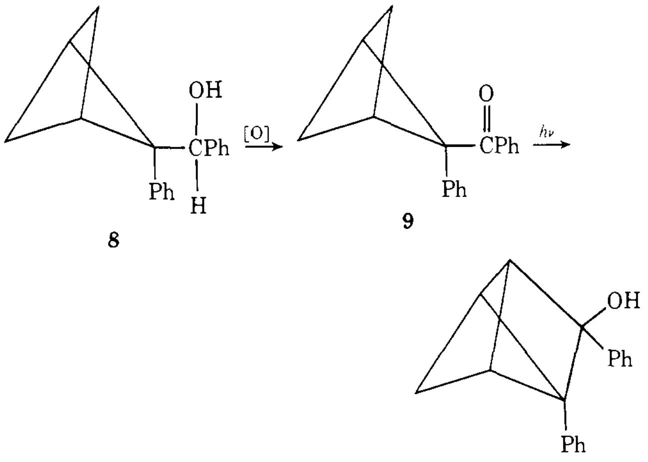
(**9**) in quantitative yield. Ketone **9** is a white solid mp 101-102° (ir (CCl_4) 3.40, 5.98, 6.26 μ; NMR (CCl_4) methylene δ 2.00 (doublet of doublets J = 2.5, 10.0 Hz (1 H)), 1.86 (doublet J = 2.5 Hz (1 H)), 1.71 (doublet J = 2.2 (1 H)), 2.06 (doublet of doublets J = 2.2, 10.0 Hz (1 H)), bridgehead δ 3.31 (singlet (2 H)), aromatic δ 7.26 (multiplet (8 H)), 7.88 (multiplet (2 H)); *m/e* 248 M^+, 233, 143, 128, 105 (base peak), 77.

Irradiation of ketone **9** at 310 nm (0.01 M in *tert*-butyl alcohol) resulted in 100% conversion to 1,2-diphenyltricyclo[2.2.0.0^{2,5}]hexan-2-ol (**4b**). The photocyclization[24] was complete after 10 min of irradiation.



8 **9** **4b**

The tricyclic alcohol **4b** was isolated as a pale yellow oil and was purified by preparative gas chromatography. Its structure is consistent with its spectral characteristics: ir (CCl_4) 2.81, 3.40 μ; NMR (CCl_4) methylene δ 2.23 (doublet J = 5.0 Hz (1 H)), 2.19 (doublet J = 5.0 Hz (1 H)), bridgehead δ 2.79 (doublet J = 17.0 Hz (1 H)), 3.65 (doublet J = 17.0 Hz (1 H)), 3.86 (singlet (1 H)), aromatic δ 7.20 (multiplet (10 H)), *m/e* 248 M^+, 233, 230, 143, 128, 105 (base peak), 77.

The tricyclohexanol **4b** is found to be thermally stable below 100 °C. When heated under vacuum to 160°, however, it undergoes rapid decomposition to a mixture of products the major of which has been identified as ketone **9**.

We are presently investigating the physical and chemical properties of the tricyclo[2.2.0.0^{2,5}]hexanol (**4b**). The general synthetic utility of mandelate ester photodecarboxylation is also being explored in our laboratory.

Acknowledgment. We are grateful to the National Institutes of Health (MBS Grant RR08135) for financial support of this work.

References and Notes

(1) For the previous paper in this series see ref 2.
(2) E. C. Alexander and R. J. Jackson, *J. Am. Chem. Soc.*, **98**, 1609 (1976).
(3) J. Meinwald and Y. C. Meinwald, *Adv. Alicyclic Chem.*, **1**, 38 (1966).
(4) D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).
(5) W. Kirmse and F. Scheidt, *Angew. Chem., Int. Ed. Engl.*, **10**, 263 (1971).
(6) S. Masamune, M. J. Bennett, J. T. Purdham, and S. Takada, *J. Am. Chem. Soc.*, **93**, 4063 (1971).
(7) W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 779 (1972).
(8) A. J. Schipperijn and J. Lukas, *Tetrahedron Lett.*, 231 (1972).
(9) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Am. Chem. Soc.*, **94**, 997 (1972).
(10) M. C. Flowers, H. M. Frey, and H. Hoepf, *J. Chem. Soc., Chem. Commun.*, 1284 (1972).
(11) C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Am. Chem. Soc.*, **95**, 861 (1973).
(12) J. Meinwald and A. Wissner, *J. Org. Chem.*, **38**, 1697 (1973).
(13) T. J. Katz and K. Nicolaou, *J. Am. Chem. Soc.*, **96**, 1948 (1974).
(14) R. B. Reinarz and G. C. Fonken, *Tetrahedron Lett.*, 4013 (1973).
(15) M. D. Newton, J. M. Schulman, and M. Manus, fiJ. Am. Chem. Soc., **96**, 17 (1974).
(16) H. Hogeveen and P. W. Kwant, *J. Org. Chem.*, **39**, 2624 (1974).
(17) M. Cristi, U. Heinemann, and W. Kristof, *J. Am. Chem. Soc.*, **97**, 2299 (1975).
(18) C. Y. Ho and F. T. Bond, *J. Am. Chem. Soc.*, **96**, 7355 (1974).
(19) E. C. Alexander and J. Uliana, *J. Am. Chem. Soc.*, **96**, 5644 (1974).
(20) S. F. Acree, *Am. Chem. J.*, **50**, 389 (1913).
(21) We have prepared 2-phenyl-2-benzylbicyclo[1.1.1]pentane by photodecarboxylation[22] of 2-phenylbicyclo[1.1.1]pentane-2-phenyl acetate. Our attempts to convert it to **8** or **9**, however, were unsuccessful.
(22) R. S. Givens and B. Matuszewski, *J. Am. Chem. Soc.*, **97**, 5617 (1975).
(23) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).
(24) (a) A. Padwa and W. Eisenberg, *J. Am. Chem. Soc.*, **94**, 5852, 5859 (1972); (b) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, **92**, 4752 (1970); (c) F. D. Lewis and R. A. Ruden, *Tetrahedron Lett.* 715 (1971); (d) K. Matsui, T. Mori and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **44**, 3440 (1971).

Edward C. Alexander,* Joseph Uliana
Department of Chemistry, B-017
University of California, San Diego
La Jolla, California 92093

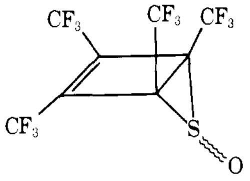
Received February 18, 1976

An Extraordinarily Facile Sulfoxide Automerization

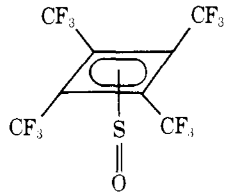
Sir:

Perfluorotetramethyl(Dewar thiophene) (**2**)[1] is rapidly transformed by peroxytrifluoroacetic acid into a very sensitive and unusual compound (**1**). Careful sublimation of the crude product at room temperature (aspirator) gives colorless blocks, mp 31-32°, with these spectral characteristics:[2] ir (CH_2Cl_2) 1664 (w), 1410 (w), 1364 (m), 1188 (br, s) cm^{-1}; ^{19}F NMR (CH_2Cl_2) δ 18.17;[2] ms 372 (parent).

Although the new compound clearly has the composition of the anticipated sulfoxide **1a**, its ^{19}F NMR spectrum down to temperatures as low as −95° (where it remains a narrow singlet) is more easily accommodated by the highly symmetrical structure **1b**. Certainly that structure is unconventional, requiring as it does that sulfur play a role previously reserved for metals,[3] but the opportunities for S-C bonding in such a C_{4v} sulfur monoxide-cyclobutadiene complex are not bad.[4]



1a

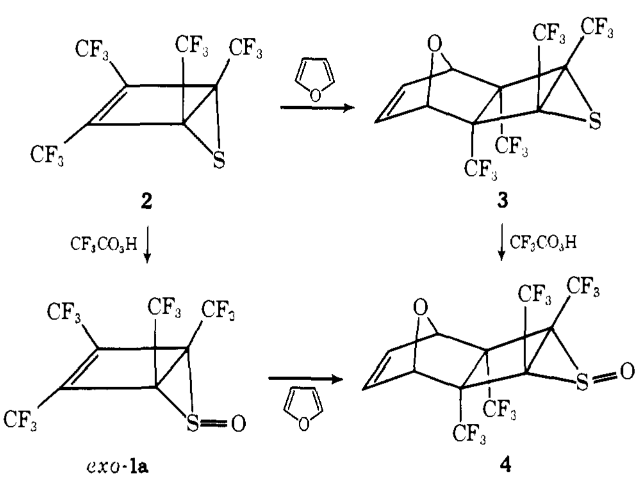


1b

The infrared and Raman spectra of **1a**, of course, should each reveal only a single C=C stretching band, at the same frequency. While the C_{4v} structure **1b** should give rise to a single ring stretching fundamental (of E symmetry) in the infrared spectrum at >1500 cm^{-1}, two may be expected in this region of the Raman spectrum (B_1, E). Since the E band should be weak,[5] the major Raman feature should appear at a different frequency from the infrared absorption. In fact, a single band was found in the 1500-1800 cm^{-1} region of the Raman spectrum,[6] identical in position and similar in shape to the infrared band.[7] Hence **1a** must be the correct structure, and the anomalous ^{19}F spectrum must reflect the existence of a degenerate rearrangement facile enough to render all 12 fluorines magnetically equivalent even at −95°. This surmise has now been confirmed by NMR measurements at still lower temperatures. Below −100° in Freon 21 the signal broadens rapidly and evolves into two resonances of equal area separated by 2.82 ppm at the slow exchange limit ($T_c = -124 \pm 3°$ [8]). The free energy of activation for exchange at −124° is thus 6.8 ± 0.3 kcal/mol.

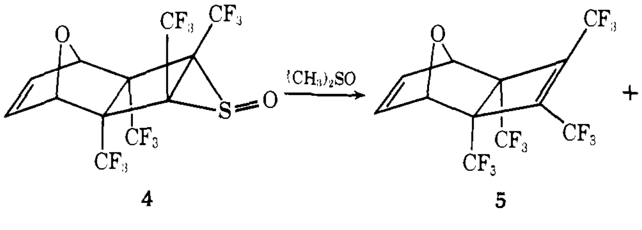
The high reactivity of **1a** is manifest in its rapid destruction at room temperature by such reagents as methanol, dimethyl sulfoxide, and furan. Reaction with the last yields a 1:1 adduct

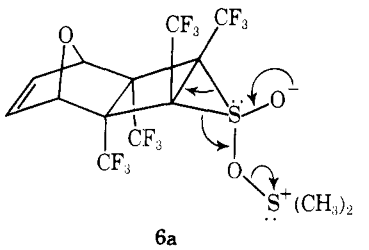
Chart I



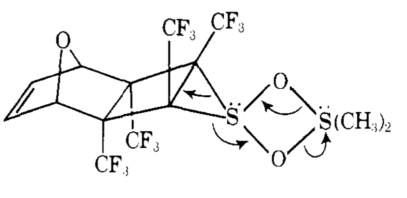
(**4**), identical with the compound obtained when the furan adduct **3** of perfluorotetramethyl(Dewar thiophene)[9] is oxidized with peroxytrifluoroacetic acid (Chart I): mp 107.5–108.5° dec; ir (KBr) 1295 (s), 1261, 1182 (br,s), 1107, 1027, 899, 818, 752, 733 cm^{-1}; ^{19}F NMR (CDCl$_3$) δ 21,98, 19.24 (br,s); ^{1}H NMR (CDCl$_3$) δ 7.12, 6.13 (unresolved m). Since the configuration of **3** has been determined by an x-ray study of a close analogue,[9] and since approach to the endo face of the sulfur in **3** is sterically hindered, one can be confident that **4** has the configuration shown. These experiments establish that the Dewar thiophene oxidation product has the exo configuration.

Remarkably, dissolution of **4** in dimethyl sulfoxide at room temperature results in fast elimination of the *elements* of sulfur monoxide to give the known tricyclic diene **5**,[10] sulfur dioxide, and dimethyl sulfide. Probably dimethyl sulfoxide attacks as a nucleophile at the electron-deficient sulfur of **4** to give a trigonal bipyramidal intermediate, **6a** or **6b**, whose demise proceeds (concertedly or stepwise) as indicated.



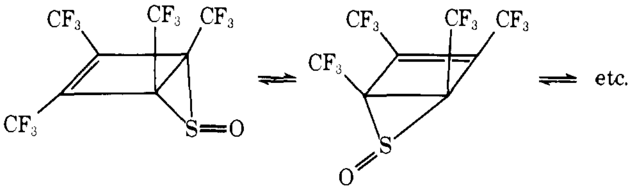


6a

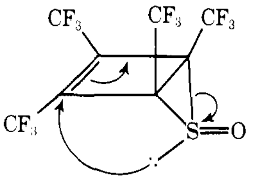


6b

The fluxional behavior of *exo*-**1a** might be interpreted in terms of **1b** (or a rectangularly distorted **1b**), cast in the role either of intermediate or transition state. Alternatively, one might invoke an automerization pathway of lower symmetry, namely, a sigmatropic change of order [1,3]:

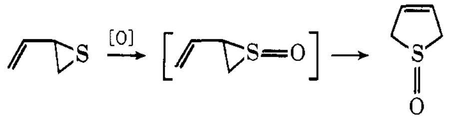


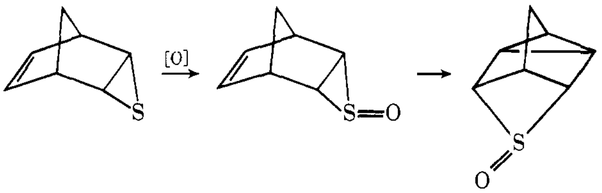
Such sigmatropic rearrangements are orbital symmetry forbidden to occur suprafacially with respect to the migrating center, and the transition state geometry for the allowed process (antarafacial at sulfur) is very unfavorable.[11] A diradical pathway appears to be out of the question, given the extremely low activation energy barrier.[12] There is a fourth possible mechanism for the allylic shift, however; here the sulfur lone pair forms the new bond to carbon, and the electrons of the cleaving C–S bond become a new lone pair, as shown in **7**. This pathway is appealing from a geometrical viewpoint, as models suggest that lone pair-π overlap is significant even in the initial state.[13] Like the allowed pericyclic rearrangement, this process inverts the sulfur, thus preserving the exo sulfoxide configuration.



7

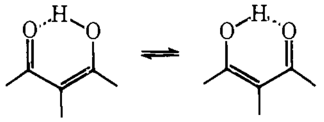
Presently available evidence does not rule out a role for **1b**, but the proposed [1,3]sigmatropic pathway for automerization derives support from studies of other sulfoxides. Lautenschlaeger observed that hydrogen peroxide oxidation of vinylthiirane (**8**) at room temperature yielded directly 3-thiolene *S*-oxide (**10**).[14] By carrying out the oxidation with peroxytrifluoroacetic acid, we have now found that the presumed thiirane oxide intermediate **9** is short-lived even at temperatures below −60°.[15] Thus the **9** → **10** transformation, a nondegenerate counterpart of the automerization postulated for *exo*-**1a**, is itself remarkably facile. The related oxidation of tricyclic thiirane **11** to rearranged sulfoxide **13** is also of interest, for it provides stereochemical information. Again the reaction was discovered by Lautenschlaeger,[14] who carried it out with periodate at 25°, obtained **13** directly, and assigned this thietane oxide the exo configuration. Low temperature oxidation with *m*-chloroperbenzoic acid allowed us to isolate and purify the intermediate thiirane oxide **12**. Through the use of Eu(fod)$_3$ the configuration at sulfur was shown to be exo.[16] Presumably because rearrangement of **12** to **13** is homoallylic



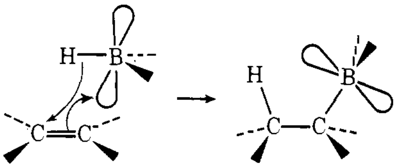


and much less exothermic than the allylic analogue **9** → **10**, the former reaction is far slower ($t_{1/2}{}^{55°} = 0.5$ h). Rearrangement of **12** was found to be stereospecific, and the exo configuration assigned to **13** was confirmed using Eu(fod)$_3$. Although there is no assurance that *exo-* **1a** and **12** react according to the same mechanism, it is striking that the rearrangement stereochemistry demonstrated for **12** matches that postulated for *exo-* **1a.**[17]

We propose the name *pseudopericyclic* to describe the [1,3]sigmatropic pathway shown in **7.** *A pseudopericyclic reaction is a concerted transformation whose primary changes in bonding compass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles.*[18,19] In a crucial sense, the role interchange means a "disconnection" in the cyclic array of overlapping orbitals because the atomic orbitals switching functions are mutually orthogonal. Hence *pseudopericyclic reactions cannot be orbital symmetry forbidden.* The mechanistic idea described here is certainly not new, but we are unaware of a clear and general statement of this concept in the literature. Many apparently pseudopericyclic reactions are known.[20] Prototropy in internally hydrogen bonded enols of β-dicarbonyl compounds (eq 1) is a prosaic example. As the proton tunnels between minima, lone pair and bonding orbitals formally interchange functions at both oxygens in the planar chelate ring.[21-23] In olefin hydroboration (eq 2) the vacant boron orbital presumably switches roles with the orbital employed in bonding to hydrogen. By this device a planar, four-center transition state, normally very high lying, becomes easily accessible.[24]



(1)



(2)

Further studies of sulfoxide rearrangement mechanisms are in progress.

Acknowledgment. The authors wish to give special thanks to Professor C. Hackett Bushweller and Dr. Charles W. Gillies for making the spectroscopic measurements cited, and to Professors Orville Chapman, Roald Hoffmann, and R. B. Woodward for valuable criticism. They are grateful as well to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

References and Notes

(1) H. A. Wiebe, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972).

(2) All ^{19}F NMR chemical shifts are expressed in parts per million downfield from external trifluoroacetic acid.

(3) A square pyramidal structure has also been postulated by R. Hoffmann and W. D. Stohrer for (CH)$_5{}^+$ and its derivatives. See H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975), and references contained therein.

(4) In the ground state of SO there is an orthogonal pair of singly occupied π^* orbitals of the proper symmetry to mix with ψ_2 and ψ_3 of the diene, which are singly occupied in the Huckel approximation. Moreover, the corresponding pair of filled π orbitals in SO could transfer charge to the diene by mixing with ψ_2 and ψ_3, while vacant d orbitals provide for back-donation to sulfur from ψ_1, ψ_2, and ψ_3. R. Hoffmann emphasizes, however, that the sulfur lone pair-ψ_1 interaction would be strongly repulsive.

(5) In local D_{4h} symmetry this transition is rigorously forbidden. While the axial perturbation should confer some intensity on this Raman band, it is expected to be weak. Similarly, the ring breathing mode (ir forbidden in local D_{4h} symmetry) of the tetramethylcyclobutadiene-nickel chloride complex gives rise to a weak band in the infrared (H. P. Fritz in *Adv. Organomet. Chem.*, **1**, 258 (1964).

(6) The Raman spectrum was measured by Dr. Charles W. Gillies at Harvard University.

(7) This band is split slightly (8-9 cm^{-1}) on the low frequency side, perhaps as a consequence of Fermi resonance with the band at 831 cm^{-1}. Incidentally, the vibrational spectra also rule out a rectangularly distorted (C_{2v}) **1b.**

(8) Professor C. Hackett Bushweller of Worcester Polytechnic Institute carried out this experiment.

(9) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*, 2841 (1974).

(10) Though reported as an oil,[9] this diene has been obtained as white crystals, mp 37-38°: ir (vapor) 1724, 1344, 1276, 1218, 1183, 1163, 714 cm^{-1}; ^{19}F NMR (CDCl$_3$) δ 17.40 (m), 15.43 (m); ^{1}H NMR (CDCl$_3$) δ 6.62 (m), 4.88 (m); MS 392 (parent).

(11) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., **1970**; (b) J. A. Berson, T. Miyashi, and G. Jones, II, *J. Am. Chem. Soc.*, **96**, 3468 (1974), and references contained therein.

(12) Even though ring opening in *cis-* and *trans-*2,3-diphenylthiirane oxide produces a biradical with benzylic stabilization, these compounds cleave only slowly at room temperature (K. Kondo, M. Matsumoto, and A. Negishi, *Tetrahedron Lett.*, 2131 (1972)).

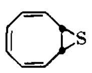
(13) Suitable geometry is a necessary, but not a sufficient criterion for a very low barrier. The Dewar thiophene (**2**) rearranges perceptibly by NMR only above 100 °C. Attempts to oxidize *exo-***1a** to the sulfone, which of course lacks the lone pair on sulfur, have met with failure.

(14) F. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969).

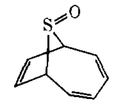
(15) Sufficient "proton sponge" was present in some runs to neutralize the trifluoroacetic acid formed, thus assuring that acid catalysis was not responsible for the rapid rate.

(16) P. Chao and D. M. Lemal, *J. Am. Chem. Soc.*, **95**, 920 (1973), and references contained therein.

(17) Oxidation of i with periodate or *m*-chloroperbenzoic acid (−30 to 0°) gives ii. With the reasonable assumption that oxidation occurs on the exo face of i, this stereochemical result parallels those under discussion. Sulfoxide **ii** is capable of further rearrangement on heating, but by a different mechanism. A. G. Anastassiou, J. C. Wetzel, and B. Y.-H. Chao, *J. Amer. Chem. Soc.*, **97**, 1124 (1975).

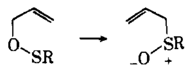


i



ii

(18) A bonding-nonbonding interchange involving *different* atoms does *not* qualify; e.g., **iii** → **iv.**, a pericyclic reaction:



iii iv

In cheletropic reactions, two atomic orbitals at the same center are intimately involved, but they do not interchange roles.

(19) For the definition of pericyclic reaction, see R. B. Woodward and R. Hoffmann, ref 11a.

(20) Numerous examples will be presented in a full paper.

(21) A bonding p orbital and a "nonbonding" lone pair orbital switch roles at the left-hand oxygen, while a complementary interchange occurs at the oxygen on the right. Although the bonding/nonbonding distinction is obviously not absolute here, the separation of this *concerted process* into persistently orthogonal σ and π components dramatizes the fact that it is not pericyclic.

(22) The crystal structure of dibenzoylmethane, as its enol, is presented in R. W. G. Wyckoff, "Crystal Structures", 2d ed, Vol. 6, Interscience, New York, N.Y., 1971, pp 125-128.

(23) Many other prototropic processes in conjugated systems are presumably pseudopericyclic, among them the proton tunneling phenomena in DNA which Lowdin has proposed as a basis for mutagenesis (W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968, pp 176-178).

(24) K. Fukui, *Bull. Chem. Soc. Jpn.*, **39**, 498 (1966).

James A. Ross, Reginald P. Seiders, David M. Lemal*
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received February 10, 1976

Novel Aromatic Systems. 6.[1] The Bis(tetramethylhomocyclopropenyl) Dication

Sir:

In view of our current interest in the two π electron homoaromatic cyclobutenyl(homocyclopropenyl) cation **1**,[2] we wish to report now the interesting and unexpected finding that the two electron oxidative ring opening reaction of the tetramethylcyclobutadiene dimer **2**[3] in antimony pentafluo-