angular distortions (Figure 1) will be more fully discussed at a later date.

Although discrete $L_3Cu_2X_2$ units have now been shown to exist in the solid state, there is not yet any evidence for the existence of such a species in solution.[1] The correct identification of various $L_nCu_mX_m$ complexes in solution is not a simple task, since rapid exchange of L and X as well as multiple, concentration-dependent equilibria involving ligand dissociation and complex oligomerization reactions are taking place.[1,2,14] The fact that $L_3Cu_2X_2$ complexes have been isolated as solids under a variety of conditions and with various L and X groups,[1,5,6] however, requires that, in any interpretation of solution data, serious consideration be given to the possibility that dimers of this stoichiometry might be present.[15]

Acknowledgment. Support of this work by the National Science Foundation under Grant No. GP-10737 is gratefully acknowledged. We also thank Dr. W. T. Reichle of Union Carbide Corporation for providing a sample of $(Ph_3P)_3Cu_2Cl_2$ prepared in his laboratory.

(14) (a) E. L. Muetterties, private communication; (b) S. J. Lippard and J. J. Mayerle, unpublished results.

(15) Note Added in Proof. Recent ^{31}P nmr studies by E. L. Muetterties and C. W. Alegranti (private communication, submitted for publication) have established the solution existence of $L_3Cu_2Cl_2$, for L = tri-*p*-tolylphosphine.

(16) Alfred P. Sloan Foundation Fellow, 1968–1970.

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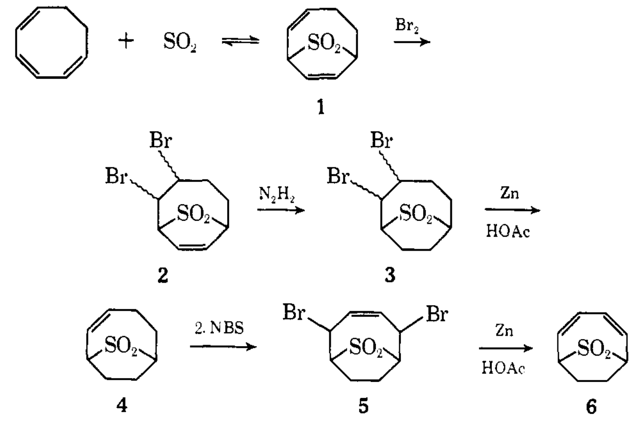
Orbital Symmetry Forbiddenness in a Suprafacial 1,6 Cycloelimination of Sulfur Dioxide

Sir:

In the absence of steric constraints, sulfur dioxide tends to interact with a 3-*cis*-hexatriene in an antarafacial manner (*trans*-1,6 addition or elimination).[1,2] We here report upon the thermal decomposition of a sulfone, **6** (9-thiabicyclo[4.2.1]nona-2,4-diene 9,9-dioxide), in which only suprafacial elimination of sulfur dioxide may take place in a concerted 1,6 fashion.[3]

The addition of sulfur dioxide to 1,3,5-cyclooctatriene produces only the 1,4 adduct, 9-thiabicyclo[4.2.1]-nona-2,7-diene 9,9-dioxide (**1**, Scheme I).[5] Bromine (1 equiv) was rapidly consumed by **1** to give **2**. Diimide reduction[6] of **2** gave **3**, which upon treatment with zinc and acetic acid produced **4**. Double allylic bromination of **4** gave the dibromide **5**, which upon treatment with zinc and acetic acid produced the diene **6**.

Scheme I



Direct, concerted fragmentation of **6** into cyclooctatriene and sulfur dioxide should be relatively[2] a disallowed process since it must proceed suprafacially (*cis* elimination) with respect to the triene component due to the constraints of the bicyclic system.[3] Molecular orbital symmetry considerations indicate that only the 1,4 process (*e.g.*, formation of **1**) should occur suprafacially with synchronous bond rupture through a symmetrical transition state (linear path).[4,7] Hence, comparison of the thermal stabilities of **1** and **6** should enable one to estimate the magnitude of symmetry factors in these electrocyclic transformations.[7]

Rates of decomposition of **1** and **6** were determined by measurement of sulfur dioxide liberated as a function of time.[8] Dissociation of **1** proceeded cleanly at conveniently measurable apparent first-order rates in the temperature range 100–120° ($k_{1,4}$ = 4.2 × 10^{-4} sec^{-1} at 110°). From the temperature dependence of the rate the following activation parameters were obtained: $\Delta H^{\ddagger} = 31.2 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger} = +7.0 \pm 3$ eu, $\Delta G^{\ddagger} = 28.5 \pm 0.9$ kcal/mol. These values are typical for sulfolene decompositions.[8] We therefore infer that the sulfone **1** is not appreciably strained and that there is no indication of greater nonsynchrony in the order of bond rupture in **1** relative to previously studied sulfolene decompositions.[8]

The sulfone **6** was completely stable at 110° and required temperatures over 100° higher for comparable rates of decomposition. Elimination proceeded less cleanly than in the case of **1**. In addition to sulfur dioxide (>80% of theory), the major volatile hydrocarbons were 1,3,5-cyclooctatriene and its valence tautomer bicyclo[4.2.0]octa-2,4-diene, which are inevitably in equilibrium at the decomposition temperature. Also detected by glpc were traces of other, unidentified products of similar volatility. Additionally, a residual tar was produced in small amount.

From the observed rate of sulfur dioxide production from **6** at 240–275° ($k_{1,6}$ = 4.2 × 10^{-4} sec^{-1} at 250°) and the temperature dependence thereof, activation parameters may be derived: $\Delta H^{\ddagger} = 30.0 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -18 \pm 5$ eu, $\Delta G^{\ddagger} = 39.5 \pm 1.5$ kcal/mol. The difference in free energy of activation between **1** and **6** ($\Delta\Delta G^{\ddagger}$) is 10 kcal/mol at intermediate decomposition temperatures (*ca.* 180°), corresponding to a rate differential of 60,000 ($= k_{1,4}/k_{1,6}$). This difference, which we suggest may be taken as a measure (minimal) of the magnitude of orbital symmetry constraints in these cycloeliminations,[9] appears to reside in the entropy

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(1) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

(2) W. L. Mock, *ibid.*, **91**, 5682 (1969).

(3) More specifically, the realistic options are a [6s + 2s] path (linear cheletropic reaction, symmetry forbidden) and a [6s + 2a] path (nonlinear process, symmetry allowed).[4]

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). See especially under cheletropic reactions.

(5) The new compounds **1–6** analyze within 0.3% carbon and hydrogen; structures are supported by ir, uv, and, in particular, nmr spectroscopy.

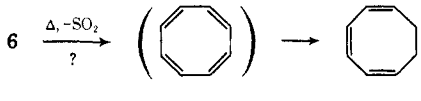
(6) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Amer. Chem. Soc.*, **83**, 2957 (1961); E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961).

(7) W. L. Mock, *ibid.*, **88**, 2857 (1966).

(8) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950).

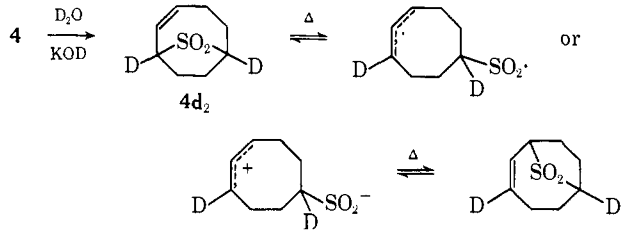
term. A fundamental difference in mechanism may underlie the latter observation, since orbital symmetry forbiddenness should be associated with enthalpy in the first approximation.

Ambiguity exists regarding the actual mechanism of decomposition of **6**. As alternatives to concerted fragmentation, other multistep (and therefore symmetry allowed) processes may be conceived. For example, fragmentation to sulfur dioxide and *cis,cis*-octatetraene is allowed;[10] subsequent conrotatory closure[11] of the latter would indeed produce 1,3,5-cyclooctatriene under the conditions prevailing.[12] At present we have no evidence excluding this mechanism. Nevertheless, we should like to give further consideration to a single step (concerted) process for the transformation of **6** directly into cyclooctatriene. In the related case of sulfur dioxide elimination from thiirane 1,1-dioxides, an allowed reaction course involving an asymmetrical transition state has been proposed (nonlinear path).[4] Stereoelectronic factors are comparable for 1,6 elimination.



In considering the possibility of a sequential (as opposed to synchronous) rupture of carbon–sulfur bonds in **6** leading directly to cyclooctatriene, it would be desirable to have some idea of the energy barrier for the formation of an intermediate diradical or zwitterion (two-step mechanism). Deuteration of **4** with basic deuterium oxide, yielding **4**-d_2, enables such an estimate to be made by nmr spectroscopy (Scheme II). When **4**-d_2 is heated in diphenyl ether solution, reappearance of a signal from the bridgehead position (as in **4**) is noted when the reaction is monitored by nmr. This allows a measurement of the rate of the process depicted (or its equivalent in a symmetry forbidden, concerted reaction[13]). Again, the reaction is not clean and experimentally does not lend itself to accurate rate determination. The estimated first-order rate constant is 5×10^{-5} sec^{-1} at 310°. An estimate of the rate of decomposition of **6** at this temperature may be obtained by extrapolation. Comparison of rate constants, with a correction for the statistical factor of two potentially rupturable carbon–sulfur bonds in **6**, reveals that **6** undergoes reaction only 100 ± 50 times more rapidly than does **4**-d_2.[14] Reaction by a mechanism analogous to that in Scheme II should indeed proceed more rapidly for **6** than for **4**-d_2 due to the additional double bond extending conjugation in the intermediate from **6**. The rate of decomposition of **6** is, then, approximately that expected from a process in which *scission of a single carbon–sulfur bond* characterizes the transition state.

Scheme II



However, on the basis of this evidence an energetic "nonlinear" concerted mechanism[4] may not be excluded relative to a two-step alternative for the elimination of sulfur dioxide from **6**. Our evidence only specifies that, if there is no actual intermediate, then the transition state is nevertheless of comparable energy to that expected for such a mechanism. A complete discussion of the possibilities, in which explicit attention must be given to the entropy factor, will be deferred until a full paper. Whatever the mechanism, it may conservatively be concluded that synchronous bond rupture in **6** through a symmetrical transition state (linear path[4]) is disallowed by at least 10 kcal/mol relative to **1** and other sulfolenes.[7,8]

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(9) In comparing the decompositions of **1** and **6**, we are assuming equivalent strain energy and other steric factors; this seems reasonable from examination of models and finds support in equilibration studies of related systems.

(10) This transformation has an analogy in the decomposition of 3-thiabicyclo[3.1.0]hexane 3,3-dioxide to 1,4-pentadiene and sulfur dioxide (W. L. Mock, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P-20) for which we have measured $\Delta G^{\ddagger} = 30.1$ kcal/mol. These fragmentations may be designated as [2s + 2s + 2s] (allowed) processes.[4]

(11) E. N. Marvell and J. Seubert, *J. Amer. Chem. Soc.*, **89**, 3377 (1967).

(12) T. D. Goldfarb and L. Lindqvist, *ibid.*, **89**, 4588 (1967).

(13) This distinction is not important to our argument; the key feature in the rearrangement of **4**-d_2 is that only a single carbon–sulfur bond participates.

(14) Actually, the $\Delta\Delta G^{\ddagger}$ for the comparison of **4**-d_2 and **6** amounts to *ca.* 5 kcal/mol near 300°. Furthermore, uncertainty in the ground-state energies of **1** *vs.* **6** are also of this magnitude.[9] Consequently, the 10 kcal/mol assigned herein to orbital symmetry constraints is a crude estimate at best.

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Transannular Photochemical Ring Closure in 1,2,5,6-Tetramethylenecyclooctane. A Novel Synthesis of [3.3.2]Propellane

Sir:

Recent syntheses of propellanes[1] containing four-membered rings have utilized intermolecular photochemical "2 + 2" cycloaddition reactions in order to produce a tricyclic [*n.m.*2]propellane skeleton from a bicyclic [*n.m.*0] precursor.[2,3] We now report that convenient entry into the [3.3.2]propellane skeleton can be obtained by transannular photo-ring closure in 1,2,5,6-tetramethylenecyclooctane (**1**).[4]

When **1** was photolyzed with a high-pressure mercury lamp in degassed hexane solution, in addition to the two products resulting from the photochemical butadiene → cyclobutene reaction,[4] a third product was produced in 50% yield and isolated by preparative vpc. Its nmr spectrum showed four vinyl (δ 4.8) and four allylic (δ 2.7) protons, indicating that the compound was tricyclic. Of the remaining eight protons, four appeared as a slightly broadened singlet (δ 2.0),

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(1) Review: D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969).

(2) R. J. Cargill and W. Crawford, *Tetrahedron Lett.*, 169 (1967), and references cited therein.

(3) P. E. Eaton, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P1.

(4) W. T. Borden, L. A. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).