Biemann's facility is supported by National Institutes of Health Grant No. RR00317 from the Division of Research Resources. Through the kindness of Professor S. Dev, I received generous samples of malabaricol and lactone IV as well as valuable synthetic details. I am also grateful to the Perkin-Elmer Corporation for use of a 900 gas chromatograph for collection of samples and for the micro ir spectra which they ran on their 180 instrument. I thank a Du Pont Fundamental Research Grant for providing financial support.

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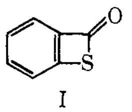
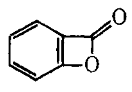
2-Thiobenzpropiolactone[1]

Sir:

We wish to record a facile synthesis of the highly reactive compound, 2-thiobenzpropiolactone (I). This substance is the thio analog of the unknown benzpropiolactone (II) which has been considered as a possible intermediate in the decomposition of *o*-diazoniumcarboxylate to benzyne.


I


II

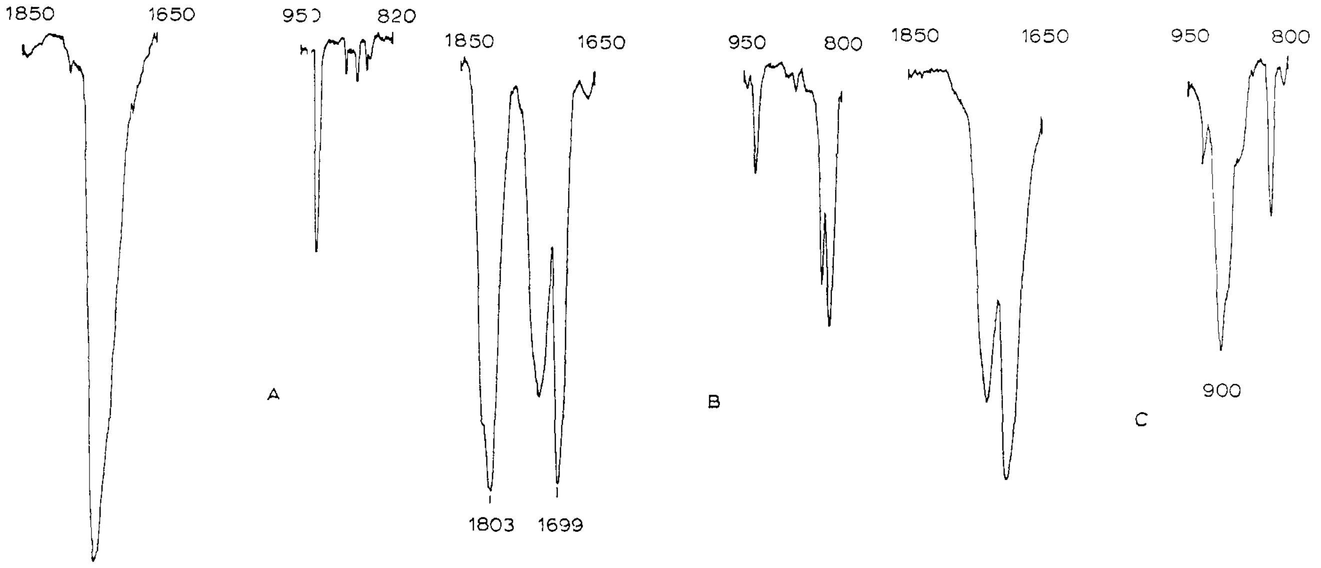
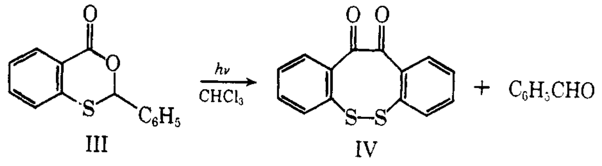


Figure 1. A. Infrared spectrum of 2-phenyl-3,1-benzoxathian-4-one at 77°K before irradiation. B. Infrared spectrum of same sample after irradiation at 77°K through Pyrex; note bands at 1803 and 1699 cm^{-1} characteristic of I and benzaldehyde. C. Infrared spectrum at 77°K of the same sample after warming to room temperature; note appearance of the band at 900 cm^{-1} characteristic of V.

Irradiation of 2-phenyl-3,1-benzoxathian-4-one (III) at room temperature in chloroform has been reported to give IV and benzaldehyde.[2] These authors considered two biradicals and a thione ketene as possible intermediates in the formation of IV.[2] Our experiments show that this reaction in fact proceeds *via* I and gives V rather than IV.[3] Irradiation of III at 77°K in an infrared cell[6] causes disappearance of III and produces bands characteristic of benzaldehyde (see ν_{CO} 1699 cm^{-1}, Figure 1) and a new species with ν_{CO} at 1803 cm^{-1} and other bands at 1570, 1430, 820, 670, and 630 cm^{-1}. No bands characteristic of V are observed at 77°K. The absence of the intense band at 900 cm^{-1} is particularly clear evidence that V is not formed during the irradiation of III at 77°K. Warming the irradiated sample to −40° gives rise to characteristic bands of V with concurrent disappearance of the 1803-cm^{-1} species. The 1803-cm^{-1} species is thus the thermal precursor of V.



When the irradiation of III is carried out in the presence of methanol at 77°K, the 1803-cm^{-1} species is observed. Warming of the irradiated sample in this case gives rise to bands characteristic of methyl *o*-mercaptobenzoate

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[1] Photochemical Transformations. LXI.

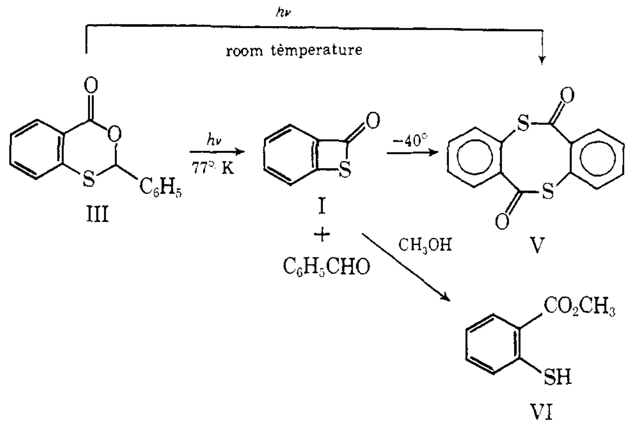
[2] A. O. Pedersen, S.-O. Lawesson, P. D. Klemmensen, and J. Kolc, *Tetrahedron*, **26**, 1157 (1970).

[3] The evidence presented for structure IV was nonidentity of IV with authentic V in melting point and tlc retention and reduction in low yield to benzil.[2] The absence of ultraviolet maxima above 240 nm in the product and the difficulty in rationalizing formation of structure IV led us to question this assignment. In our hands, the photoproduct from III and authentic V[4] are identical in melting point and infrared absorption after the trimer has been separated from authentic V. The reduction of V to benzil probably occurs *via* a transannular reduction analogous to that observed by Metlesics and Sternbach[5] in the zinc–acetic acid reduction of dibenzocine derivatives. The identity of the photoproduct from III and authentic V has been confirmed by Dr. J. C. Clardy by comparison of X-ray powder patterns.

[4] W. Baker, A. S. El-Nawawy, and W. D. Ollis, *J. Chem. Soc.*, 3163 (1952).

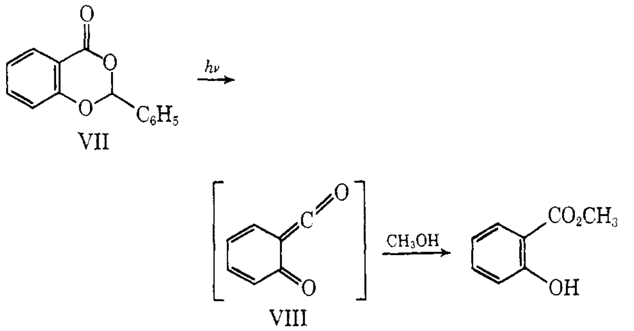
[5] W. Metlesics and L. H. Sternbach, *J. Amer. Chem. Soc.*, **88**, 1077 (1966).

[6] O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).



(VI).[7] The infrared spectrum and the formation of VI identify the intermediate as 2-thiobenzpropiolactone (I).

The facile synthesis of 2-thiobenzpropiolactone (I) from III led us to attempt the synthesis of the parent benzpropiolactone (II). Irradiation of VII at 77°K gave rise to a ketene band (2118 cm^{-1}) but no bands which could be attributed to the β-lactone. Irradiation of VII in methanol at room temperature gave methyl salicylate. This latter result suggests that the ketene observed at low temperature may be VII.



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(7) Ethyl 2-mercaptobenzoate has been observed in the irradiation of III at room temperature in the presence of ethanol.[2]

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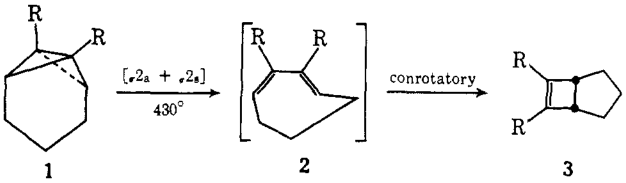
Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. IV. The Fate of Tricyclo[4.1.0.0^{2,7}]heptane[1,2]

Sir:

Earlier studies in this laboratory have elaborated upon the remarkable facility with which Ag$^+$ can induce thermally disallowed [$_\sigma2_a$ + $_\sigma2_a$] skeletal isomerizations of homocubyl and 1,1′-bishomocubyl systems.[1,3] We now report an extension of this fascinating development to bicyclo[1.1.0]butane derivatives.

Despite the fact that the bicyclobutane ring system possesses a remarkably high strain energy (63–68 kcal/mol[4]), thermal reorganization of its derivatives requires elevated temperatures, usually in excess of 150°.[5,6] The activation energy for isomerization to butadiene resides in the vicinity of 41–43 kcal/mol.[5a,7] Nevertheless, the highly stereoselective nature of the reaction provides compelling evidence that the process is a concerted [$_\sigma2_s$ + $_\sigma2_a$] chemical transposition.[5d,e] In particular, such observations have revealed that electronic factors clearly outweigh thermodynamic considerations in determining the stereochemistry of the diene product.

A case in point is tricyclo[4.1.0.0^{2,7}]heptane (**1a**) which affords *cis*-bicyclo[3.2.0]hept-6-ene (**3a**) when heated above 300°. *cis,trans*-1,3-Cycloheptadiene (**2a**) justifiably has been postulated as the requisite intermediate.[5d] The gas-phase pyrolysis of **1b**, performed during the course of the present study (Table I), is likewise best accommodated by this mechanism. The resulting *cis*-bicyclo[3.2.0]hept-6-ene was deuterated



1 **2** **3**

a, R = H; **b**, R = D

Table I. Pyrolysis[a] of Tricyclo[4.1.0.0^{2,7}]heptane-*1,7-d$_2$* (**1b**)

Temp, °C	Yield, %	Composition of pyrolysate, % **3b**	Recovd **1b**	1,3-Cycloheptadiene[b]
430	86	50	32	18
440	91	56	16	28
490	91	33	10	57
500	91	5	10	85

[a] Gas-phase conditions under a nitrogen atmosphere at 12–16 mm in a quartz tube (28 cm × 16 mm) packed with quartz chips. [b] The 1,3-cycloheptadiene-d_2 had undergone virtually complete deuterium scrambling *via* consecutive [1,5]-sigmatropic hydrogen shifts, as established by nmr analysis of the hydrocarbon and its maleic anhydride adduct.

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(1) Paper III: L. A. Paquette and J. C. Stowell, submitted for publication.

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research.

(3) (a) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970); (b) L. A. Paquette, *ibid.*, **92**, 5765 (1970); (c) see also W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).

(4) (a) R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, Jr., *ibid.*, 997 (1965); (b) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); (c) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (d) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

(5) (a) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); (b) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (c) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); (d) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (e) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968); (f) W. Mahler, *ibid.*, **84**, 4600 (1962); (g) D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963); (h) R. Srinivasan, A. A. Levi, and I. Haller, *J. Phys. Chem.*, **69**, 1775 (1965); (i) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966); (j) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968).

(6) Note, however, R. B. Woodward and D. L. Dalrymple, *ibid.*, **91**, 4612 (1969).

(7) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964).