assorted Lewis acids and metal carbonyls have thus far met with frustration. The molecule quantitatively consumes 2 mol of sodium in tetrahydrofuran, probably yielding the nido anion $B_9H_9S^{2-}$. Degradation of 1-B_9H_9S is facile in methanolic KOH and gives various air and moisture sensitive thiaborane anions which have thus far eluded very definitive characterization. We feel that such degradation reactions and oxidative closure of the resulting deltahedral fragments[1] portend the isolation of an entire series of new thiaboranes. Such reaction chemistry is now under investigation as is a small yield of a less volatile pyrolysate of $B_9H_{11}S$ which contains a mixture of higher thiaboranes as shown by mass spectral analysis.

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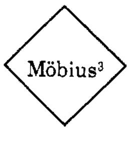
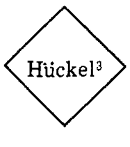
Electron Repulsion in Pericyclic Transition States

Sir:

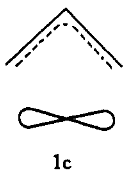
In a recent communication[1] Berson and Salem have shown that subjacent orbital interactions should, in principle, favor concerted "symmetry-forbidden"[2] over purely nonconcerted diradical pathways in certain pericyclic reactions. The one-electron energies of three model transition states for a 1,3-sigmatropic shift were found to be in the order: **1a**, symmetry allowed, aromatic Möbius array[3] ($4\sqrt{2}\beta$) < **1b**, symmetry forbidden, antiaromatic cyclobutadienoid ring (4β) < **1c**, noninteracting allyl plus p, diradical ($2\sqrt{2}\beta$). Berson and Salem point out, however, that "it is not inconceivable that the important two-electron energies characteristic of open shells could reverse, in certain cases, the ordering of the nonconcerted and forbidden transition-state energies."[1] In this communication we investigate the effect of electron repulsion on the relative energies of model aromatic, antiaromatic, and diradical transition states. We show that, in both $4n$ Hückel and $4n + 2$ Möbius "forbidden" transition states, the open-shell electrons can correlate their positions so as to interact with minimal repulsion, thereby making such a reversal of energies unlikely. In contrast, in a planar trimethylenemethane model transition state the open-shell electrons cannot avoid each other, and the large resulting repulsion is responsible for raising the total energy above that of a twisted biradical.



1a



1b



1c

The electron repulsion energies of **1a–c** were calculated from the orbital coefficients using the standard approximation of zero differential overlap.[4] The coefficients were obtained by assuming all β's equal in **1a** and **1b** and a value of zero for the resonance integral between the p and allyl π orbitals in **1c**. The calculated two-electron energies for the *lowest singlet* state of each system are tabulated below, where γ_{11} is the one-center repulsion integral, while γ_{12} and γ_{13} are respectively the repulsion integrals between adjacent and nonadjacent orbitals.

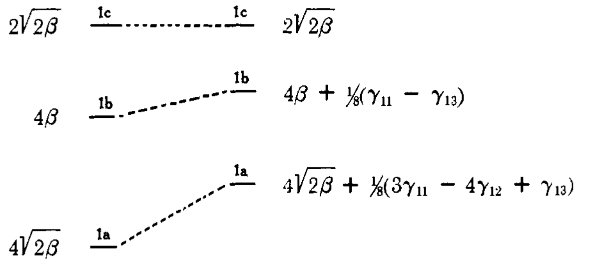
$$\mathbf{1a}:\quad \gamma_{11} + 3\gamma_{12} + 2\gamma_{13}$$

$$\mathbf{1b}:\quad {}^{3}/_{4}\gamma_{11} + {}^{7}/_{2}\gamma_{12} + {}^{7}/_{4}\gamma_{13}$$

$$\mathbf{1c}:\quad {}^{5}/_{8}\gamma_{11} + {}^{7}/_{2}\gamma_{12} + {}^{15}/_{8}\gamma_{13}$$

Assuming that the latter two integrals are independent of the orientation of the orbitals involved, the two-electron energies of **1a** and **1b** relative to **1c** are easily computed. Employing typical[5] values of the repulsion integrals, the electron repulsion energy in **1a** is found to be 0.6 eV and in **1b** 1.2 eV *greater* than that in **1c**. The lower two-electron energy of **1c** can be ascribed to the fact that in this system one electron is "isolated." Therefore, it cannot at any time appear simultaneously in a p orbital with an electron of opposite spin.[6]

The most important question now is whether the subjacent orbital stabilization of **1b** relative to **1c** can be reversed by the greater electron repulsion energy present in the former, and the answer depends on the relative values of $(4 - 2\sqrt{2})\beta$ and $^1/_8(\gamma_{11} - \gamma_{13})$. However, even for a conservative value of $\beta = -1.0$ eV the subjacent orbital stabilization of **1b** predominates, and the forbidden concerted transition state model **1b** is lower in total energy than the model for the diradical **1c**. The effect of the one- and two-electron terms in the Hamiltonian on the stability of **1a–c** is shown schematically below.



The dominance of the subjacent orbital effect in determining the relative stability of **1b** and **1c** does not mean that in other systems a reversal of the one-electron energy ordering cannot occur when electron repulsion is included. Comparison of **2a**, a trimethylenemethane model for the transition state in the Woodward–Hoffmann "forbidden" ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ concerted pathway for the degenerate rearrangement of methylenecyclopro-

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(1) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

(4) For a discussion see R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1963.

(5) Calculated for the cyclobutadienoid geometry as suggested by M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969). Any reasonable set of repulsion integrals gives approximately the same quantitative result.

(6) The simultaneous occupancy of an orbital by two electrons of opposite spin is, of course, not prohibited by the Pauli principle and gives rise to ionic terms in the wave function. These terms have high two-electron energy because of the large value of the one-center repulsion integral.

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

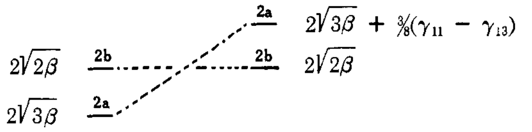
$$\mathbf{2a}:\quad \gamma_{11} + {}^{5}/{}_{2}\gamma_{12} + {}^{5}/{}_{2}\gamma_{13}$$

$$\mathbf{2b}:\quad {}^{5}/{}_{8}\gamma_{11} + {}^{5}/{}_{2}\gamma_{12} + {}^{23}/{}_{8}\gamma_{13}$$


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.

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(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.

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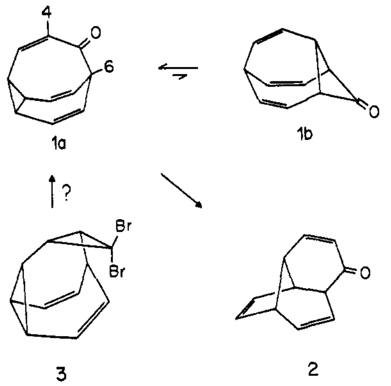
The Vinyl Ketene Rearrangement Mechanism of Homobullvalenone

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 synthesis, 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]

Scheme I



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** → **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

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(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[4.3.2.0^{2,9}]undeca-3,7,10-trien-5-one; **2**, tricyclo[5.4.0.0^{4,11}]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 (CCl_4) 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]