CHEMISTRY LETTERS, pp. 71-74, 1973. Published by the Chemical Society of Japan

ON THE BIRADICAL VS. CONCERTED MECHANISMS FOR THE THERMAL REARRANGEMENT OF TRICYCLO[3.3.0.0^{2,6}]OCTA-3,7-DIENE TO SEMIBULLVALENE(1)

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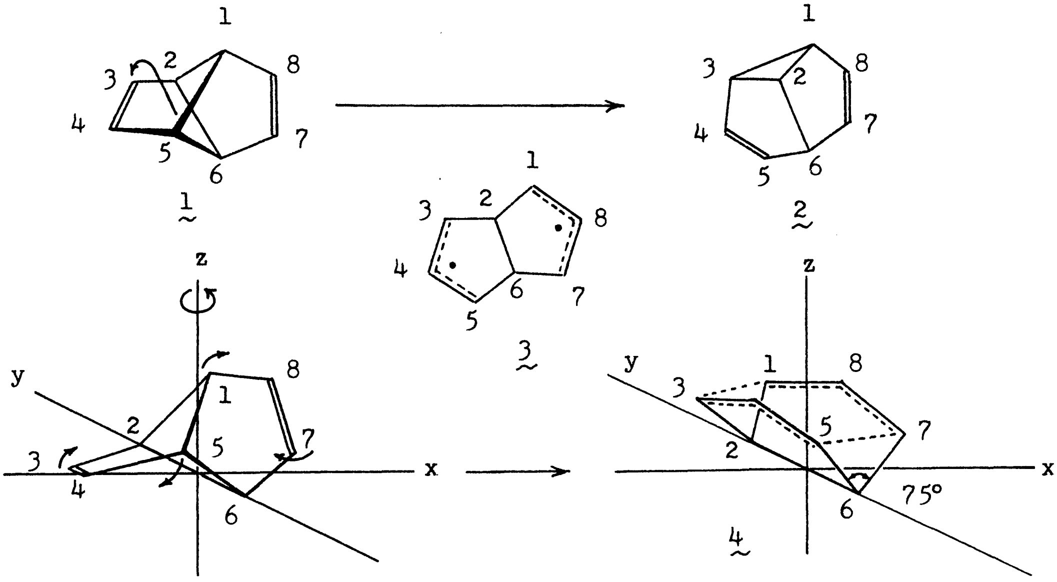
A symmetry-allowed concerted process is proposed by the MINDO/2 MO study for the facile rearrangement of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene **1** to semibullvalene **2**. The reaction path involves the cleavage of an allylic bond by twisting the molecule with C_2 symmetry operation kept until the geometry corresponding to the transition state for the Cope rearrangement of **2** is obtained.

The formal application of the orbital symmetry rules for the extremely facile rearrangement of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene **1** to semibullvalene **2** discovered by Meinwald and co-workers(2) and by Zimmerman and co-workers(3) leads to a prediction that the suprafacial 1,3-sigmatropic shift as represented in Eq. 1 is thermally forbidden as a concerted process. Thus an intermediacy of "stable bis-allyl radical" **3** has been postulated for the reaction by the original authors. When there is a face to face overlap between both ends of two allyl groups, however, the degenerate non-bonding orbitals split into the bonding and anti-bonding orbitals, and the ground state of the interacting system can be described by a closed shell singlet. Goldstein and Hoffmann proposed a symmetry-allowed concerted mechanism in which the cleavage of a vinyl bond rather than an allyl bond is involved.(4) A most likely precedent in favor of the latter mechanism may be the ring opening of bicyclo[2.1.0]pent-2-ene.(5) However, the experimental findings by Baldwin and Andrist was recently questioned by McLean and co-workers.(6) Thus two alternative mechanisms are considered to be susceptible of criticism.

We wish to report here the MINDO/2 MO study(7) which clearly indicates that there is a reaction path from **1** to **2** in which the interaction between two allyl moieties in species **3** is always kept sizable and therefore the intermediate species can not at any stage of the reaction coordinates be entitled as biradical. The new reaction path starts with the cleavage of an allylic bond, e.g., C_1-C_5, followed by twisting of the molecule symmetrically so that the C_2 symmetry operation is kept around the z axis passing through the centers of bonds C_1-C_5 and C_2-C_6, the latter lying on the y axis (Eq. 2). The twisting process is continued up until species **4** is obtained which corresponds exactly to the transition state geometry for the Cope rearrangement of semibullvalene **2**. The intermediate has been shown experimentally[8)] as well as theoretically[9)] to lie very close to **2** on the ground state potential energy hypersurfaces interrelating $(CH)_8$ isomers. The subsequent process from **4** to **2** should, therefore, be spontaneous.



(1)

(2)

Although a minimum energy reaction path has not yet been attained by the present calculations, several snapshots of the geometries along the proposed reaction coordinates and of the corresponding MO's are instructive to help construct MO correlation diagram for the reaction (Fig. 1) and disclose some interesting features of the electronic structure of the rearrangement of **1** to **2** by way of **4**. These are : 1) In the equilibrium geometry of the starting molecule **1** obtained by minimizing the MINDO/2 energy with respect to all independent internal coordinates, we note strong mixing between the ethylenic π-bonds and the high-lying σ-orbitals of the cyclobutane ring. The overlap integral between the p_π-orbital on C_3 and the parallel p-orbital on C_2 amounts to 0.20, and an incomparably large value (-0.26 eV) of resonance energy due to this interaction is calculated. As a result, the four highest occupied 17 to 20th MO's out of 20 occupied MO's of the 40 valence electron system are approximated as in Figure 1.10, 11) 2) As C_1-C_5 bond cleaves and the distance between the two carbon atoms increases from 1.534 Å in 1 to 2.90 Å in 4, the degenerate pairs start to split, 18 and 20th MO's destabilizing. However, nowhere on the reaction coordinates the energy gap between these occupied levels and the lowest unoccupied level is less than 7 eV, nor the calculated destabilization in total energy is more than 30 kcal/mole relative to 1. Note that the word biradical can be used in the sense of MO theories for the systems with two degenerate or nearly degenerate non-bonding levels half-filled. We also find that the energy gap between HOMO and LUMO becomes less than 5 eV and inclusion of the lowest doubly excited configuration may lead to an appreciable decrease in energy only when the

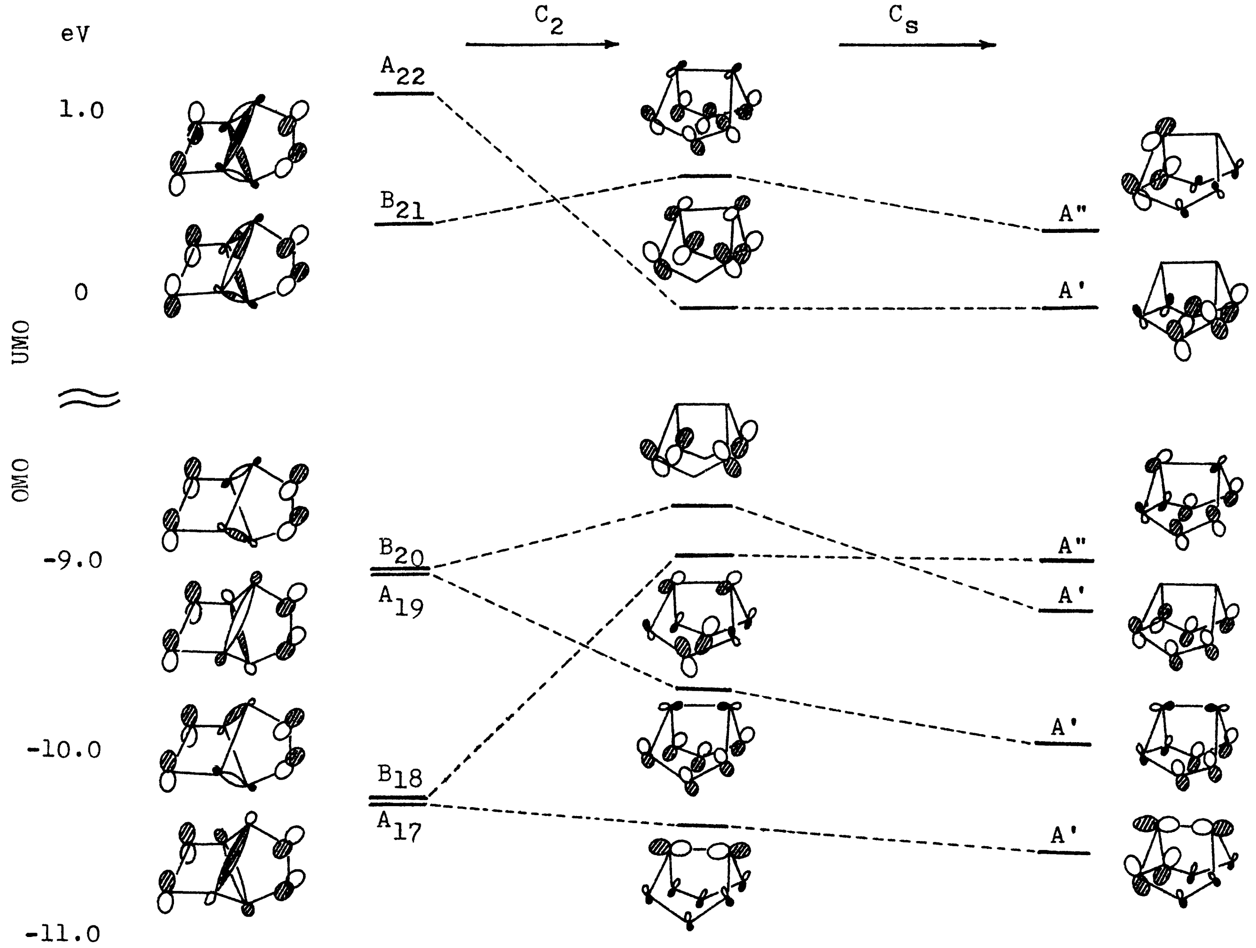


Figure 1. Approximate MINDO/2 MO correlation diagram for the thermal rearrangement of 1 to 2.

dihedral angle between two five-membered rings in **3** is expanded as large as 120°. 3) The driving force of the exothermic reaction (Eq. 1, $\Delta\Delta H_f = -12$ kcal/mole[12]) is found by the energy partitioning study to be due primarily to the release of steric strain in **1** as revealed by decrease in two center energy terms.

Thus the rearrangement of **1** to **2** by the mechanism proposed in this paper is concluded to be an allowed process under thermal conditions.

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(Received November 20, 1972)