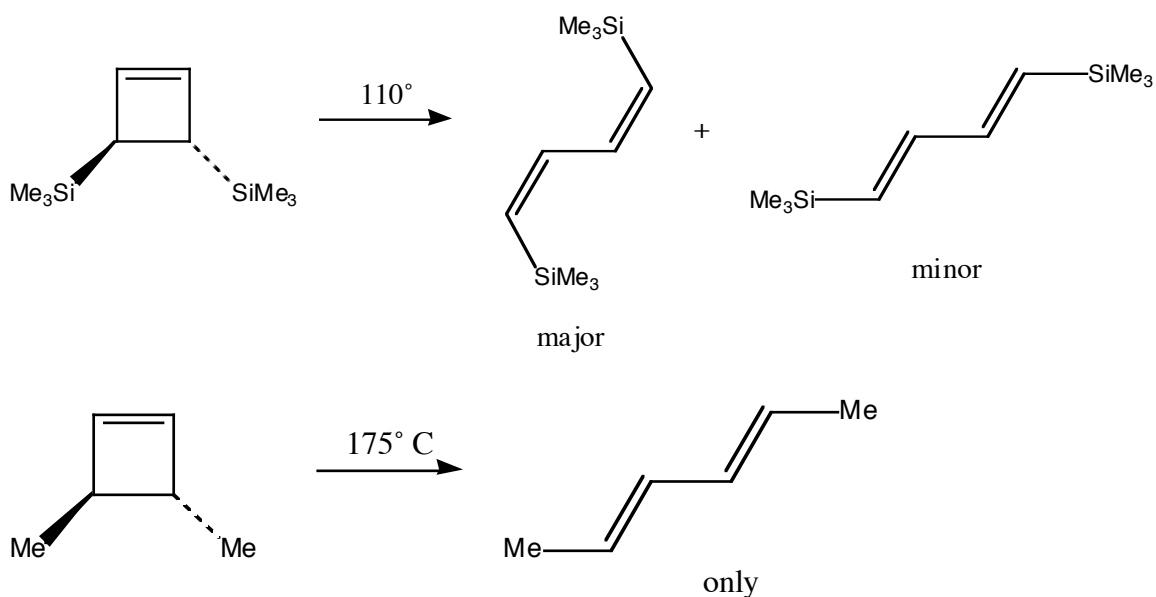


ORGANIC CUMULATIVE EXAM
April 24, 2004
Theory and Mechanism of Pericyclic Reactions

Number _____

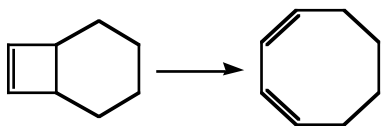
Question	Points
1.	<u> /25 </u>
2.	<u> /25 </u>
3.	<u> /15 </u>
4.	<u> /25 </u>
5.	<u> /10 </u>
Total	<u> /100 </u>

1. (25 points) M. Murakami and M. Hasegawa, Tokyo, unpublished results, and *Angew. Chem. Int. Ed.* **1995**, *34*, 1476-1477 (see also Lee, Zhang, and Houk, *J. Am. Chem. Soc.* **2003**, *125*, 5072-5079), reported the following:

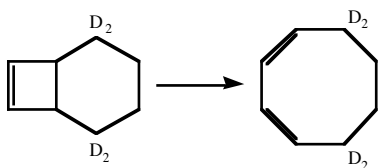


Why do silyl and methyl give different results? Please provide an explanation based upon MO theory.

2. (25 points) Baldwin *et al.*, *Org. Lett.* **2004**, ASAP, studied the following reaction:

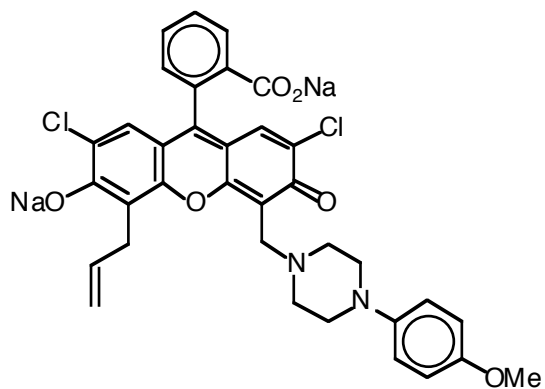


It had been proposed earlier that this reaction might be a two-step process involving a conrotatory opening and 1,5-sigmatropic hydrogen shift. The authors now measured the rate of the following reaction:



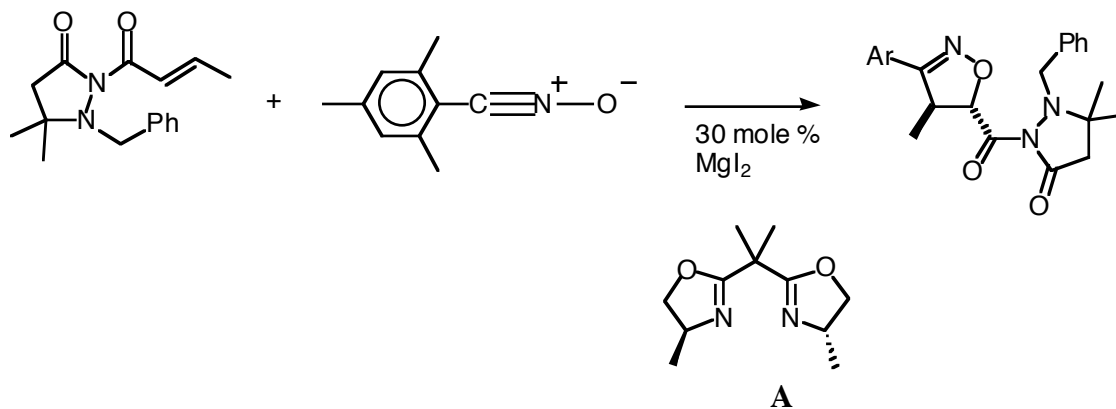
From the rate of this and the first reaction, they found that $k_H / k_{D_4} = 1.17$. Is the originally proposed mechanism consistent with this result? Explain your answer. If the original mechanism is wrong, propose a mechanism that is consistent with the isotope effect.

3. (15 points) In his April 8, 2004, Colloquium, Kazunori Koide reported that

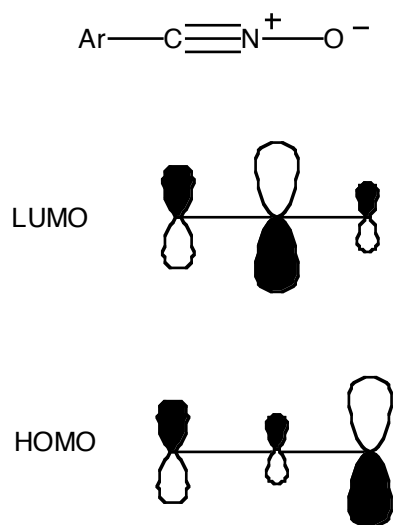


can be prepared by a Claisen rearrangement. Show the Claisen reaction that can be used to make this compound.

4. (15 points) Sibi *et al*, *J. Am. Chem. Soc.* **2004**, ASAP, report that the chiral Lewis acid, **A**, catalyzes the formation of the adduct shown.



Is this major regioisomer consistent with frontier molecular orbital control or steric control of regioselectivity – or both? Please explain what you think is a good explanation of regioselectivity. The FMOs of a nitrile oxide are sketched below:



5. (10 points) Explain if the following reactions are allowed or forbidden according to the Woodward-Hoffmann rules. Explain your answer.

