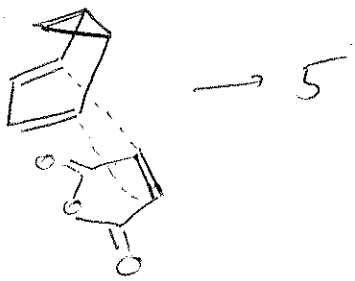




A

5

ENDO T.S.



→ 5

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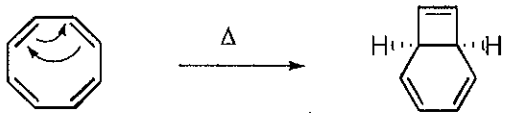
5 (a) Upon discovering the thermal rearrangement of **1** to **2**, an overly excitable scientist wrote the mechanism below.

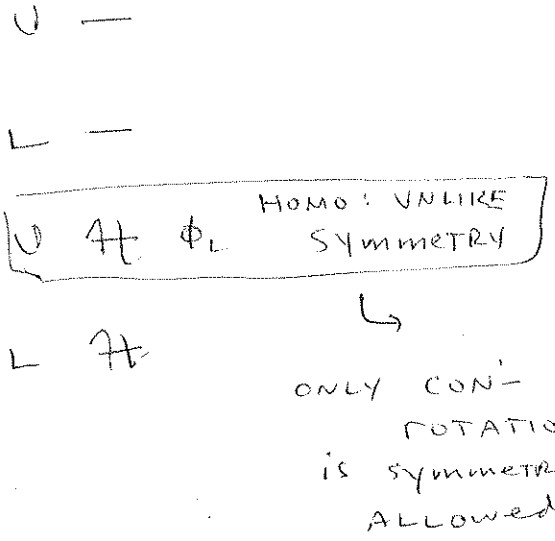
(15 points)

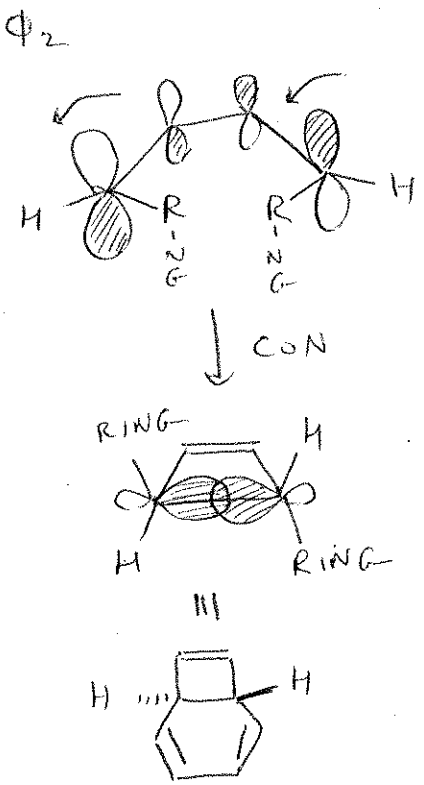


1 **2**

However, the mechanism as written above is NOT reasonable. Provide a detailed explaination (using molecular orbital analysis) that explains why this mechanism is incorrect.

• Draw MO energy levels & Determine Symmetry of HOMO

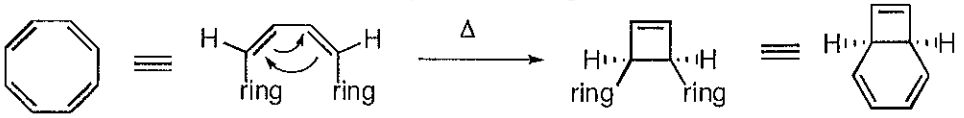




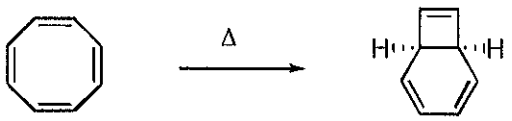
THIS MODEL PREDICTS A TRANS- RING FUSION, WHICH WOULD BE IMPOSSIBLY STRAINED AND INCONSISTENT WITH THE STRUCTURE OF 2.

• Hint: the mechanism drawn above is a 4π process that is analogous to the electrocyclic ring closure of butadiene. When crafting your answer to the question above, do not worry about the electrons that are 'not involved' in the rearrangement.

It may be helpful to label the 'uninvolved' part of the ring as follows:

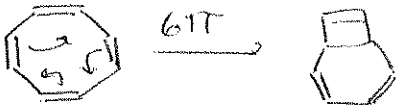


5 (continued) However, structure **1** does indeed undergo electrocyclic ring closure to form **2**.



1 **2**

(b) provide an arrow pushing mechanism (5 points)



(c) Using molecular orbital analysis, explain why the concerted reaction that you just illustrated is permitted under thermal conditions. (10 points)

6 π

U — ϕ_6

L — ϕ_5

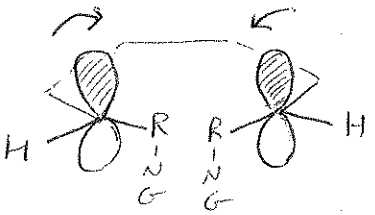
U — ϕ_4

L ~~π~~ ϕ_3 HOMO HAS LIKE SYMMETRY

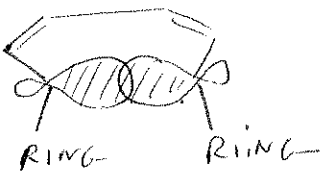
U ~~π~~ ϕ_2 ↳ PREDICTS DIS-ROTATION

L ~~π~~ ϕ_1

ϕ_3



↓ dis



III