straints become so extreme that the reaction is forced to follow an unfavorable symmetrical path.

These arguments imply that the transition state of any "forbidden" electrocyclic reaction should be unsymmetrical unless symmetry is enforced by severe geometrical constraints and that in general the transition state of such a reaction will precede the HOMO–LUMO crossing.[19] Biradical intermediates should not therefore play any mechanistic role in such reactions, except as transition states in the exceptional cases where symmetry is enforced.

(19) Bauld, et al.,[20] have suggested that "forbidden" electrocyclic reactions take place via unsymmetrical transition state; which in our terminology would be described as biradicals. It is of course well recognized that other "forbidden" pericyclic reactions take place via unsymmetrical transition states so the same would also be expected of "forbidden" electrocyclic reactions. However, the present discussion shows that the latter do show a novel feature; i.e., the transition states occur before the biradical intermediate is reached.

(20) N. L. Bauld, F. R. Farr, and C. S. I-Chang, Tetrahedron Lett., 2443 (1972).

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Dimerization of Ethylene to Cyclobutane[1]

Sir:

The dimerization of ethylene (1) to cyclobutane (2) and the reverse conversion of 2 to 1 have been the subjects of much recent discussion.[2-9] The mechanisms which have been considered are first an "allowed" reaction proceeding with inversion about one double bond via a skew transition state 3, secondly, a "forbidden" reaction proceeding via an antiaromatic rectangular transition state 4, and thirdly, a reaction involving the biradical 5 as a stable intermediate. The latter mechanism has been favored by Benson[5-7] on the grounds that the observed activation energy for conversion of 2 to 1 is greater than the estimated difference in energy between 2 and 5.

| 1 | 2 | 3 | 4 | 5 |
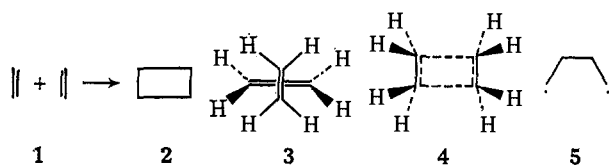
We have studied these processes in detail, using the MINDO/3 semiempirical SCF MO method.[10] The path of lowest energy was found to be via structures

(2) L. Salem and C. Rowland, Angew. Chem., Int. Ed. Engl., 11, 92 (1972).
(3) L. M. Stephenson, J. H. Gibson, and J. I. Brauman, J. Amer. Chem. Soc., 95, 2849 (1973).
(4) R. Hoffmann, S. Swaminathan, B. Odell, and R. Gleiter, J. Amer. Chem. Soc., 92, 7091 (1970).
(5) S. W. Benson, J. Chem. Phys., 34, 521 (1961).
(6) S. W. Benson and M. F. O'Neal, J. Phys. Chem., 72, 1866 (1968).
(7) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968 Section 3.10.
(8) G. R. Freeman, Can. J. Chem., 44, 245 (1966).
(9) R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969).
(10) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

analogous to 5. In view of the biradical-like nature of such intermediates, CI with the lowest doubly excited configuration was included.[11] The potential surface had the "two-valley" structure typical of forbidden pericyclic reactions.[12] The surface is divided in two by a ridge corresponding to the biradical intermediates, separating the lumomeric species on either side of it.[13] In the vicinity of the transition state, the system exists as one of two biradicaloid[14] structures, 6 and 7. In 6, which is homomeric with 1, the radical centers are coupled hyperconjugatively via the intervening C–C $p\sigma : p\sigma$ bond,[14] while in 7, which is homomeric with 2, the coupling is across space.[14] In each case the "radical" centers are nonplanar, as in the analogous biradicaloids derived from bicyclo[2.2.0]hexane.[14] The biradicaloid 6 is most stable, as indicated, in a trans conformation while 7 is most stable in cis. Neither biradicaloid is a stable species but there is a ridge in the potential surface for conversion of 2 to 1 at ca. 60 kcal/mol above 2. The conversion of 7 to 6, and hence 1, involves rotation about the central bond and inversion of both terminal methylene groups. The reaction involves a HOMO–LUMO crossing, i.e., is "forbidden," and so requires activation. The overall activation energy for conversion of 2 to 1 (62 kcal/mol) agrees well with experiment (62.5 kcal/mol[7]).

Simple dimerization of ethylene in this way via 6 and 7 would give a cyclobutane in which the geometry of both ethylene units is retained. In order to get inversion of one methylene moiety, it is necessary to rotate one of the terminal methylene groups in 6, e.g., CH_1H_2, about 180° to form, e.g., 8. This is a "forbidden" process, precisely analogous to the corresponding rotation of one terminal methylene in 1,3-butadiene, though the activation energy here will naturally be much smaller since the AO's of the two terminal carbon atoms are coupled much less strongly in 6 than in butadiene. "Forbidden" inversion of 8 to 9 can then lead to the

| 6 | 7 |
| 8 | 9 |
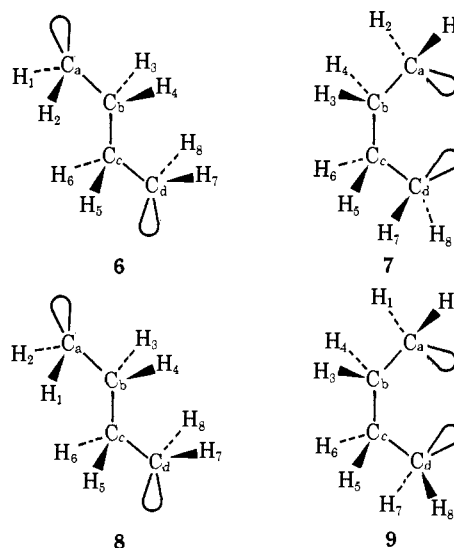
isomeric cyclobutane. The amount of 9 formed, and

(11) Cf. R. C. Bingham and M. J. S. Dewar, J. Amer. Chem. Soc., 94, 9107 (1972).
(12) M. J. S. Dewar and S. Kirschner, J. Amer. Chen. Soc., 93, 4290, 4291, 4292 (1971).
(13) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, J. Amer. Chem. Soc., 96, 5240 (1974).
(14) M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, J. Amer. Chem. Soc., 96, 5242 (1974).

so the extent to which configuration is lost during dimerization of **1** to **2**, will depend on the relative activation energies of the two "forbidden" processes **6 → 7** and **6 → 8**. Since both have very low activation energies, the difference between them must be correspondingly small. The conversion of **1** to **2**, or of **2** to **1**, should therefore take place with partial retention, but much loss, of configuration. This is the case.[15]

The loss of configuration in these reactions is due to the formation first of the "wrong" intermediate (**6** in the case of **1 → 2**) which has to undergo a "forbidden" conversion to the "right" one (**7**). If the latter were formed directly, it should collapse to cyclobutane with little or no loss of configuration. Bartlett and Porter[16] have indeed found that photolysis of **10** gives **12** with little of the trans isomer; in this case loss of N_2 from **10** gives the biradicaloid **11** analogous to **7**.
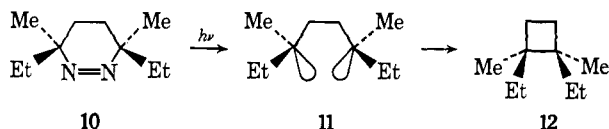
Benson[7] estimated the heat of formation (ΔH_f) of the biradical **5** assuming it to have a classical localized structure, the difference between it and 1-n-butyl radical being the same as that between 1-n-butyl and n-butane. Apart from general objections to the use of the localized bond model for biradicals, this argument specifically neglects the effects of spin correlation. The biradical can exist as a singlet state or a threefold degenerate triplet. Benson's method gives an average of the four. His value is therefore less than that of the singlet by three-quarters of the singlet–triplet separation or $1.5K_{\mu\nu}$ where $K_{\mu\nu}$ is the exchange integral between the two singly occupied orbitals. Since the latter are not localized AO's but delocalized MO's, and consequently overlap with one another, $K_{\mu\nu}$ would not be expected to vanish. MINDO/3 indeed predicts a value of 5 kcal/mol for $K_{\mu\nu}$ for the cis structure **5**. It is therefore not surprising that Benson's value of ΔH_f for the biradical was less (by 6 kcal/mol) than that observed for the transition state for conversion of **1** to **2** and his conclusion that the biradical must consequently be a stable intermediate is therefore not valid.

(15) C. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, **73**, 4497 (1951).
(16) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

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η^2-Cyclobutadienoid Transition Metal Complexes. The Preparation and Characterization of a Binuclear Complex Possessing a Bridging Cyclobutadiene Ligand

Sir:

We wish to report the first example of a complex in which a cyclobutadiene ligand is simultaneously η^2 bonded to two metals. Although binuclear η^2-cyclobutadienoid complexes have been proposed as intermediates in ligand transfer reactions,[1,2] no previous

(1) D. F. Polluck and P. M. Maitlis, *Can. J. Chem.* **44**, 2673 (1966).

experimental evidence has been presented supporting the existence of such species.

Our recent preparation of η^2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**2**)[3] suggested that the analogous binuclear cyclobutene
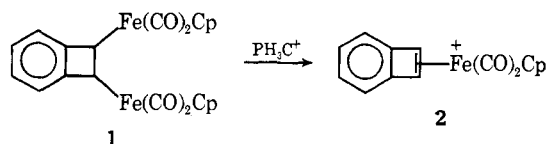
complex (**3**) might serve as a precursor for the preparation of a cationic η^2-cyclobutadiene complex (**9**) *via* oxidative demetallation. The reaction between 3,4-dichlorocyclobutene and sodium η^5-cyclopentadienyldicarbonylferrate is known to yield the binuclear butadiene complex **5**,[4–9] the structure of which has been determined both in the crystal[5,6] and in solution.[7–9] We have reinvestigated this reaction and found that the progenitor of **5**, the binuclear cyclobutene complex **3**, is readily prepared in 47% yield. The preparation of **3** was effected by the sequential mixing of tetrahydrofuran solutions of sodium η^5-cyclopentadienyldicarbonylferrate and the dichlorocyclobutene at $-78°$, allowing the reaction mixture to warm to $0°$, filtering, rotary evaporating the filtrate (without external heating), washing the residue with cold ($0°$) petroleum ether, and finally recrystallizing from carbon disulfide at $-78°$ to afford **3** as dark yellow-brown crystals. The spectroscopic properties (^{1}H nmr and ir) of **3** and of all other new compounds are presented in Table I. The

Table I. ^{1}H Nmr and Ir for New Complexes[a]

3	Nmr (CS$_2$) τ 6.33 (m,[b] 2, H^1), 5.38 (s, 5, Cp), 4.29 (m,[b] 2, H^2); ir[c] 1981, 1922 cm^{-1} (C≡O)
4	Nmr (CS$_2$) τ 6.17 (m,[b] 1, H^1), 5.59 (m,[b] 1, H^2), 5.18 (s, 5, Cp), 4.37 (m,[b] 1, H^3), 3.72 (m,[b] 1, H^4); ir 2000, 1950 cm^{-1} (C≡O)
6	Nmr (CD$_3$NO$_2$) τ 4.53 (s, 4, H), 4.26 (s, 10, Cp); ir 2080, 2040 cm^{-1} (C≡O)
7	Nmr (CS$_2$) τ 6.45 (s, 3, OCH$_3$), 5.17 (s, 5, Cp), 4.79 (d, 1, H^1, $J_{1,2}$ = 15 Hz), 3.27 (m, 2, H^2 and H^3, $J_{2,3}$ = 10.5 Hz), 2.21 (d, 1, H^4, $J_{3,4}$ = 15 Hz); ir 2000, 1938 cm^{-1} (C≡O)
8	Nmr (CD$_3$)$_2$CO τ 6.57 (m,[b] 1, H^4), 5.46 (m,[b] 1, H^3), 4.98 (m,[b] 1, H^2), 4.69 (s, 5, Cp), 4.23 (s, 5, Cp^1), 3.20 (m,[b] 1, H^1); ir 2060, 2025, 2000, 1944 cm^{-1} (C≡O)

[a] All new compounds gave satisfactory analyses for carbon and hydrogen. [b] Narrow multiplet. [c] Ir spectra were taken as Nujol mulls.

assignment of the trans orientation of the metals in **3** is based on the quantitative electrocyclic isomerization of **3** to **5**, which in the absence of any special electronic effects requires a trans disubstituted cyclobutene. We have also isolated, by fractional recrystallization of the

(2) P. M. Maitlis and A. Efraty, *J. Organometal. Chem.*, **4**, 175 (1965). Reviews: A. Efraty, *J. Organometal. Chem.*, **57**, 1 (1973); P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 95 (1966); A. Z. Rubezhov and S. P. Gubin, *Advan. Organometal. Chem.* **10**, 347 (1972).
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(5) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969).
(6) R. E. Davis, *Chem. Commun.*, 1218 (1968).
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(8) W. P. Giering *Chem. Commun.*, 4 (1971).
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