

Chem 332

Exam 2

2010

Prof Fox

50 minutes

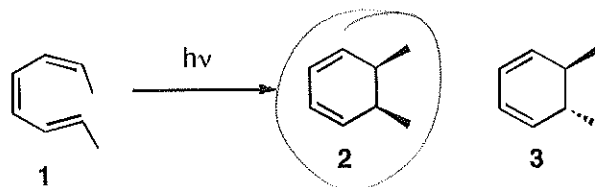
80 points

The exam is closed book

Write your name on every page

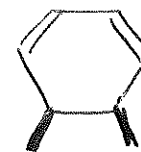
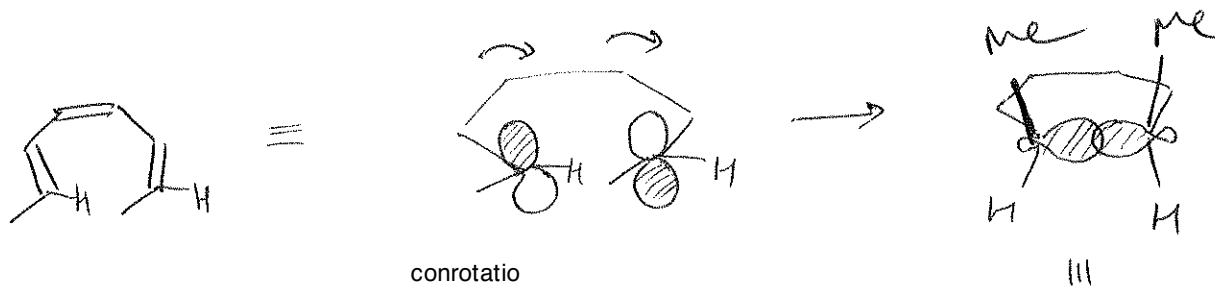
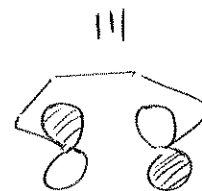
Name KEY

1. Does the photochemical isomerization of **1** lead to compound **2**, compound **3**, or a mixture of both? Circle the correct product(s). Explain your answer in detail using an argument based in molecular orbital theory; a correct answer will predict if this reaction will proceed via conrotatory or disrotatory electrocyclic ring closure. (15 points)  
NO CREDIT will be awarded for simply circling the correct product



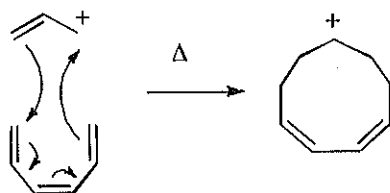
$\phi_6$	U	—	—
$\phi_5$	L	—	—
$\phi_4$	U	—	$\oplus$
$\phi_3$	L	$\oplus$	$\oplus$
$\phi_2$	U	$\oplus$	$\oplus$
$\phi_1$	L	$\oplus$	$\oplus$

$\xrightarrow{h\nu}$  PHOTOHOMO is  $\phi_4$ : UNLIKE SYMMETRY.

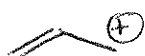


(25 points)

2. Consider the thermal reaction shown below. Would you expect this to be a concerted process under thermal conditions? Explain in detail using an argument based in molecular orbital theory.



CycloADDITIONS require COMBINATION of the HOMO of ONE REACTANT + LUMO of the OTHER.

 $3\pi, 2e^-$ 

 $6\pi, 6e^-$ 

 $L \Phi_3$  —

 $U \Phi_2$  — LUMO

 $L \Phi_1$   $\overline{\overline{H}}$  HOMO

 $U \Phi_6$  —

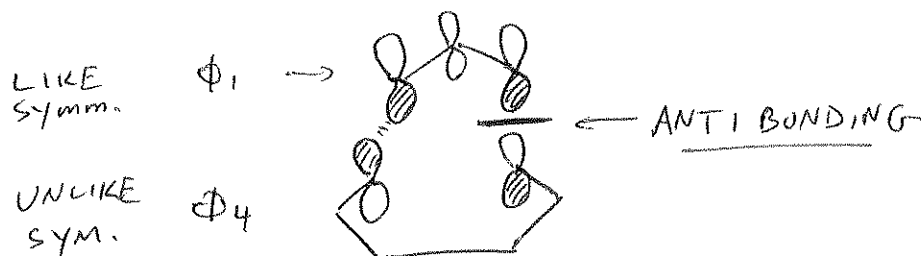
 $L \Phi_5$  —

 $U \Phi_4$  — LUMO

 $L \Phi_3$   $\overline{\overline{H}}$  HOMO

 $U \Phi_2$   $\overline{\overline{H}}$ 
 $L \Phi_1$   $\overline{\overline{H}}$ 

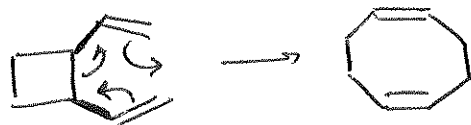
WE CAN CONSIDER THE COMBINATION OF  $\Phi_1$  (allyl) &  $\Phi_4$  (1,3-butadiene)



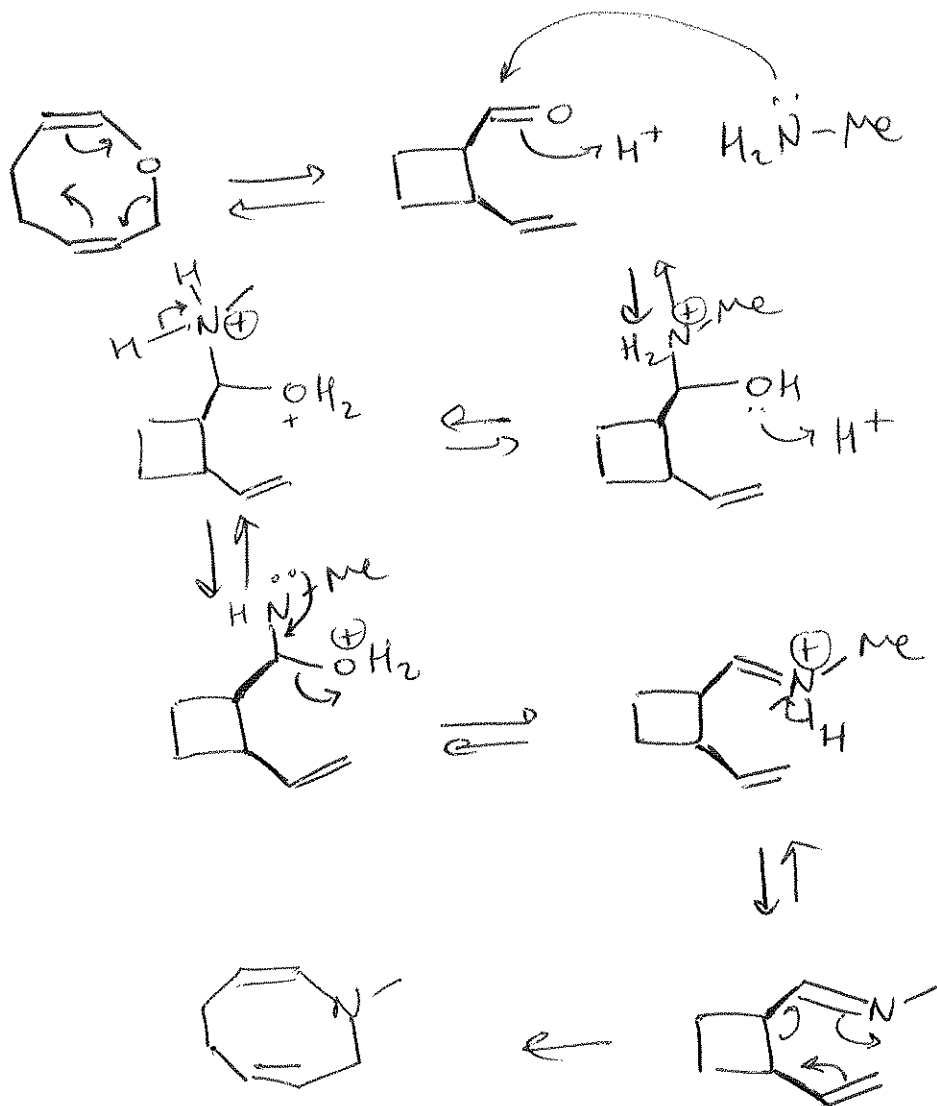
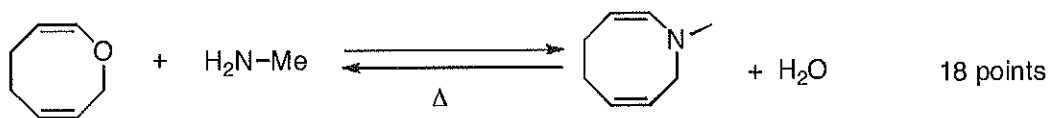
BECAUSE THE SYMMETRY RESULTS IN AN ANTI BONDING INTERACTION, THIS CYCLOADDITION IS NOT CONCERTED.<sup>3</sup>

• ANALYSIS WITH  $\Phi_2$  (allyl) +  $\Phi_3$  (1,3-butadiene) REACHES A SIMILAR CONCLUSION

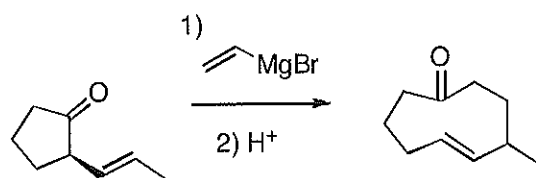
3. Provide a detailed arrow pushing mechanism. Your answer does NOT require molecular orbital analysis.



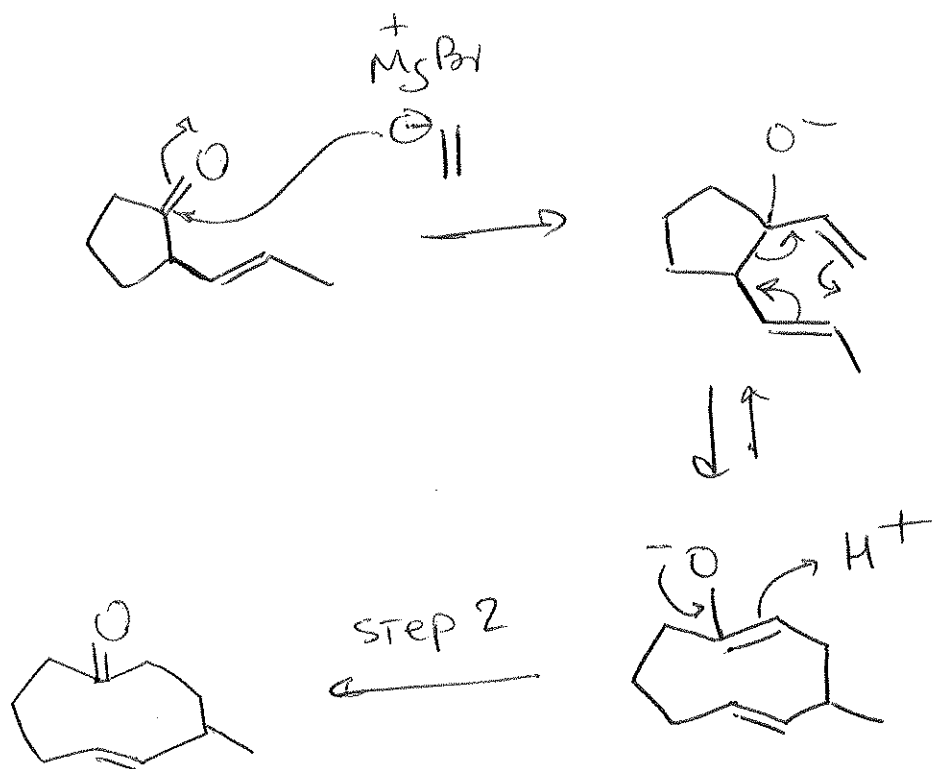
4. Provide a detailed arrow pushing mechanism. Your answer does NOT require molecular orbital analysis.



5. Provide a detailed arrow pushing mechanism. Your answer does NOT require molecular orbital analysis.



17 points



Scratch paper