

213 POSSIBLE

Chemistry 302
Spring, 2003
Exam 2

KEY

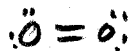
Topics: MO Theory, Pericyclic Reactions, Molecular Properties

Instructions: Please write your name on the last page of this exam. You may use a model kit and the periodic table on the wall. No other aids are allowed. Please make sure that your answers are shown clearly in the space provided, and show your work where appropriate. Structural drawings should include stereochemistry when relevant.

Part 1: Molecular Orbital Theory

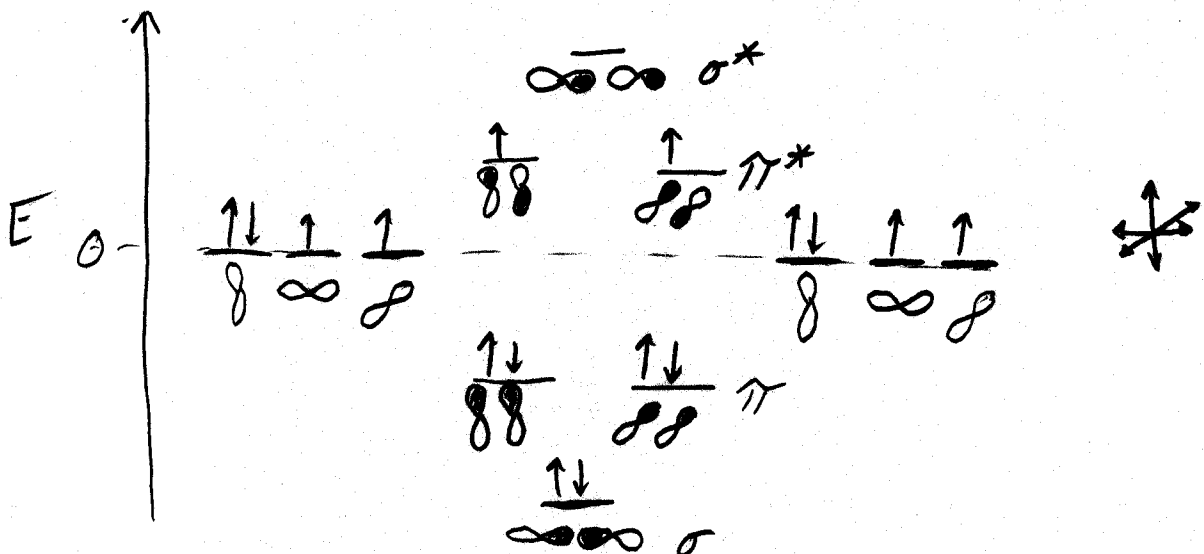
1) (10) Why is MO theory more successful in describing the structure of molecular oxygen (O_2) than Lewis Theory? Use an occupied MO diagram as part of your answer.

LEWIS THEORY PREDICTS THAT THE O_2 MOLECULE WILL HAVE A BOND ORDER OF 2, AND THAT ALL ELECTRONS WILL BE PAIRED:



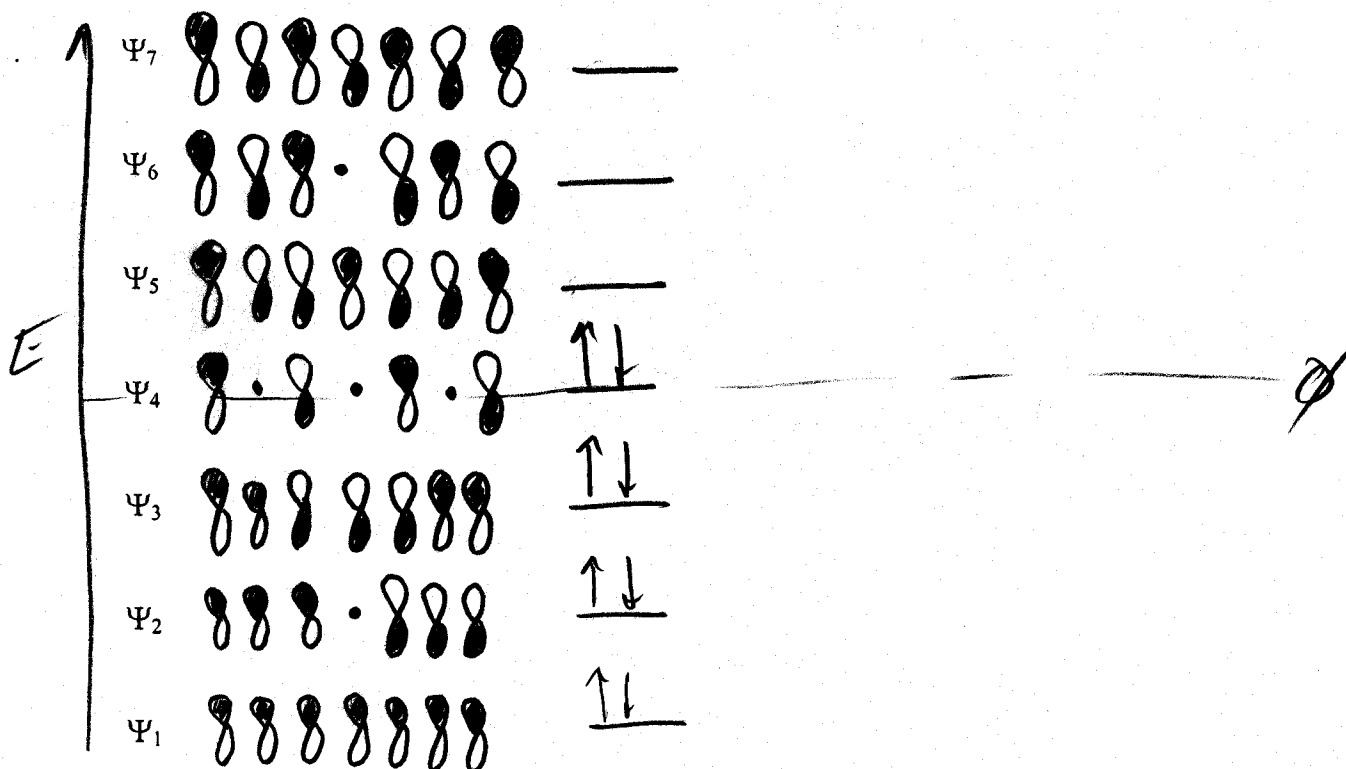
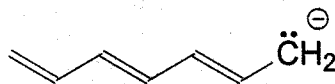
WHILE LABORATORY OBSERVATIONS CONFIRM THE BOND ORDER OF 2, THEY ALSO INDICATE THAT O_2 IS A DIRADICAL. THUS, LEWIS THEORY DOES NOT ACCURATELY DESCRIBE THE STRUCTURE OF O_2 .

MO THEORY, BASED ON THE IDEA THAT e^- OCCUPY MOLECULAR ORBITALS THAT ARE FORMED FROM ATOMIC ORBITALS, CAN ACCOUNT FOR BOTH THE BOND ORDER AND THE ELECTRON PAIRING:



2) (30 total)

a) (14) Draw all the linear combinations of atomic p orbitals (\uparrow or \downarrow): which represent the molecular orbitals Ψ_1 through Ψ_7 of the 1,3,5-heptatrienyl anion:



b) (2) Which orbitals are occupied?

 $\Psi_1 - \Psi_4$

c) (2) Which orbital is the HOMO?

 Ψ_4

d) (2) Which orbital is the LUMO?

 Ψ_5

e) (2) What is the bond order of this molecule?

3

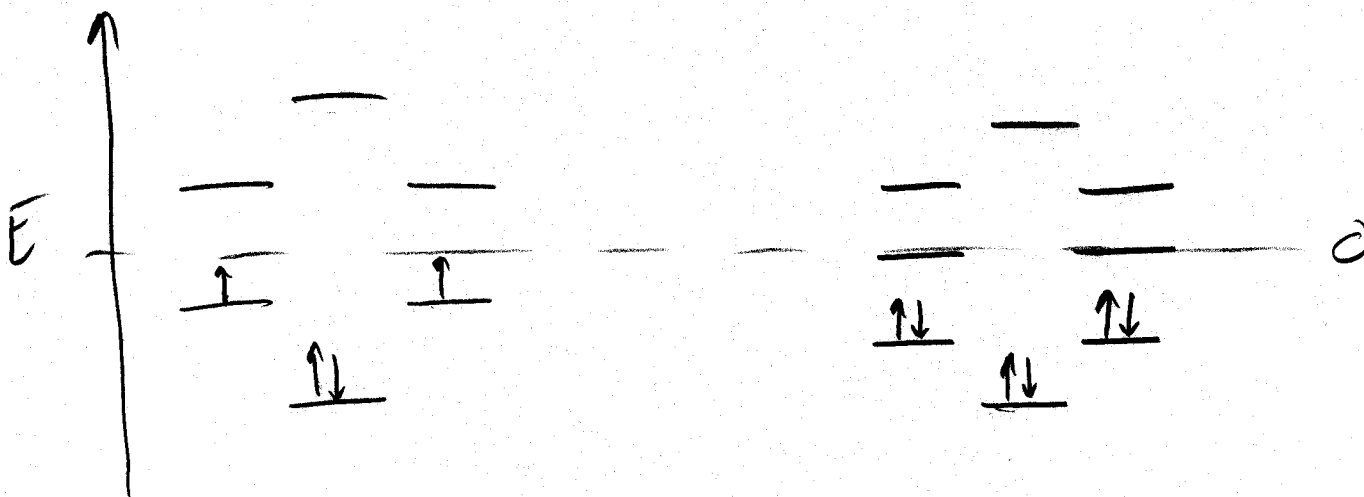
f) (2) Which orbital would be the HOMO for the 1,3,5-heptatrienyl cation?

 Ψ_3

g) (6) Identify the following orbitals as bonding, non-bonding, or antibonding.

 Ψ_4 NONBONDING Ψ_5 ANTIBONDING Ψ_6 ANTIBONDING

3) (10+3) Provide an occupied MO diagram for the following molecules. Indicate which orbitals are bonding, non-bonding, or antibonding. You do not have to provide the "p orbital notation" for each molecular orbital, only the relative energies of the MO's.

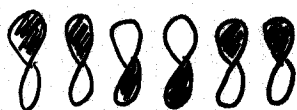


b) Which of the structures is more stable? Why?

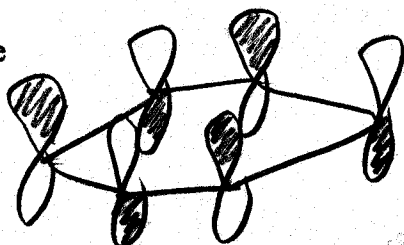
THE CYCLOOCTATRIENYL DICTION HAS ALL BONDING ORBITALS FILLED WITH e^- . IT IS MORE STABLE. IT'S AROMATIC!

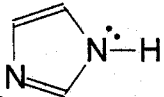
4) (12) Draw the following molecular orbitals, representing individual atomic p orbitals as \uparrow or \downarrow :

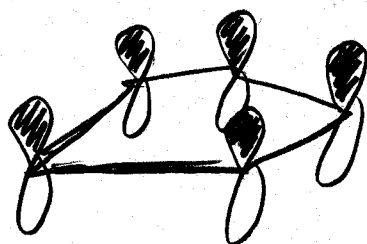
a) The HOMO of 1,3,5-hexatriene



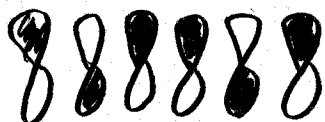
b) Ψ_6 of benzene



c) Ψ_1 of imidazole, \therefore 



d) The LUMO of the excited state of 1,3,5-hexatriene



Part 2: Pericyclic Reactions

5) (9) Provide brief, correct definitions for the following terms:

a) pericyclic reaction

A concerted reaction that proceeds through a cyclic transition state, and in which 2 or more bonds are made/broken.

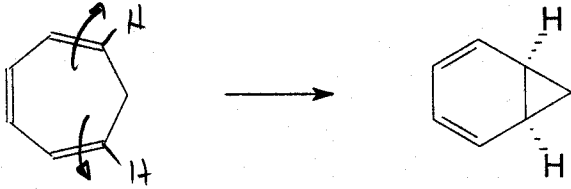
b) electrocyclic reaction

A pericyclic reaction that forms a sigma bond between the two terminal atoms of a series of conjugated pi bonds in a molecule.

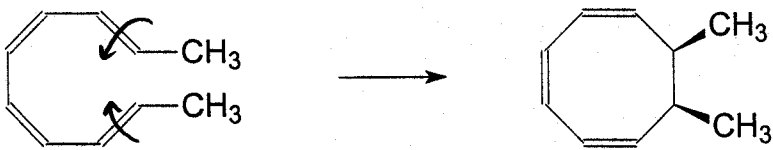
c) cycloaddition reaction

A concerted reaction in which 2 sigma bonds are formed between the end atoms of two pi systems, resulting in the formation of a ring.

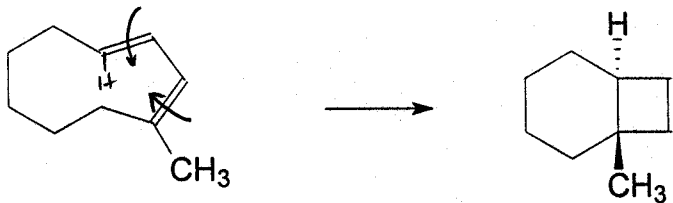
6) (18) Based on the stereochemistry of the reactant and of the product, indicate if a conrotatory or disrotatory process is responsible for each transformation.



DIS



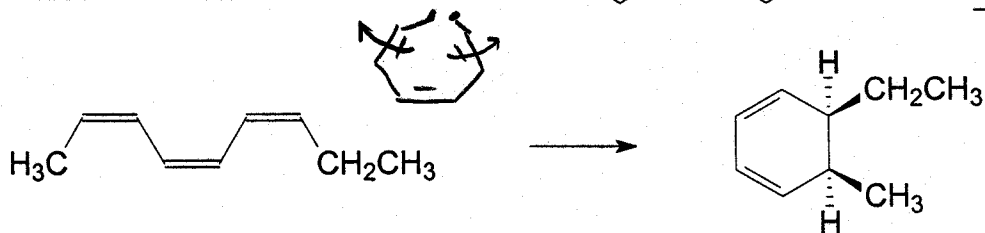
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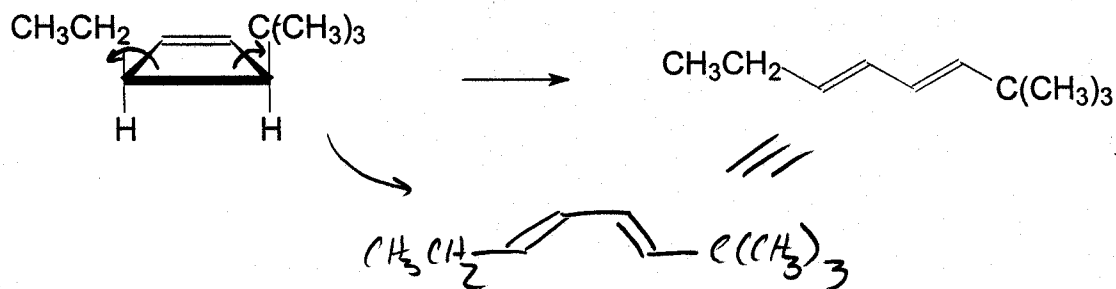
DIS



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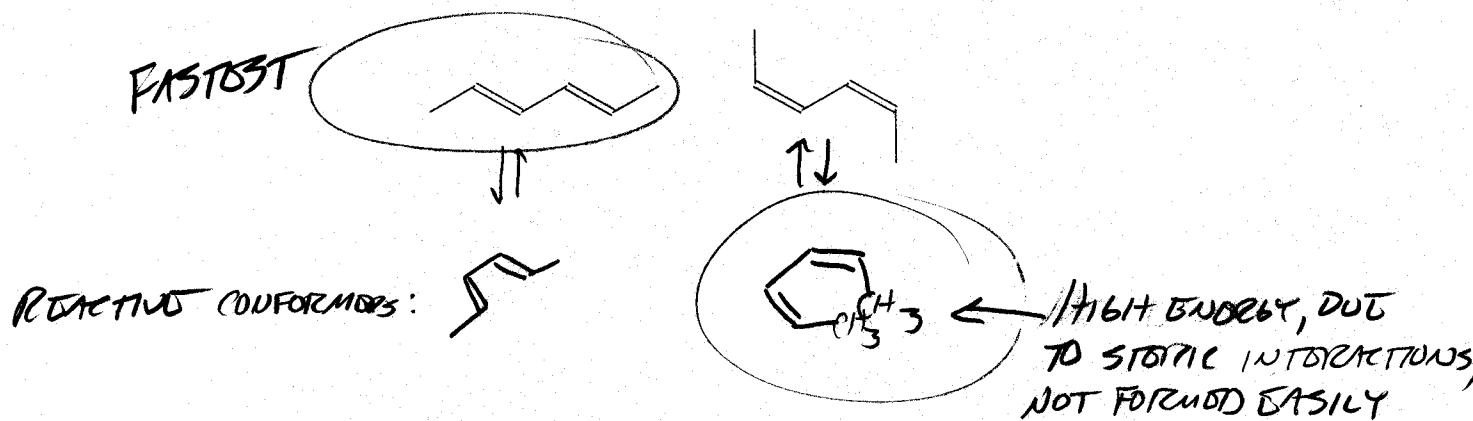


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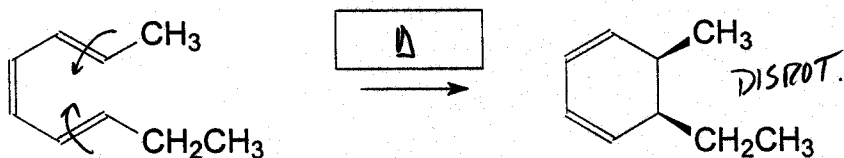
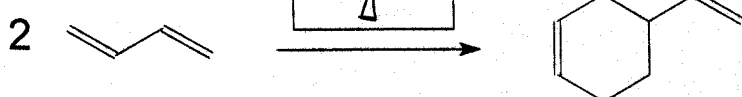
DIS

7) (5) Of the two compounds shown, which will undergo electrocyclic ring closure more rapidly? Explain your answer for full credit.

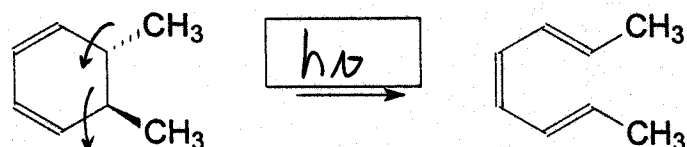
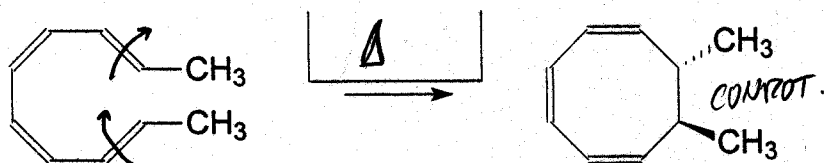
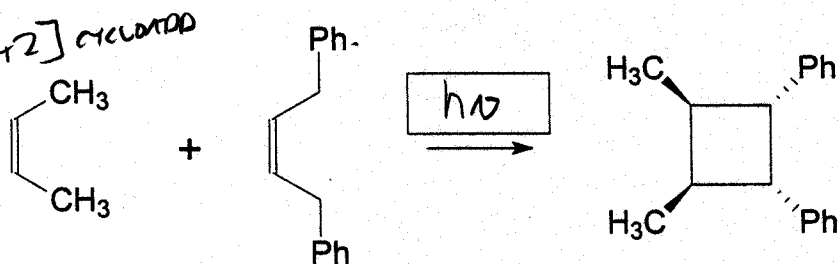


8) (15) What conditions are used to effect each of the following transformations? Write your answer in the space provided.

$[4+2]$ CYCLOADD.



$[2+2]$ CYCLOADD.



① DETERMINE IF ELECTROCYCLIC OR CYCLOADDITION.

② IF ELECTROCYCLIC, DET. IF CON- OR DISROTATORY.

③ APPLY SELECTION RULES
COUNT e^- PAIRS

ELECTROCYCLIC

ODD # PAIRS

DISROT. \rightarrow Δ ALLOWED

CONROT \rightarrow $h\nu$ ALLOWED

EVEN #

DISROT \rightarrow $h\nu$ ALLOWED

CONROT \rightarrow Δ ALLOWED

CYCLOADDITION

ODD # PAIRS

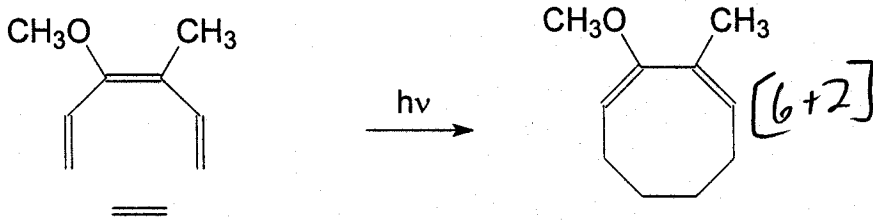
Δ ALLOWED

EVEN #

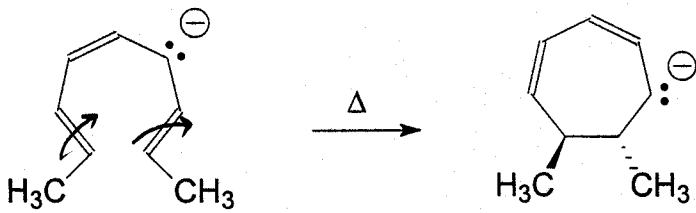
$h\nu$ ALLOWED

500 # 8

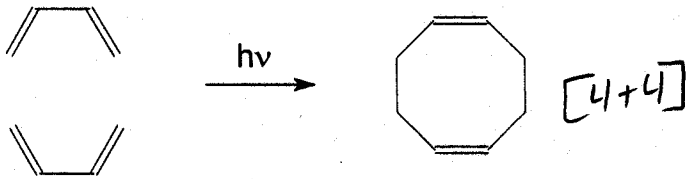
9) (9) Indicate whether each reaction is allowed or forbidden



ALLOWED

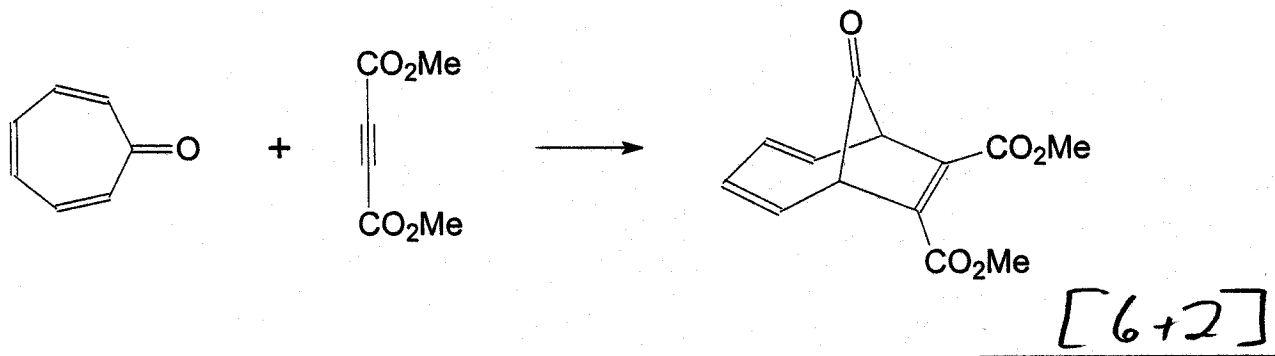
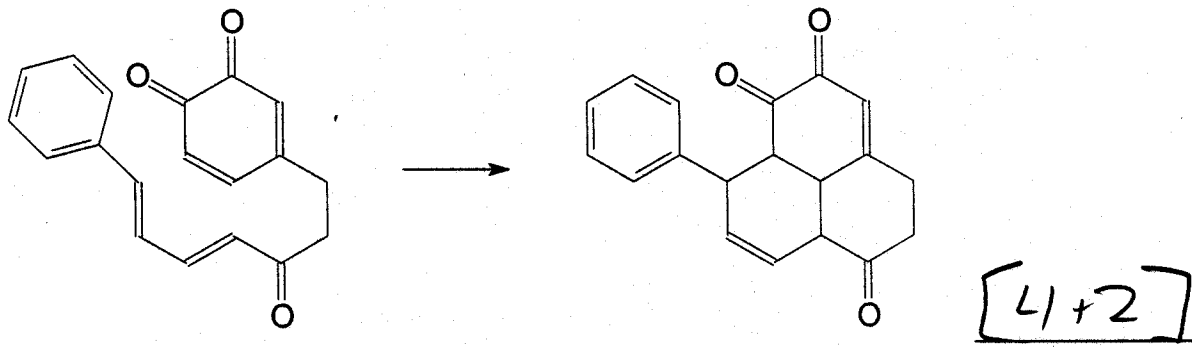
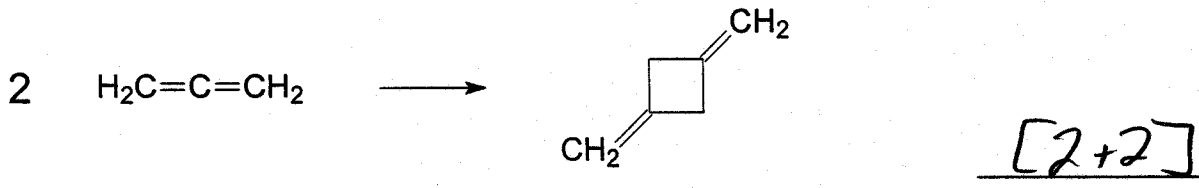


ALLOWED

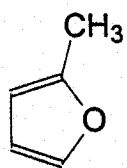
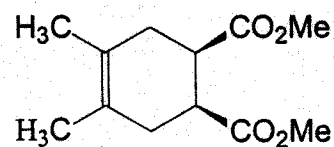
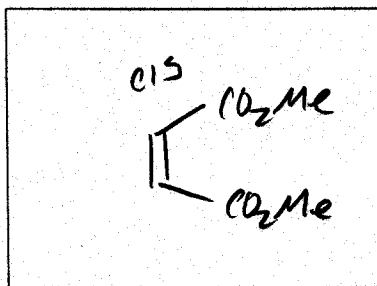
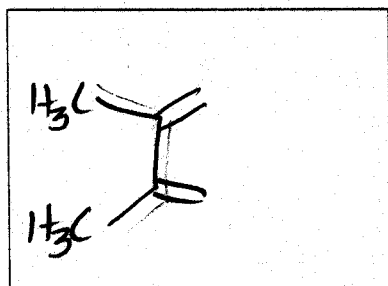


ALLOWED

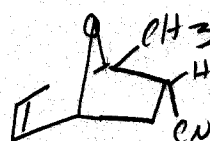
10) (9) Classify each of the following cycloadditions as [2+2], [4+2]. Etc



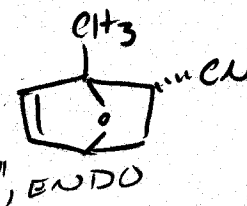
11) (68 total) For each of the following Diels-Alder reactions, provide the structure of the missing reagent(s) or product. To receive full credit, be sure to include stereochemistry when appropriate.



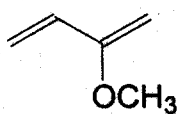
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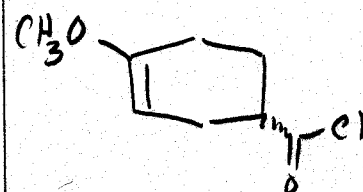
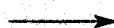
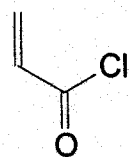
OR



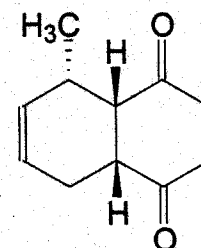
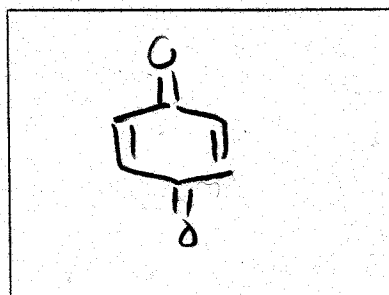
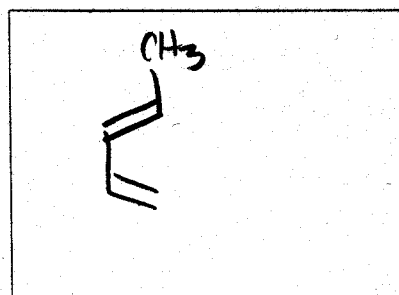
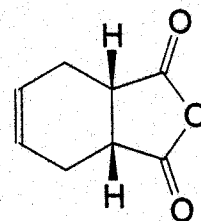
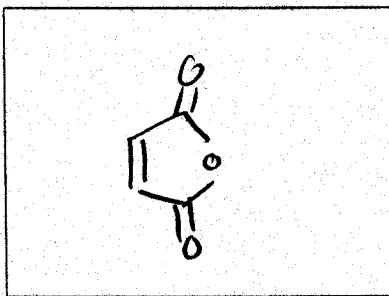
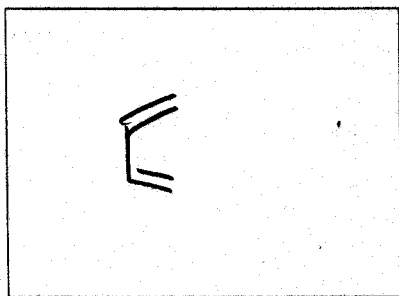
"HORIZONTAL", ENDO

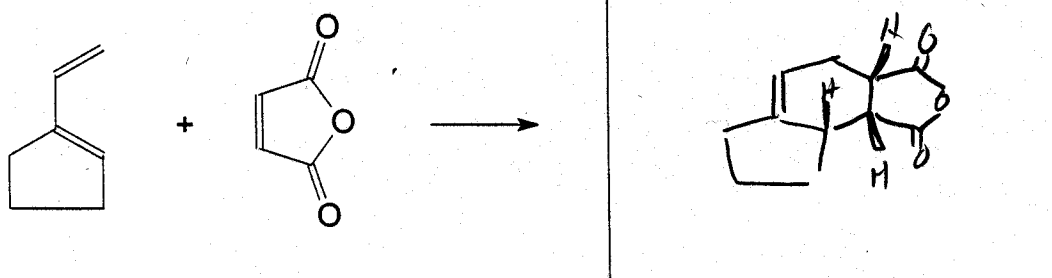
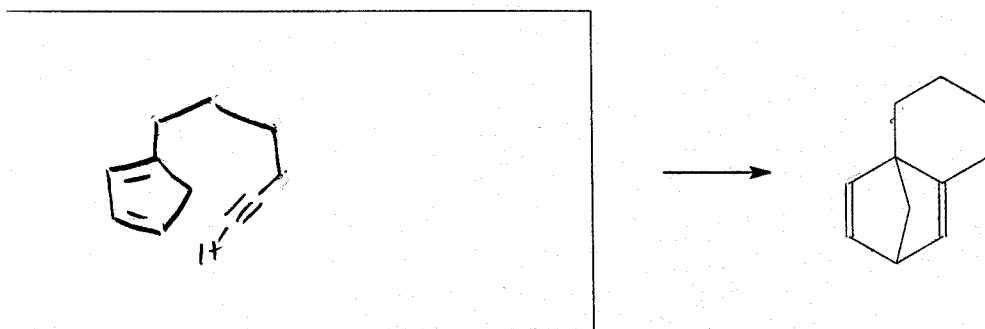
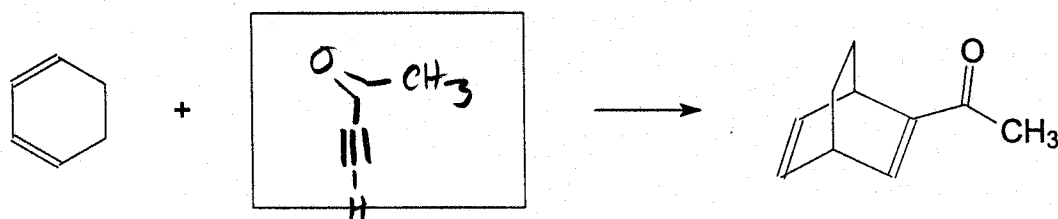
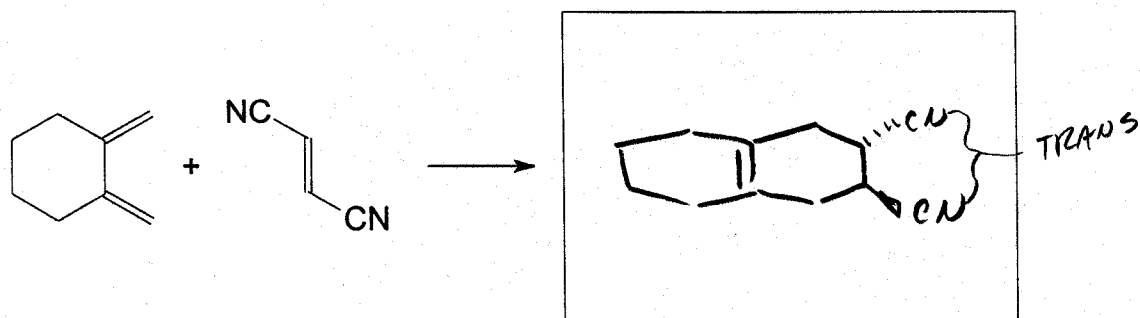
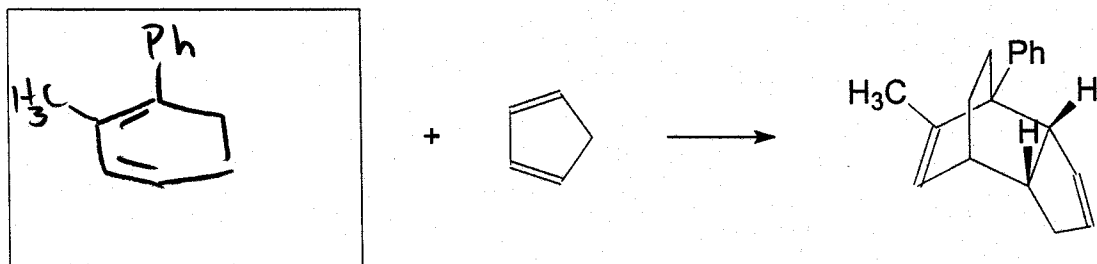


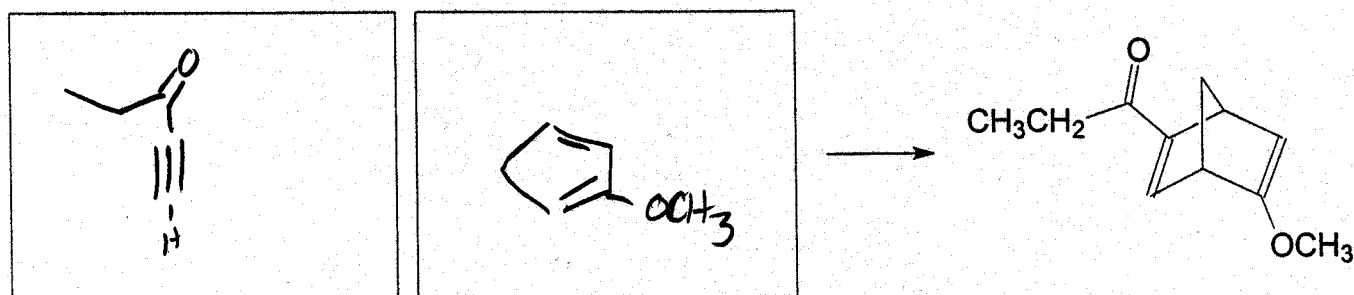
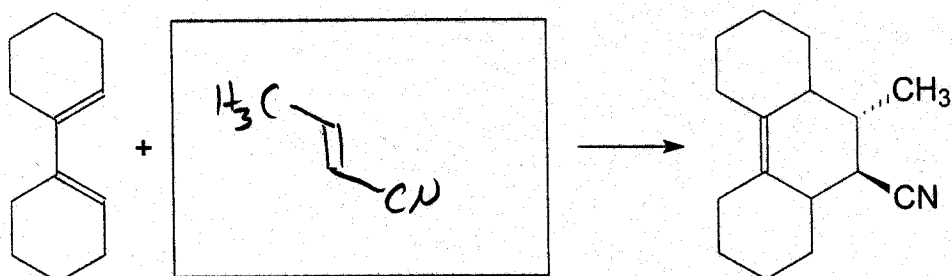
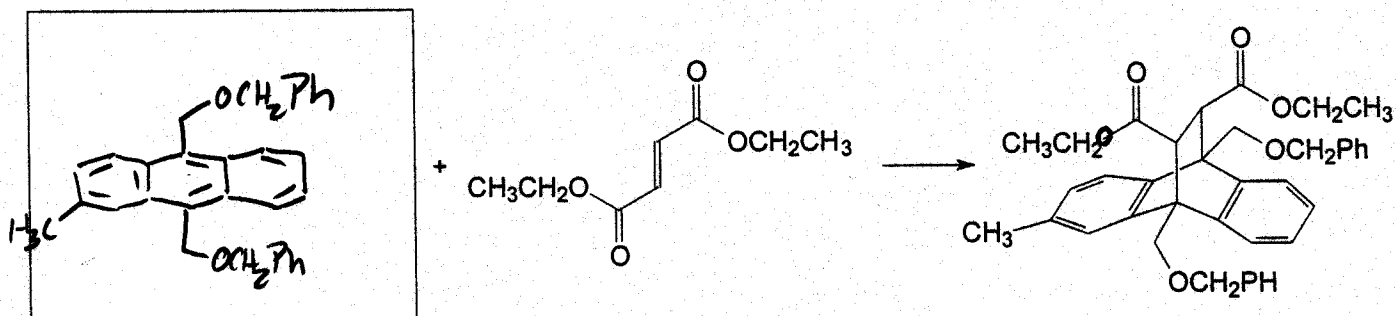
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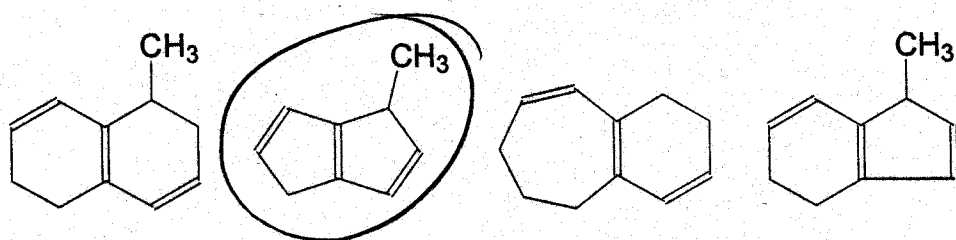
"PARA" ENDO





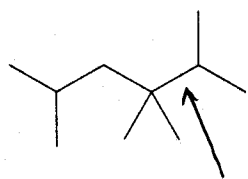


12) (5) Circle the compound with the longest λ_{max} . Explain your response for full credit.

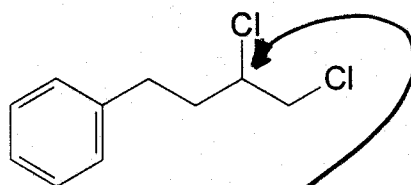


All are conjugated, but the smaller rings in the 2nd structure "lock" the π system into a conformation that allows constant conjugation. \uparrow conjugation $\downarrow \lambda_{\text{max}}$

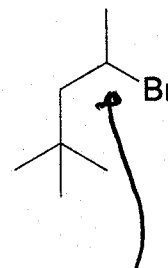
13) (15) For each compound, draw an arrow that points to the weakest bond. Please make sure that your response is clear. Explain your responses for full credit.



MOST
SUBSTITUTION

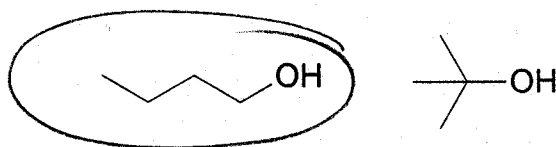


C-X AND
MOST
SUBSTITUTION



C-Br IS
WEAKER THAN
ANY C-C

14) (5) One of these isomeric alcohols has a boiling point of 82 °C, the other has a boiling point of 117°C. Explain which isomer has the higher boiling point.



GREATER DISPERSION (LONDON) FORCES.

Honor Statement (required for credit, regardless of number of correct responses above)

I have neither provided nor received any unauthorized aid for this assignment.

Signature

N. OTME HOWAY

(Printed Name)

You may also decide to sign the following (not required)

I have witnessed unauthorized aid for this assignment.

Signature

J. VIDENOT