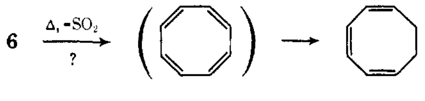
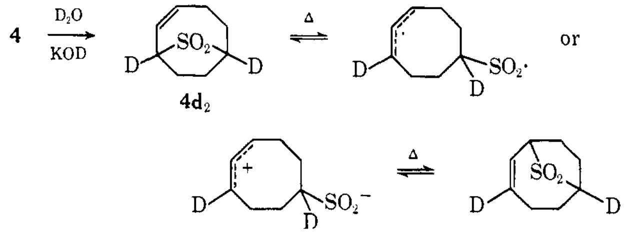
term. A fundamental difference in mechanism may underlie the latter observation, since orbital symmetry forbiddenness should be associated with enthalpy in the first approximation.

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).

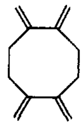
(2) R. J. Cargill and W. Crawford, *Tetrahedron Lett.*, 169 (1967), and references cited therein.

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

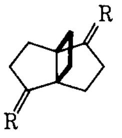
(4) W. T. Borden, L. A. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).

suggesting that the product was, in fact, **2**, formed by a 1,5-transannular photo-ring closure.[5]

The structure **2** was confirmed by ozonolysis to the crystalline diketone **3**[7] (mp 75–76°). The ir of the diketone showed a sharp absorption at 5.75 μ, indicating that both carbonyls were contained in five-membered rings. The rather complex nmr spectrum of the diketone could be greatly simplified by stirring a CCl_4 solution with D_2O containing Na_2CO_3. This resulted in the exchange of four protons (mass spectrum) and caused the nmr spectrum to collapse to an A_2B_2 pattern (4 H) centered at δ 2.27 and a broad singlet (4 H) at δ 2.00. The diketone underwent smooth Wolff–Kishner reduction to give the parent [3.3.2]propellane (**4**), whose nmr spectrum displayed a sharp singlet at δ 1.63 for the four equivalent cyclobutyl protons.



1



2, R = CH$_2$
3, R = O
4, R = H$_2$

The geometry of **2**, which causes the orbitals of the central single bond to lie in a plane almost orthogonal to the π lobes of the methylene groups, confers on this compound a reasonable degree of thermal stability. We have used this fact to develop a scheme which allows separation of **2** from the by-products in the photolysis of **1**, all of which contain a cyclobutene ring which can be reopened by pyrolysis in a flow system under conditions where **2** is stable. The mixture of **2** and conjugated dienes which is obtained from pyrolysis of the crude photolysate is allowed to react with maleic anhydride in refluxing $CHCl_3$. Since **2** does not react, it can be separated from the Diels–Alder adducts by simple column chromatography and thus obtained essentially pure without the necessity of tedious vpc collection.[8]

We are currently exploring ring contraction reactions in the diketone **3**, which would lead to [2.2.2]propellane.[1,3,8a]

[5] For a review of 1,5-transannular reactions in cyclooctane derivatives, see A. C. Cope, *Quart. Rev. Chem. Soc.*, **20**, 119 (1966). Our expectation that the structure of **1** would dispose it favorably toward such a reaction was based in part on the fact that the 1,3,5,7 isomer of **1** undergoes a 1,5 transannular cycloaddition reaction with tetracyanoethylene.[6]

[6] J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 1257 (1962).

[7] All compounds gave elemental analyses and mass spectra in accord with the proposed formulas.

[8] This scheme also allows the use in the photolysis of unpurified **1**, which contains an isomer that is converted by photolysis to a product containing a cyclobutene ring.[4] Thus, **2** can be obtained from 1,2-dimethylenecyclobutane in three steps without purification of any of the intermediates.[4]

[8a] Note Added in Proof. Professor Cargill has kindly provided us with the ir and nmr spectra of [3.3.2]propellane prepared in his laboratory by a route different from ours;[2] these proved to be indistinguishable from those obtained from **4**. Preliminary experiments in our laboratory indicate unusual reactivity of the central C-C single bond in this molecule toward free-radical addition.

[9] NIH Postdoctoral Fellow, 1969–1970.

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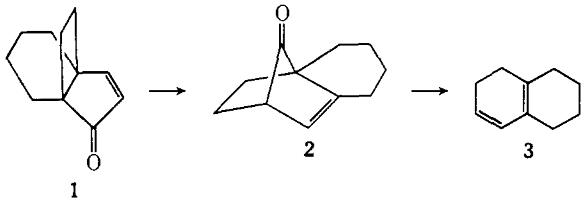
Received March 19, 1970

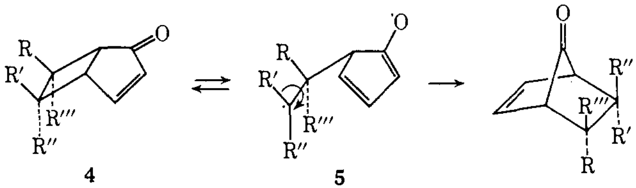
Stereochemistry of a Photochemical Allylic Rearrangement[1]

Sir:

Irradiation of tricyclo[4.3.2.0^{1,6}]undec-3-en-2-one (**1**) in methylene chloride (0.83 *M*) with the output from ten "blacklights" (General Electric F15-T8-BL) through Pyrex yielded only ketone **2** (crude yield, 95%). Similar irradiation of bicyclo[3.2.0]hept-3-en-2-one (**4a**) in pentane (0.014 *M*) gave 7-ketonorbornene (**6a**) in 10–20% yield along with one or more dimers, mp 174–177°, in 60–70% yield. These photoisomerizations, as well as the analogous verbenone–chrysanthenone rearrangement,[2a,b] represent photochemical allylic shifts in which the migrating atom is carbon,[2] and which are restricted by the geometry of the substrates to being suprafacial. If these reactions proceed with simultaneous bonding of the migrating carbon to the α and γ positions (concerted reactions), we may expect, based on consideration of the symmetry of the first antibonding MO (ψ_3) of the allyl radical,[3] that the stereochemistry of the migrating carbon will be retained.[4] A nonconcerted, or "diradical," process should result in randomization of configuration, provided the diradical is relatively long-lived. We have investigated the stereochemistry of the **4** → **6** change and we report our findings here.



1 2 3



4 5 6

a, R = R′ = R″ = R‴ = H
b, R = R′ = D; R″ = R‴ = H
c, R = R″ = D; R′ = R‴ = H
d, R = R′ = H; R″ = R‴ = D

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the National Science Foundation for a grant toward the purchase of the mass spectrometer used in this work.

[2] (a) J. J. Hurst and G. W. Whitham, *J. Chem. Soc.*, 2464 (1960); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967). See also (c) H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966); (d) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 964 (1968); (e) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Chem. Commun.*, 823 (1967); (f) R. C. Cookson and D. C. Warrell, *J. Chem. Soc., C*, 1391 (1967); (g) R. C. Cookson, *Quart. Rev. Chem. Soc.*, **22**, 423 (1968); (h) L. A. Paquette, G. V. Meehan, and R. F. Eizember, *Tetrahedron Lett.*, 995, 999 (1969); (i) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); and (j) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 1126 (1967).

[3] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). The constructive comments of Professor Hoffmann are greatly appreciated.

[4] Retention is expected if the rearrangement occurs in an excited state; however, if the change occurs in a vibrationally excited, electronic ground state inversion of configuration is predicted. An excellent discussion of thermal 1,3-sigmatropic reactions obviates the necessity of further elaboration here: J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).