1. (6) Offer a detailed explanation for the following observations.

(a) The barrier for rotation about the bond marked with an arrow below is only about 14 kcal/mol, significantly lower than a ‘regular’ C=C double bond.

\[
\text{\[
\begin{array}{c}
\text{\[
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\end{array}\]
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\]

(b) The molecule below is easily reduced to a dianion. The proton NMR spectrum of the dianion shows an average downfield shift, relative to the neutral hydrocarbon. The center carbon for the dianion shows a very large upfield shift in the $^{13}$C NMR spectrum relative to the neutral hydrocarbon.

2. (9) In class we discussed two different tetramethylcyclooctatetraenes, the 1,2,3,4- and the 2,3,4,5-isomers:

(a) Where do these two compounds fit on the 'isomer family tree'?

(b) It is known that if either isomer is heated to 160 °C for about 6 hours, an equilibrium mixture of both compounds results, favoring one isomer in about 70:30 ratio. Which compound do you predict would be the one in greater amount (i.e., which one isomer is thermodynamically more stable)? Why?
(c) Can you think of any other pair of tetramethyl COT isomers that might be isomeric in the same way as the 1,2,3,4- and 2,3,4,5-isomers (meaning, they could be isolated as distinct compounds at room temperature but are interconvertible at higher temperature)?
3. (6) (a) Propose a mechanism to account for the formation of products formed by decomposition of diazocyclooctadecane in the following reaction:

![Image of reaction](image_url)

(b) Other fused-ring bicyclooctadecanes could have formed. Propose why only those above are found and not others.

4. (6) Although the following two reactions below are not under the same conditions, explain why the top reaction occurs readily, while the bottom reaction does not, even when under fairly severe thermal conditions of upwards of 350 °C.

![Image of reactions](image_url)

5. (6) Predict whether orbital symmetry rules allow or forbid each of the following reactions to occur as a concerted process.
\[
\text{C}_{2}\text{H}_{4} + \text{C}_{3}\text{H}_{4} \xrightarrow{\Delta} \text{C}_{10}\text{H}_{10}
\]

\[
2 \text{C}_{2}\text{H}_{4} \xrightarrow{h\nu} \text{C}_{10}\text{H}_{10}
\]
6. (6) The following thermal cycloaddition has been reported, but the stereochemistry of the product has not been established with certainty. What would you predict for the relative stereochemistry of the indicated hydrogens (meaning, are they cis or trans)? Explain.

7. (6) Explain why each of the following reactions is, or is not, allowed to occur as a concerted process if the starting material is heated or if the starting material is subjected to photoirradiation.

8. (5) Summarize in four pages or less the "non-classical ion problem" involving the 2-norbornyl cation. Do you agree with the view that the author presents?

As a reminder, you are welcome to use any textbooks or reference books, etc., to help you with this take-home exam. You are not allowed to consult with
anyone for help, except me. If you really have no idea how to get started on a problem, call or e-mail me and I'll try to push you forward a bit.