Molecular Orbital Study of the Cycloaddition Reactions
of Cyclopentyne Lumomer

John C. Gilbert* and Steven Kirschner*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, and

Department of Chemistry, Austin Community College, Riverside Campus, Austin, Texas 78741.

Key Words: Cyclobutylidenylcarbene, cyclopentyne, lumomer, orbital crossing, cycloaddition

Abstract: AM1 molecular orbital calculations of the reaction path for [2+2] and [2+4] cycloaddition reactions of cyclopentyne lumomer, **2**, with ethylene and 1,3-butadiene show concert for the former process and stepwise character for the latter. The results are consistent with Dewar's theory of orbital isomerism in pericyclic reactions.

Ring expansion of cyclobutylidenylcarbene (**1**) has been predicted computationally to produce an isomer, **2**, of cyclopentyne (**3**), rather than **3** itself.[1] The relationship between **2** and **3** is that of lumomers, in the language of Dewar's theory of orbital isomerism;[2] that is, a HOMO-LUMO orbital crossing is required for the conversion. As a consequence of this enforced crossing, there is an enthalpic activation barrier of over 10 kcal/mol for the transformation of **2** to **3**.[1]

Application of the theory of orbital isomerism leads to the proposition that the thermal [2+2] and [2+4] cycloaddition reactions of **2** would be allowed (concerted) and forbidden (stepwise), respectively, with the suprafacial participation of the relevant p-orbitals. This prediction is perhaps most easily understood in the following way. The HOMO of cyclopentyne (**3**) is basically a *symmetrical* π-like in-plane orbital[3] and may be likened to that of ethylene itself; thus **3** is predicted to undergo a thermal [2+2] cycloaddition in a stepwise manner, for example. The lumomeric relationship of **2** and **3** then requires that the predictions of the allowedness of pericyclic reactions involving **2** be precisely the opposite of those for **3**. We now report the results of molecular orbital calculations supporting the proposal that **2** does indeed undergo cycloaddition reactions according to these mechanistic motifs.
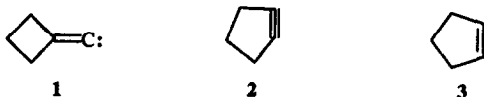

The conversion of lumomer **2** and ethylene to bicyclo[3.2.0]hept-1(5)-ene (**4**, equation 1) was studied using the AM1 method[4] with 3 x 3 configuration interaction. The C-2 - C-3 distance was selected as the reaction coordinate, and all other molecular parameters were optimized as this distance was varied. Because **2** has a higher enthalpy than its orbital isomer, cyclopentyne, most optimization procedures would tend to

produce points on the lower energy portion of the potential energy hypersurface and not on the more interesting lumomeric component of this surface. To ensure that this did not take place, all geometrical optimizations were computed using the Jacob-Thompson-Bartel (JTB) method,[5] a non-linear least-squares gradient minimization known to be capable of finding points of local minima on a potential energy hypersurface.[6]

$$\text{(structures)} \qquad (1)$$

2   188.10   4

172.19   188.10   45.93
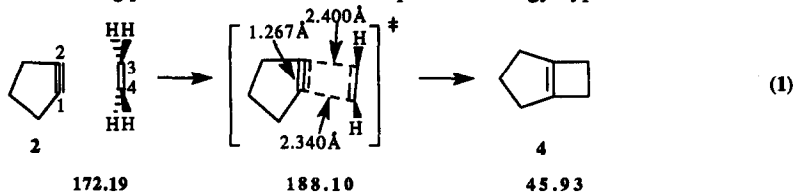
Using this procedure, the [2+2] cycloaddition reaction having *suprafacial* participation at all four of the relevant carbon atoms was found to proceed in a *concerted* manner, with nearly synchronous formation of the two new sigma bonds. The approximate[7] transition state for the reaction has a calculated ΔH_f of *188.10* kcal/mol, making the enthalpy of activation only 15.91 kcal/mol, a value commensurate with the experimental observations for this reaction.[10] Examination of all points along the reaction coordinate failed to reveal the existence of any intermediates other than the reactants and product or to show any changes in orbital occupations. This is entirely consistent with an allowed (concerted) reaction. When the identical computational procedure was employed in the study of the [2+2] cycloaddition of cyclopentyne and ethylene, a two-step reaction mechanism involving an unsymmetrical biradicaloid intermediate resulted.[9,11] This strongly indicates that the concerted reaction with nearly synchronous bond formation observed for cyclopentyne lumomer (2) is not an artifact of the computational procedure employed.

The [2+4] cycloaddition reaction of 2 and *cis*-1,3-butadiene to afford bicyclo[4.3.0]nona-1(5),3-diene (6, equation 2) was studied in a like manner, using the C-2 - C-3 bond distance as reaction coordinate and initiating the calculation with the carbon skeleta of the two reactants in a coplanar relationship.[12] Optimization of geometries using the JTB methodology provided a reaction path that was significantly different from that obtained for the [2+2] analog. In this case a biradicaloid intermediate 5 intervened between reactants and product. The transition state for formation of 5 has an enthalpy some 28 kcal/mol greater than that of the reactants. Given the considerably lower enthalpy of activation for the concerted [2+2] process, it is clear that [2+4] cycloaddition would not be competitive in alkenic substrates capable of both modes of reaction.

$$ (2) $$

2   **5**   **6**

184.47   212.70   126.07   147.72   2.98
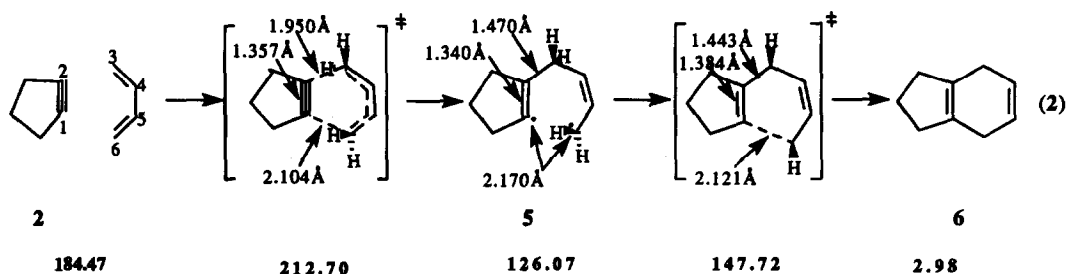
Further investigation of the biradicaloid intermediate **5** showed that conversion of this species to the cycloaddition product **6** involves an orbital crossing and consequently involves a transition state of relatively high energy, the activation enthalpy required to reach it being some 22 kcal/mol. Thus, the [2+4] reaction of lumomer **2** with 1,3-butadiene is clearly a forbidden two-step process and proceeds through a biradicaloid intermediate that lies in a rather deep potential energy well.[13]

These results, which are predicted using Dewar's theory of orbital isomerism, provide a clear distinction between this theory and that of Woodward and Hoffmann.[14] It is incorrect to state that any type of reaction is formally forbidden or allowed since this will depend not only upon the correlation of molecular orbitals but also upon the orbital occupation of reactants. For this reason the allowedness or forbiddenness of any reaction should depend only upon whether there is an orbital crossing of the HOMO and the LUMO during the course of the reaction. To paraphrase Dewar, et al.,[2a] the interconversion of homomers provides an allowed process whereas that of lumomers is forbidden.

Footnotes and References

1. Gilbert, J. C.; Kirschner, S. *Tetrahedron Lett.*, accompanying Communication.

2. (a) Dewar, M. J. S.; Kirschner, S., Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240-5242. (b) Dewar, M. J .S.; Kirschner, S.; Kollmar, H. W.; Wade, L. E. *J. Am. Chem. Soc.* **1974**, *96*, 5242-5244. (c) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 5244-5246.

3. Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884-6888; Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Chem. Res.* **1985**, 328-329.

4. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909.

5. Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736-3753. Bartell, L. S.; Burgi, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 5239-5245.

6. Dennington II, R.; Healy, E. F. *AMPAC Manual, Version 2.1*, The University of Texas at Austin, 1989.

7. Exact location of the transition state for the reaction was not possible with the JTB method. Consequently, force constant calculations could not be performed.[8] Based on unpublished work concerning the *allowed* [2+4] cycloaddition of cyclopentyne with 1,3-butadiene,[9] it is evident that the simultaneous formation of two bonds results in a rather flat potential energy maximum with several shallow local maxima. Thus there are several stationary points present and, while only one of them can be the true transition state, all have approximately the same enthalpy of formation. Consequently, although an exact transition state has not been found, the computed enthalpy of activation computed is undoubtedly close to the actual value.

8. See footnote 9 of accompanying paper.

9. Gilbert, J. C.; Kirschner, S. unpublished results.

10. Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23* , 1661-1664. Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1983**, *105* , 664. Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24* , 5495-5498. Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106* , 1885-1886.

11. A similar result has been reported using MNDO methodology; in this case an erroneously high activation enthalpy of 21.92 kcal/mol was found for formation of the biradicaloid from reactants: Olivella, S.; Pericàs, M.A.; Riera, A.; Solè, A. *J. Chem. Soc. Perkin Trans. II* **1986**, 613-617. Our full paper will describe the source of this discrepancy.

12. This starting geometry is the same as that found for the reaction of cyclopentyne with 1,3-butadiene.[8] Other possible trajectories are currently being explored computationally, but it is considered very unlikely that they will provide reaction channels of lower energy than those described herein.

13. Indeed, biradicaloid 3 is found to have available lower energy forbidden reaction paths than the one described here,[9] thus showing that the [2+4] cycloaddition reaction of lumomer 2 is not even the most preferred forbidden reaction on the potential energy hypersurface.

14. Woodward, R. B.; Hoffmann, R., *The Conservation of Orbital Symmetry*, Weinheim, Germany: Verlag Chemie, 1970.