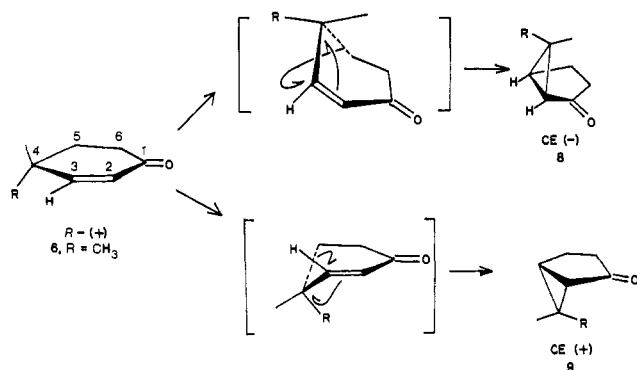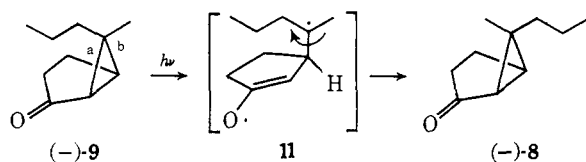figuration at C_4 (see Scheme I). Similarly, formation

Scheme I

of **9** from **6** occurs by downward movement of C_4, bonding between C_3 and C_5 on the top face and formation of the 2–4 bond on the bottom face of the ring, once again with inversion at C_4. The results exclude the involvement of any diradical along the reaction coordinate which can undergo rotation about the former C_3–C_4 bond, since this would lead to loss of stereospecificity in lumiketone formation as well as to racemization in the route to cyclopentenone **10**.[14]

Photolysis of (−)-**9** at 300 nm in *tert*-butyl alcohol gives (−)-**8** as well as racemic **10**. Thus, the photochemical epimerization does not alter the configuration of the cyclopropyl ketone chromophore and must take place by cleavage of bond a in **9** and pivoting around bond b.[16] Thus, the intermediate diradical in the epimerization, presumably **11**, is also specifically ex-

cluded from the pathway utilized in conversion of cyclohexenone **6** to the lumiketones **8** and **9**.

These results, coupled with the observation of retention of configuration at C_1 in **3** → **4**,[6] suggest that the conversion of cyclohexenones to lumiketones is a completely concerted $_\sigma 2_a + _\pi 2_a$ process.[17] This is despite the fact that the reaction originates from a triplet excited state and occurs with very low quantum efficiency.[18] Furthermore, energy wastage cannot be due to reversion to **6** from diradicals generated along the reaction pathway.[19] All the data are consistent with a very rapid relaxation of the spectroscopic enone triplet[20] by torsion around the carbon–carbon double bond to give a twisted triplet,[21,22] which partitions between

decay to the ground state potential surfaces of starting material (major pathway) and products (minor pathway). One would expect that these S_0 surfaces have energy maxima in the region corresponding to the "twisted π-bond biradicaloid,"[21] which therefore serves as an ideal point ("funnel") for crossing from T_1 to S_0. Partitioning ratios, and therefore quantum efficiencies, should depend critically on the exact shapes of the S_0 and T_1 surfaces in this region.

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MINDO/3 Study of Some Diels–Alder Reactions[1]

Sir:

The mechanism of the Diels–Alder reaction has been the subject of much discussion during the last 40 years.[2–11] Initially two limiting processes were considered, *i.e.*, a pericyclic reaction involving a more or less symmetrical cyclic transition state and a two-step process involving a biradical as a stable intermediate. In recent years it seems to have been generally agreed that the reaction is concerted, but varying opinions have been expressed concerning the symmetry of the transition state.

Problems of this kind, involving the detailed timing of individual bond forming and bond breaking processes during a reaction, are notoriously incalcitrant to experimental solution. Equally, until very recently, no theoretical procedures were available that could give reliable predictions in such cases. The development of MINDO/3[12] seems to have met this requirement, judging by the results of a number of investigations of pericyclic and other reactions.[14] We have therefore

(16) This is the same route as found for interconversion of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one: H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, 90, 4892 (1968).

(17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH–Academic Press, 1970, p 89 ff.

(18) Φ for disappearance of **6** in t-BuOH at >290 nm is 0.017, and the reactions of **6** can be quenched by oxygen and by naphthalene ($k_q\tau$ = 7.5 M^{-1}).

(19) Studies to be described elsewhere indicate that reversible formation of diradicals by α-cleavage of the C_1–C_6 bond does not occur.[4]

(20) Defined as having the geometry corresponding to the minimum in the S_0 potential surface.[21]

(21) J. Michl, *Mol. Photochem.*, 4, 243, 257 (1972).

(22) P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, 91, 5090 (1969).

(1) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

(2) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

(3) A. Wassermann, "Diels-Alder Reactions," Elsevier, Amsterdam, (1965).

(4) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, 6, 16 (1967).

(5) H. Kwart and K. King, *Chem. Rev.*, 68, 415 (1968).

(6) H. Wollweber in "Methoden der Organischen Chemie," Vol. V/lc, George Thieme Verlag, Stuttgart, 1970.

(7) M. J. S. Dewar and R. S. Pyron, *J. Amer. Chem. Soc.*, 92, 3098 (1970).

(8) R. B. Woodward and T. Katz, *Tetrahedron*, 5, 70 (1959).

(9) S. W. Benson, *J. Chem. Phys.*, 46, 4920 (1967).

(10) W. v. E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, 94, 3833 (1972).

(11) J. W. McIver, *J. Amer. Chem. Soc.*, 94, 4782 (1972).

(12) MINDO/3 is an improved version of the MINDO[13] semiempirical SCF-MO method.

(13) See N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 94, 5303 (1972) and earlier MINDO papers cited there.

(14) See, *e.g.*, M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 96, 5244, 5246 (1974), and in press; R. C. Bingham, M. J. S. Dewar, and R. C. Haddon, *ibid.*, submitted for publication; R. C. Bingham, M. J. S. Dewar, and H. W. Kollmar, *ibid.*, submitted for publication; M. J. S. Dewar and R. C. Haddon, to be published.
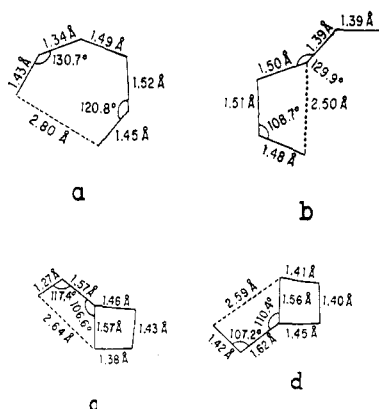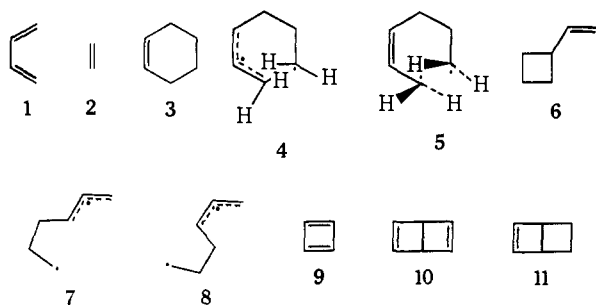
Figure 1. Calculated interatomic distances (Å) and angles (deg) in the transition states for reaction of (a) 1 with 2 to form 4, (b) 1 with 3 to form 5, (c) 9 with acetylene to form 10, and (d) 9 with ethylene to form 11.

used it to study the simplest of Diels–Alder reactions, i.e., that between 1,3-butadiene (1) and ethylene (2) to form cyclohexene (3).

The reaction was first followed by using the distance (r) between the midpoints of the C_2C_3 bond in 1 and the CC bond in 2 as the reaction coordinate,[15] the energy being minimized with respect to all other coordinates for each value of r. The results indicated that the transition state is very unsymmetrical (cf. ref 11), one new CC σ bond having been almost completely formed while the other had hardly begun to form at all. As a check the calculation was repeated enforcing C_s symmetry; the calculated activation energy was then 70–80 kcal/mol, implying that such a symmetrical concerted path is very unfavorable.

The extreme asymmetry of the transition state implied a high degree of biradical character. In such cases it is necessary[16] to include CI with the lowest doubly excited configuration. The MINDO/3 calculations were therefore repeated with such CI. The transition state found in this way (see Figure 1a) was indeed very unsymmetrical, corresponding to a biradical-like structure with a weak interaction between the radical centers, i.e., a biradicaloid.[17] The calculated activation energy (28.2 kcal/mol) was in very good agreement with experiment (27.5 kcal/mol[18]).

The transition state differs very significantly from the classical biradical 4 in structure, the terminal methylene groups being nonplanar and the "allyl" carbon-carbon bonds dissimilar in length, in the manner indicated in 5.

(15) See M. J. S. Dewar and S. Kirschner, J. Amer. Chem. Soc., 93, 4290 (1971).
(16) See R. C. Bingham and M. J. S. Dewar, J. Amer. Chem. Soc., 94, 9107 (1972).
(17) See M. J. S. Dewar, H. W. Kollmar, S. Kirschner, and L. E. Wade, J. Amer. Chem. Soc., 96, 5242 (1974).
(18) D. Rowley and H. Steiner, Discuss. Faraday Soc., 10, 198 (1951).

While the reaction of 1 with 2 leads predominantly to cyclohexene, Bartlett and Schueller[19] have found that 0.02% of vinylcyclobutane (6) is also formed. This could arise either by an "allowed" $[_\pi2_s + _\pi2_a]$[20] cycloaddition or by a "forbidden" $(_\pi2_s + _\pi2_s)$ one. The latter is more likely since MINDO/3 calculations[21] have shown that the $(_\pi2_s + _\pi2_a)$ dimerization of ethylene to cyclobutane is extremely unfavorable. The "forbidden" reaction involves the conversion of (1 + 2) into a lumomer;[22] it must therefore be accompanied by a HOMO–LUMO crossing and so take place via an intermediate biradical,[22] which presumably can be represented by 4. There are, however, two distinct paths by which such a reaction could take place, corresponding to association of 2 with cis- or trans-1. We investigated the reaction by following its reverse, i.e., the dissociation of 6 into 1 + 2.

Here again only one CC bond is weakened initially, leading to a biradicaloid corresponding to the classical structure 7 (see Figure 1b). As in the corresponding reaction of cyclobutane itself,[21] the transition state occurs at the point when the HOMO and LUMO cross and it can therefore be represented as a "true" biradical species. Of the two possible isomeric biradicaloids 7 and 8, that (7) with trans geometry in the nascent butadiene moiety was favored. We therefore conclude that 6 is formed by the reaction of 2 with trans-1,3-butadiene. The calculated activation energy (31.8 kcal/mol) is greater by 3.6 kcal/mol than that for the normal Diels–Alder reaction to form 3. The frequency factor for formation of 6 is not known.

We have also studied in a similar manner, including CI, the Diels–Alder reactions of cyclobutadiene (9) with acetylene and with ethylene to form, respectively, Dewar benzene (10) and its dihydro derivative 11. The calculated activation energies were very low (4.7 and 1.7 kcal/mol, respectively), in agreement with the experimental evidence[23] that reactions of this type are extremely facile. The transition states (Figure 1c and d) are again very unsymmetrical, corresponding to biradicaloid structures.

The transition states for these three typical Diels–Alder reactions, covering a span from very low to very high reactivity, thus differ from classical biradicals only because the latter are inherently unstable.[17] It is clear that the reactions cannot properly be classed as concerted pericyclic processes. Since it seems equally clear from our calculations that no stable intermediates are involved, the term "two-stage" reaction proposed by Woodward and Katz[8] seems very appropriate. While the reaction does not take place in kinetically distinct steps, the two new bonds appear to be formed at different stages, one on the way to the transition state and the other after the transition state has been passed.

(19) P. D. Bartlett and H. E. Schueller, J. Amer. Chem. Soc., 90, 6071 (1968).
(20) R. B. Woodward and R. Hoffmann, Angew. Chem., Int., Ed. Engl., 8, 781 (1969).
(21) M. J. S. Dewar and S. Kirschner, J. Amer. Chem. Soc., 96, 5246 (1974).
(22) M. J. S. Dewar, H. W. Kollmar, and S. Kirschner, J. Amer. Chem. Soc., 96, 5240 (1974).
(23) R. Pettit, Pure Appl. Chem., 17, 253 (1969).

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