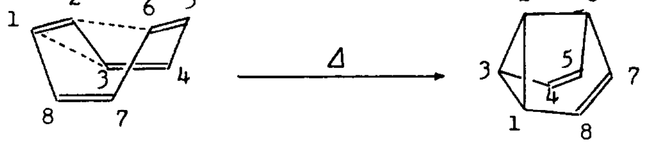
Tetrahedron Letters No. 5, pp 369 - 372, 1973. Pergamon Press. Printed in Great Britain.

A THEORETICAL ASPECT ON THE THERMAL ISOMERIZATION OF CYCLOOCTATETRAENE TO SEMIBULLVALENE

Hiizu Iwamura
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

(Received in Japan 21 October 1972; received in UK for publication 2 January 1973)

The thermal conversion of cyclooctatetraene to semibullvalene has been the subject of considerable controversy. Criegee and Askani were the first to find efficient conversion at elevated temperatures of octamethylcyclooctatetraene to the semibullvalene (1). 1,3,5,7-Tetramethylcyclooctatetraene is similarly transformed into the corresponding semibullvalenes by heating at 250° for 15 hr (2). In the case of parent semibullvalene, all experimental efforts to detect this in the gaseous and condensed phase pyrolysates of cyclooctatetraene have proved to be totally unsuccessful. The products are styrene and dihydropentalene as well as benzene and acetylene (3,4). Semibullvalene can, in contrast, be formed by the acetone sensitized photolysis of cyclooctatetraene (2,5). We interpreted the last results as a stepwise reaction by assuming the concerted 1,3;2,6 double cyclization of cyclooctatetraene to be symmetry allowed in the ground state (2). Recently, however, our photochemical results were cited as an example of the allowed reaction in the excited state (6,7). With no operational test to settle the controversy available, we present here the detailed analyses of the electronic structure of isomerization reaction;



The theoretical methods employed here are to draw correlation diagram of the MINDO MO's (8) for the above reaction. Correlation between the MO's of the species in either side of the equation is not straightforward because cyclooctatetraene and semibullvalene lack any common symmetry element. However, it is made possible to find MO correlation by imposing in the reaction coordinate close to the end an intermediate which corresponds to the transition state structure for the degenerate Cope rearrangement of semibullvalene (9,10, 11). The C_2 symmetry operation is kept for the first half and the C_s symmetry element holds throughout the last half of the reaction coordinate. Since the activation energy for the Cope rearrangement is known to be exceptionally low (9,10,11,12), the above specification of the reaction as passing through this intermediate does not necessarily mean to restrict the course of the reaction to two steps. The intermediate and semibullvalene are energetically too close to be separated on the potential energy supersurface interrelating the $(CH)_8$ isomers.

In the MO correlation diagram obtained by application of symmetry operation and the non-crossing rule to the resulting MO's, the occupied levels are satisfactorily correlated between starting cyclooctatetraene and product semibullvalene. Although separation of the σ and π characters of a given MO in the all-valence-electron SCF MO methods is not clear, the higher occupied MO's and lower unoccupied MO's can still be reasonably approximated by those constructed in terms of the π-orbital approximations. Starting from cyclooctatetraene in which the occupied levels are made of four ethylene groups weakly coupled through σ-bonds, we end up, as illustrated in Figure 1, with a σ- and three π-charactered orbitals of semibullvalene by way of the bonding levels of two interacting allylic orbitals of the intermediate. In reality all these levels split further on mixing with a combination of σ-orbitals of the same symmetry.

The second clear-cut criterion obtained in the present study which supports the thermal route is that the heat of formation of cyclooctatetraene (66.4 kcal/mole) is higher than that of semibullvalene (53.0 kcal/mole) (13); the forward reaction of the equation is predicted to be exothermic.

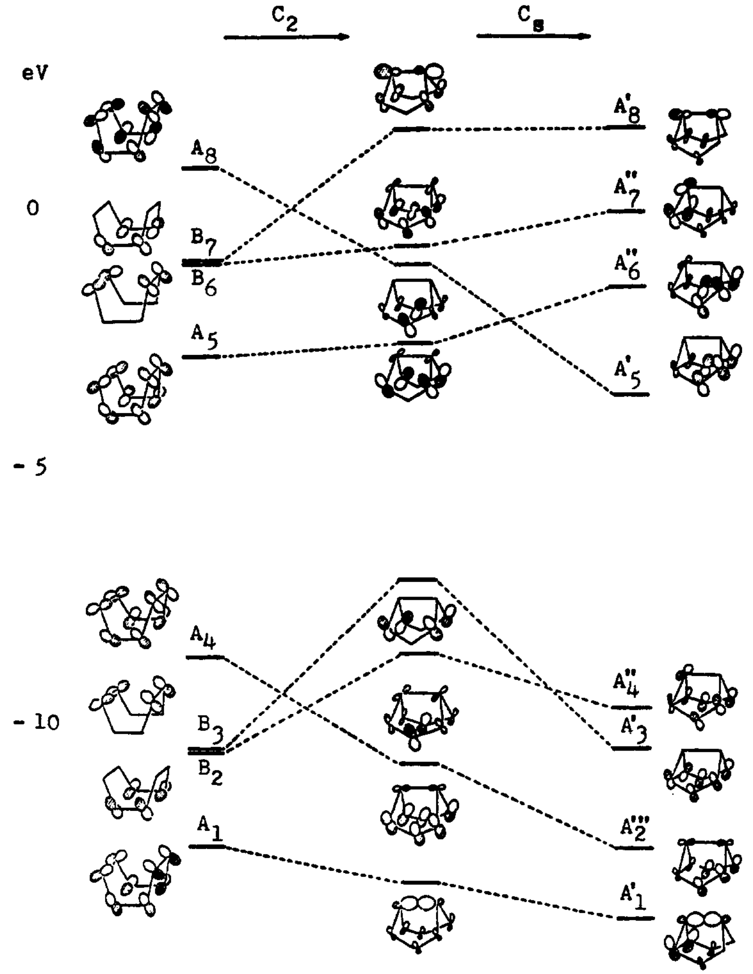
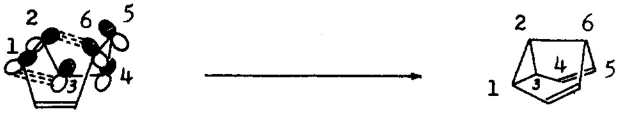


Figure 1. MO correlation diagram for the 1,3;2,6 cyclization of cyclooctatetraene to semibullvalene.

Thus it is conclusive on the theoretical bases that the isomerization reaction is an allowed process as a concerted cyclization in the ground state. The reaction may figuratively be regarded as an intramolecular Diels-Alder reaction between the C-1, C-2 ene unit and the diene C-3 $\sim$ C-6. Instead of suprafacial overlap (${}_{\pi}2_s + {}_{\pi}4_s$) between the front lobes of C-2 and C-3, and C-1 and C-6, which leads to bicyclo[4.2.0]octa-2,4,7-triene, the opposite lobes (${}_{\pi}2_a + {}_{\pi}4_a$) of the p-orbitals on C-1 and C-2 are involved to form the new σ-bonds of semibullvalene with the top p-lobe of C-6 and the bottom lobe of C-3, respectively. Prediction to the contrary, i.e., allowedness of the same 1,3; 2,6 double cyclization in the excited state, in the literature (6,7) is now found to be due to wrong drawing of the orbital overlap in which the ring closure should lead to unrealistic semibullvalene with the cyclopropane and cyclopentene rings fused *trans*.



References

1. R. Criegee and R. Askani, *Angew. Chem*., **80**, 531 (1968).
2. H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc*., **92**, 2015 (1970).
3. M. Jones, Jr. and L. O. Schwab, *ibid*., **90**, 6549 (1968).
4. H. E. Zimmerman and H. Iwamura, unpublished work.
5. H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc*., **90**, 4763 (1968).
6. K. Fukui, *Accounts Chem. Res*., **4**, 57 (1971).
7. R. C. Dougherty, *J. Amer. Chem. Soc*., **93**, 7187 (1971).
8. MINDO/1: N. C. Baird and M. J. S. Dewar, *J. Chem. Phys*., **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar and R. Sustman, *ibid*., **50**, 1275 (1969). MINDO/2: M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc*., **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget and E. Haselbach, *ibid*., **92**, 3854 (1970).
9. R. Hoffmann and W.-D. Stohrer, *ibid*., **93**, 6941 (1971).
10. M. J. S. Dewar and D. H. Lo, *ibid*., **93**, 7201 (1971).
11. H. Iwamura, K. Morio and T. Kunii, *Bull. Chem. Soc. Japan*, **45**, 841 (1972).
12. H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc*., **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald and M. A. Sherwin, *ibid*., **91**, 3316 (1969).
13. By MINDO/1. See also H. Iwamura, K. Morio and T. L. Kunii, *Chem. Commun*. 1408 (1971).