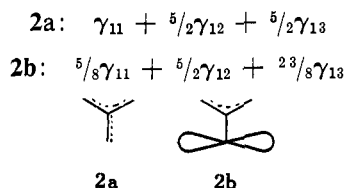pane, and **2b**, a model for the noninteracting biradical transition state, shows that in this system such a reversal does, in fact, take place. The two-electron energies are

$$\textbf{2a:}\quad \gamma_{11} + {}^5\!/_2\gamma_{12} + {}^5\!/_2\gamma_{13}$$

$$\textbf{2b:}\quad {}^5\!/_8\gamma_{11} + {}^5\!/_2\gamma_{12} + {}^{23}\!/_8\gamma_{13}$$

2a   **2b**

The electron repulsion energy of the lowest *singlet* of **2a** is more than 2 eV greater than that of **2b**. For any reasonable value of β, the two-electron energy difference is far greater than that in the one-electron energies,[7] and the one-electron energy ordering is reversed by electron repulsion as shown schematically below.
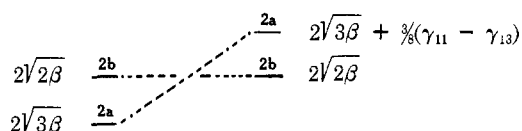
The larger destabilization by electron repulsion of **2a** relative to **2b** (>2 eV) compared with that of **1b** relative to **1c** (0.6 eV) can easily be understood from previously published theoretical work.[8] In cyclobutadiene the two open-shell electrons can occupy molecular orbitals which are confined to *different* atoms [*i.e.*, $(1/\sqrt{2})(\phi_1 - \phi_3)$ and $(1/\sqrt{2})(\phi_2 - \phi_4)$]. Repulsion between this pair of electrons is thereby minimized.[9] However, in trimethylenemethane and, more generally, in fully conjugated cyclic systems not comprised of a $4n$-membered ring, two such MO's cannot be found.[10] Indeed, the two nonbonding MO's, whatever the choice, always both have nonzero amplitude on at least one common atom. Thus, even the lowest singlet wave function for the two electrons in the degenerate MO's in trimethylenemethane contains ionic terms which are absent from the wave function for these two electrons in cyclobutadiene. The large ionic component in the singlet wave function for planar trimethylenemethane is responsible for its high energy.[11]

Acknowledgment. One of us (W. T. B) makes acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support during the period in which this work was carried out.

(7) M. J. S. Dewar and J. W. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971), have found that the total energy of **2a** is some 24 kcal/mol greater than that of **2b**.

(8) W. T. Borden, *Chem. Commun.*, 881 (1969).

(9) In fact, this singlet has the same energy as the lowest triplet in the most symmetrical cyclobutadiene geometry.[8]

(10) This is only true in Hückel systems.[8] In Möbius systems it can be shown that the degenerate nonbonding MO's in the antiaromatic $4n + 2$ atom rings can, in fact, be confined to different sets of atoms. Thus, one-electron effects probably also dominate in the relative stabilities of forbidden Möbius and noninteracting biradical transition states.

(11) The spin polarization effect, proposed as an intuitive explanation by Dewar and Wasson,[7] need not be invoked in accounting for the high energy of this species.

(12) Laboratoire de Chimie Théorique (490), Université de Paris-Sud, Centre d'Orsay, France.

Weston Thatcher Borden,* **Lionel Salem**[12]

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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The Vinyl Ketene Rearrangement Mechanism of Homobullvalenone

Sir:

Two limitations restrict practical exploitation of the thermal Woodward–Hoffmann sum rule (or its equivalents).[1] Substituent effects—particularly those of heteroatoms—are not easily accommodated.[2] Neither is there yet an adequate body of empirical mechanistic generalization which might serve to rank the numerous symmetry-allowed possibilities that are most often available.[3]

As a small contribution to this last goal, we here report the discovery and limited mechanistic analysis of the thermal rearrangement of homobullvalenone (**1a**) to its isomer **2**[4] in 93% yield (Scheme I). The syn-

Scheme I
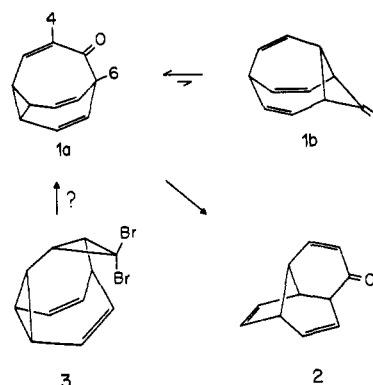
thesis, characterization, and reversible Cope equilibration of **1a** are previously described.[5] Groves[6] has since independently isolated and characterized **2** as the major product of silver trichloroacetate induced acetolysis of **3**.[7]

His suggestion, that **1a** be an intermediate in the solvolytic transformation, is consistent with our preliminary kinetic observations:[8] $10^5\lambda_{C_2Cl_4}{}^9 = 1.26$ (85.7°) and 9.15 (103.6°), whence $\Delta H^{\ddagger} = 29$ kcal/mol and $\Delta S^{\ddagger} = -0.5$ cal/(mol deg) for **1a** $\rightarrow$ **2**. His suggested mechanism, however, is quite unambiguously excluded.

Table I and Figure 1 summarize the complete pmr assignment of **2** and the evidence used to achieve it. The previously described[5] **1a-**d, its label equally distributed between C-4 and C-6, can then distinguish

(1) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) Two recent attempts to do so: (a) L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924, 1935 (1972).

(3) A completely defined subset of such possibilities is illustrated: M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 7149 (1972).

(4) *Chemical Abstracts* names: **1a**, tricyclo[4.3.2.0²·⁹]undeca-3,7,10-trien-5-one; **2**, tricyclo[5.4.0.0⁴·¹¹]undeca-2,5,9-trien-8-one.

(5) M. J. Goldstein, R. C. Krauss, and S.-H. Dai, *J. Amer. Chem. Soc.*, **94**, 680 (1972).

(6) J. T. Groves and B. S. Packard, *ibid.*, **94**, 3253 (1972). We are grateful to Professor Groves for providing us with a copy of this manuscript prior to publication.

(7) The reported[6] properties of **2** differ inconsequentially from those we observe: mp 15°; ir (CCl₄) 3050, 3030, 2950, 2920, 1682, 1623, 1380, 1365, 1323, 1240, 1197, 1148, 1118, 948, 867, and 690 cm⁻¹; uv max (isooctane) and ϵ 215 (11,000), 264 (980), 322 (98), 335 (144), 349 (164), 365 (139), and 383 (59) nm. *Anal.* Found: C, 83.35; H, 6.48.

(8) From the disappearance of the τ 4.65 absorption of **1a**.[5]

(9) An experimental rate constant (λ) is distinguished from a mechanistic one (k) by a symbol which indicates that it is the eigenvalue of a mechanism matrix.[3]
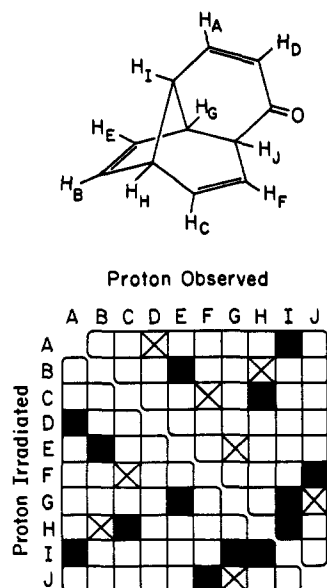
Figure 1. Complete spin decoupling of 2: (■) multiplet simplification or collapse, (□) no discernible effect, (⊠) ambiguous effect.

Table I. Pmr Spectrum of 2[a]

Assignment	A^b	τ	S^c	Appearance[d]
H_A	1.05	3.30	-2.57	ddd (J = 10.0, 5.1, 1.0)
H_B	1.02	3.47	-1.17	dd (J = 6.0, 2.8)
H_C	1.00	3.96	-2.16	ddd (J = 9.5, 6.2, 1.0)
H_D	1.03	4.08	-9.61	ddd (J = 10.0, 1.0, 1.0)
H_E	0.97	4.38	-1.44	ddd (J = 6.0, 3.0, 1.0)
H_F	1.00	4.51	-5.27	dddd (J = 9.5, 5.0, 1.5, 1.5)
H_G	0.98	7.07	-4.50	ddd (J = 5.0, 3.0, 3.0)
H_H	0.95	7.14	-2.79	ddd (J = 6.2, 5.0, 2.8)
H_I	1.00	7.32	-2.21	ddd (J = 5.1, 5.0, 5.0)
H_J	0.99	7.32	-9.15	ddd (J = 5.0, 3.0, 1.0)

[a] CCl₄ solution. [b] Areas normalized to ten protons. [c] Slope of τ vs. molar ratio [Eu(fod)₃]/[substrate]. Corresponding slopes of Table I, ref 5, should be multiplied by 0.047 for comparison. [d] Reported J (Hz) are first-order splittings as observed at appropriate lanthanide concentrations.

among the five possibilities of Scheme II.[10] Of these, **b**,[11] **c**, **d**,[12a,b,13] and **e**[12a,c,13] are symmetry allowed and not entirely without analogy. The forbidden possibility, **a**, is included only to represent the necessary consequence of previous proposals (both catalyzed and thermal).[6]

The results of Table II implicate **e** as the preferred (if not the exclusive) path. Such small discrepancies as do exist, between calculated and observed areas,

(10) Selected for their illustrative value, this inadequate number precludes any attempt at a rigorous proof. Nor can any be attempted until the remaining C₁₁H₁₀O isomers are prepared and their potential as reactive intermediates becomes better known.

(11) G. L. Closs and P. E. Pfeffer, J. Amer. Chem. Soc., **90**, 2452 (1968); J. A. Berson, W. Bauer, and M. M. Campbell, ibid., **92**, 7515 (1970); M. J. Goldstein and M. S. Benzon, ibid., **94**, 5119 (1972).

(12) (a) M. J. Goldstein and B. G. Odell, ibid., **89**, 6356 (1967); (b) O. L. Chapman and J. D. Lassila, ibid., **90**, 2449 (1968); O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, ibid., **91**, 6856 (1969); A. S. Kende, Z. Goldschmidt, and P. T. Izzo, ibid., **91**, 6858 (1969); (c) L. L. Barber, O. L. Chapman and J. D. Lassila, ibid., **91**, 531 (1969); and references there cited.

(13) For reviews of ketene cycloaddition reactions, cf. H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, Chapter II; D. Seebach, in Houben-Weyl, "Methoden der Organischen Chemie," Vol. IV/4, Georg Thieme Verlag, Stuttgart, 1971, p 174 ff.

Scheme II. Five Possible Mechanisms[a]
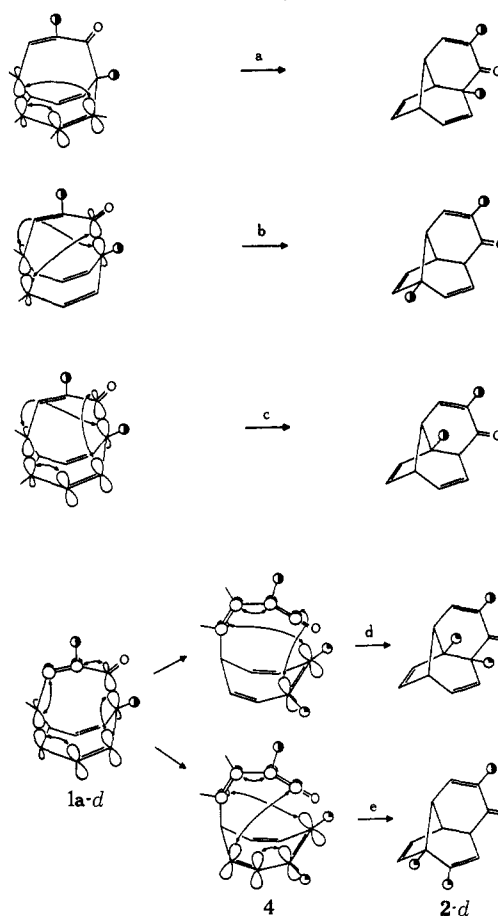
[a] Key: (◑) 50% deuterated, (◔) 25% deuterated. Note that a, b, and e generate the enantiomer of the 2-d shown.

Table II. Normalized Pmr Areas of 2-d

| Assignment | Predicted by mechanism | | | | | Obsd[a] |
	a	b	c	d	e	
H_D	0.5	0.5	0.5	0.50	0.50	0.58 ± 0.01
H_C	1.0	1.0	1.0	1.00	0.75	0.78 ± 0.01
H_G	1.0	1.0	0.5	0.75	1.00	0.98 ± 0.01
H_H	1.0	0.5	1.0	1.00	0.75	0.75 ± 0.03
H_J	0.5	1.0	1.0	0.75	1.00	0.94 ± 0.03

[a] Mean and standard deviations of five 60-MHz scans normalized to 9 protons. Each of the remaining five areas differ insignificantly from unity.

conform to expectation for intramolecular α-deuterium kinetic isotope effects.[14]

The possibility that an alternative (such as **b**) might be obscured by mechanistically irrelevant scrambling of H_C and H_H is excluded in several ways. The simplest such hypothesis—equilibration of either the reactant or the product with the vinyl ketene **4**—is a circumambulatory process,[15] one that can scramble half the label about seven equivalent positions, not merely two. Nor does the pmr spectrum of incompletely reacted **1a** reveal any obvious change in deuterium distribution. Finally, **2** is recovered unchanged from

(14) J. E. Baldwin and R. H. Fleming, Fortschr. Chem. Forsch., **15**, 281 (1970); S.-H. Dai and W. R. Dolbier, Jr., J. Amer. Chem. Soc., **94**, 3946, 3953 (1972), and references there cited.

(15) Cf., Chapter 7.2 in ref 1; J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, J. Amer. Chem. Soc., **93**, 4958 (1971); P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, ibid., **93**, 1551 (1971).

an environment (MeOH, 95°, 8 hr) which irreversibly transforms **1a** to an ester, presumably methyl (4Z)-(7′-cyclohepta-2′,4′,6′-trienyl)but-3-(and/or 2-)enoate,[16] in 85% yield.

The synthetic implications of mechanism **e** are apparent: **2**, but not **1a**, should also be accessible by an independent synthesis of **4**, e.g., through the readily available 7-vinylcycloheptatrienes.[12a,17]

Mechanistically more instructive is the apparent need of a two-step sequence to break and to form precisely those same bonds as would otherwise be achieved by the one-step mechanism **b**.[18] The subsequent choice of eight-electron (**e**) rather than six-electron (**d**) cycloaddition recalls the exclusively four-electron *intermolecular* cycloadditions of ketenes[13] and the otherwise unexpected thermal stability of barbaralone.[19] More diverse are the previous reports of *intramolecular* thermal ketene cycloadditions. Examples of *apparent* six-electron,[12a,b] as well as four-[12a,20] and/or eight-electron[12a,c] processes suggest opportunities for closer scrutiny.

Finally, we note the illustration of a more general suggestion. Symmetry-forbidden processes (such as **a**) ought to be regarded with some skepticism until the full scope of symmetry-allowed processes has been considered, much less excluded by experiment.

(16) Ir (CCl₄) 3000, 2905, 1730, 1602, 1428, 1240, 1190, 1165, and 700 cm⁻¹ but *not* at 960–970 cm⁻¹; pmr (CCl₄) τ 3.38 (2 H, tt), 3.70–4.53 (4 H, m), 4.93 (2 H, dd), 6.38 (3 H, s), 7.05 (2 H, d), 7.66 (1 H, m).

(17) J. Daub and P. v. R. Schleyer, *Angew. Chem.*, **80**, 446 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 468 (1968).

(18) *Cf.*, J. E. Baldwin and M. S. Kaplan, *J. Amer. Chem. Soc.*, **93**, 3969 (1971); **94**, 4696 (1972).

(19) T. Mukai and K. Kurabayashi, *ibid.*, **92**, 4493 (1970).

(20) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968); H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971).

M. J. Goldstein,* S.-H. Dai

Department of Chemistry, Cornell University
Ithaca, New York 14850
Received July 12, 1972

A C₁₁H₁₁ Cation of Unusual Structure[1]

Sir:

The modal description of the isomeric C₁₁H₁₁ longicyclic cations (**1a–c**) is uniformly (2,2,0).[2] All should therefore be stabilized. The further adjective, "bicycloaromatic," compares these with their isoconjugate homoantiaromatic pericyclics (**2a–d**) in a way that disparages potential isomerization, at least into the latter topology. We now report that conventional low-temperature FSO₃H extraction of the immediate alcohol precursor of **1b**[3] in fact provides *none* of these.

The observed pmr spectrum,[4] τ_A 1.91 (d, J = 7.0 Hz,

(1) Taken in part from the Ph.D. Thesis of S. A. Kline, Cornell University, 1972.

(2) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(3) The unambiguous synthesis and structure proof of *syn*- (to diene) bicyclo[4.3.2]undeca-2,4,8,10-tetraen-7-ol is described elsewhere: M. J. Goldstein and S. A. Kline, submitted for publication to *Tetrahedron Lett.*

(4) FSO₃H–CD₂Cl₂ solutions also containing SO₂, SO₂ClF, and/or SO₂F₂ at 60 and 90 MHz for protons, at 22.62 MHz with proton decoupled Fourier transform accumulation for ¹³C.
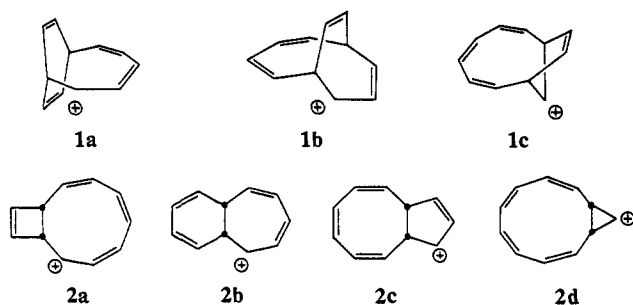
4.1), τ_B 2.41 (t, J = 7.0 Hz, 2.1), and τ_C 7.31 (s, 4.8) ppm with unresolved fine splitting (J_AC), suggests **3a** ⇌ **3b** as a first approximation to the structure of the (presumably more stable) cation.[5] Each such step, the corner alkylation of cyclopropane by an allyl cation, corresponds in stereochemistry both to that of the *exo*-deltacyclyl cation,[6] where it leads to twofold degeneracy, and of the cyclopropylcarbinyl cation,[7] where the degeneracy becomes threefold. The fivefold degeneracy of **3** is attained by a double circumambulatory
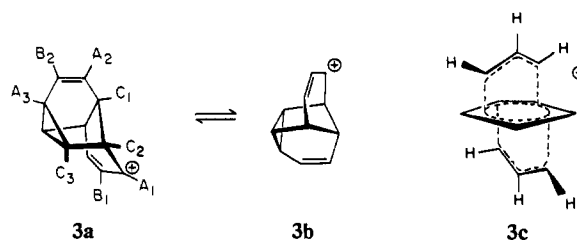
process, one that has previously been anticipated but never heretofore achieved.[8,9]

The barrier to such rotation must be lower than that of any single cationic circumambulation that we know;[8e,10] nmr spectra remain unchanged between −20° and the lowest easily accessible temperatures (−150° for pmr, −60° for cmr). At this level of approximation, the *transition state* **3c**—two mutually perpendicular 1,3-dehydroallyl cationic ligands, above and below the plane of a cyclopentadienyl anion—provides an attractive rationale. Such a geometry, accurately either C₂ (as shown) or C_s but approximately D_{2d}, permits stabilization to follow from mixing one of the vacant cyclopentadienyl π orbitals with the a₂ combination of allyl ψ₂. It requires both a negligible rotational barrier and an incomplete transfer of negative charge to the ligands.

Can such stabilization suffice to make **3c**, instead, the

(5) The role of **1a** and **1b**, as potential intermediates in the formation of **3**, will be described separately.

(6) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).

(7) K. B. Wilberg and G. Szeimies, *ibid.*, **92**, 571 (1970); Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971).

(8) (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1613 (1965); (b) P. v. R. Schleyer and R. E. Leone, *ibid.*, **94**, 4164 (1968); (c) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **87**, 1053 (1968); (d) J. J. Gajewski and C. N. Shih, *Tetrahedron Lett.*, 2967 (1970); (e) For a comprehensive review, *cf.* R. E. Leone and P. v. R. Schleyer, *Angew. Chem.*, **82**, 79 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(9) A topologically analogous process, however, provides an alternative interpretation of results observed in more complicated environments: (a) H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6264 (1971); (b) H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

(10) (a) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971); J. A. Berson and J. A. Jenkins, *ibid.*, **94**, 8907 (1972); W. J. Hehre, *ibid.*, **94**, 8908 (1972). (b) For two recently reported exceptions, *cf.* S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972), and ref 9b.