1 is apparently *not* generated in vibrationally excited form. The runs at higher temperatures demonstrate that at 341 °C spiropentane undergoes very slight decomposition to methylenecyclobutane, but temperatures in excess of 400 °C are required to produce any detectable secondary allene and ethylene, presumably by thermal decomposition of methylenecyclobutane.

The results for **6** are strikingly different. Once again, spiropentane is the major product of the reaction. Methylene cyclobutane is also formed, as are ethylene and allene, but in amounts significantly larger than those observed from **4**; small amounts of unidentified hydrocarbons are also detected. One possible way for the methylenecyclobutane to arise is via a second ring opening in **3** (Scheme II) leading to the "allylically stabilized diradical" **9** which has been discussed by Flowers and his co-workers.[1b,c] However, if this were the only route to fragmentation products, *all* the deuterium label in the decomposition of **7** should appear in the ethylene product. The actual observation is that the label is distributed *nearly equally* in the two fragmentation products (Table II). This suggests strongly that the ultimate source of the ethylene and allene is a compound which has spiropentane symmetry. Controls again show that no fragmentation products are formed thermally at these temperatures. That *both* vibrationally excited **1** and **8** must intervene in this reaction is confirmed by variable pressure studies (Table I)—in this case (unlike that of **4**) both the spiropentane and methylenecyclobutane yields are now pressure dependent.

Why does unsymmetrical pyrazoline **6** give rise to vibrationally excited spiropentane (**1**), but symmetrical pyrazoline **4** does not? One possible explanation for this might be found in differing heats of formation for the diradicals **2** and **3** or for the transition states leading to them. However, although there is some uncertainty in the group equivalent calculations needed to make such estimates,[6] it is difficult to make a case that these heats of formation will differ by more than a few kilocalories per mole in the two cases. A much more convincing explanation is provided by a postulate put forward by Bauer several years ago, suggesting that the distribution of vibrational energy in fragmentation reactions of the type discussed here might be determined by their decomposition mechanisms.[7]

Translated into terms applicable to azo compounds **4** and **6**, Bauer's postulate[7a] suggests the following: symmetrical compound **4** probably decomposes by simultaneous cleavage of both C–N bonds, passing through a short-lived, symmetrical transition state in which coupling of the N–N vibration with vibrational modes in the organic fragment is very poor. Thus the nascent N_2 molecule is generated initially with an N–N bond that is "stretched"—i.e., the N_2 is formed vibrationally excited, and carries off much of the excess energy of the decomposition, leaving an essentially thermalized organic fragment. Pyrazoline **6**, however, has one strong and one weak C–N bond; there is now good precedent that such azo compounds decompose by sequential C–N cleavage,[8] initially generating diazenyl (i.e., R–N_2·) radicals. Bauer suggests[7a] that such nitrogen-containing diradical intermediates should have time to allow efficient coupling between the N–N vibration and the vibrational modes of the organic fragment; thus the N_2 will be extruded "cold", leaving most of the excess energy behind in the organic fragment. This explanation accounts very nicely for our observations, and provides strong encouragement to the search for spectroscopically observable "hot" nitrogen extruded in the thermal decomposition of *symmetrical* cyclic azo compounds.

Acknowledgments. We are grateful to the National Science Foundation for financial support of this work (Grant No. CHE-74-14711), to Mr. John Burke for assistance in carrying out GC-mass spectrometric experiments, and to Drs. Peter Dervan, L. M. Stephenson, J. I. Brauman, David Golden, and Yuan Lee for helpful discussions.

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(4) (a) Perhaps the most careful previous search was reported by F. H. Dorer, E. Brown, J. Do, and R. Rees, *J. Phys. Chem.,* **75,** 1640 (1971). (b) For an interesting discussion of some of the possible consequences of chemical activation in pyrazoline pyrolyses, see L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.,* **93,** 1988 (1971). (c) Hot hydrocarbons have been detected in pyrazoline *photochemical* decompositions; see, for example, F. T. Thomas, C. I. Sutin, and C. Steel, *J. Am. Chem. Soc.,* **89,** 5107 (1967); F. H. Dorer, *J. Phys. Chem.,* **73,** 3109 (1959); **74,** 1142 (1970). (d) For evidence that hot *tert*-butyl radicals are generated in the decomposition of azo-*tert*-butane, see D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.,* **94,** 4403 (1972).

(5) Compounds **4–7** were prepared by allowing methylenecyclopropane and diazomethane (or diazomethane-d_2) to stand in diethyl either solution at ca. 3 °C for 2 weeks. The mixture of two azo compounds was obtained in 90% yield; the ratio of **4**:**6** was 45:55. The isomers were separated by preparative VPC on a 20 ft by ¼ in. QF1 glass column and characterized by standard spectral and analytical techniques.

(6) Azo compound heats of formation are discussed by P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, *J. Am. Chem. Soc.,* **96,** 2381 (1974). The activation energy for thermal decomposition of **4** in solution is 39.9 ± 1.5 kcal/mol at 160 °C; we estimate that E_a for decomposition of **6** is 3–4 kcal/mol higher than that of **4**.

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Kelvin Kei-wei Shen, Robert G. Bergman*
Contribution No. 5421
Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

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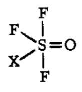
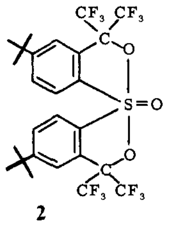
The Acid Catalyzed Fragmentation of a Spirobicyclicsulfurane Oxide: Sulfone Formation as a Driving Force for Reaction[1]

Sir:

Sulfurane oxide intermediates or transition states have often been proposed in nucleophilic substitution reactions on sulfur.[2] The preparations of sulfur oxytetrafluoride and a number of other halogen substituted sulfurane oxides, including **1a–c**, have also been reported.[3] Sulfurane oxide **2**, the only reported ketal analogue of a sulfone,[4] was found to be inert toward aqueous acid or base.

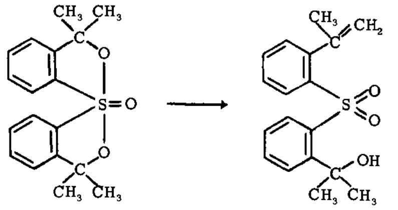


1a, X = $N(CH_3)_2$
b, X = $N(C_2H_5)_2$
c, X = OPh



2

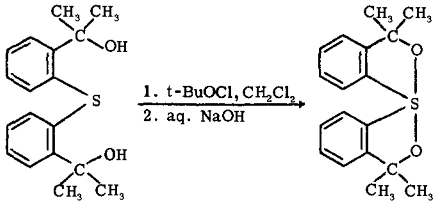
We report here the first example of a new type of fragmentation reaction which involves the smooth transformation of spirobicyclicsulfurane oxide **3** to sulfone-ene-ol **4**. The formation of the very stable, neutral, sulfone function of **4** provides a strong driving force for this reaction. The energy of the S=O bond of diphenyl sulfoxide is 96.4 kcal mol^{-1},[5] and the energy of the second S=O bond added in going from a sulfoxide to a sulfone is an even larger 115.7 kcal mol^{-1}.[5] The strong tendency for **3** to fragment to **4**, when a suitable pathway is available, is therefore not surprising.



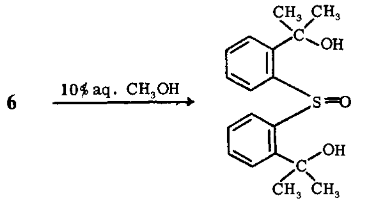
3 **4**

This quantitative and irreversible fragmentation occurs rapidly under acidic conditions but very slowly under basic conditions. For example, a sample of **3** in dry CH_2Cl_2 at 44 °C will fragment completely within seconds to sulfone **4** when one drop of HCl saturated methylene chloride is added.[6] In contrast, a pyridine solution of **3** at 100 °C undergoes fragmentation to the extent of only 12.5% after 42 min.[7] It should also be noted that stronger bases such as hydroxide retard the rate even more than pyridine alone. For example, a 15% aqueous pyridine (v/v) solution 0.251 M in sulfurane oxide **3** and 0.251 M in KOH fragmented to the extent of only 14% after 88 h at 86 °C.

The parent sulfurane (**6**) of **3** was synthesized in 82% yield by the pictured route from diol **5**.[8,9] Compound **6** is a crystalline white material (mp 155–155.5 °C) whose ^1H NMR spectrum in pyridine-d_5 shows diastereotopic methyl singlets at δ 1.60 and 1.67, each of which is split into two peaks when **6** and a chiral alcohol interact in CCl_4.[10,11] This is consistent with a chiral trigonal-bipyramidal geometry about sulfur. Spirosulfurane **6** is not affected by atmospheric moisture nor by water in $CHCl_3$ but can be hydrolyzed to sulfoxide diol **7** when boiled for 2 h in 10% aqueous methanol. Cyclodehydration of **7** to regenerate **6** occurs slowly at room temperature in chloroform containing a trace of HCl.[12]



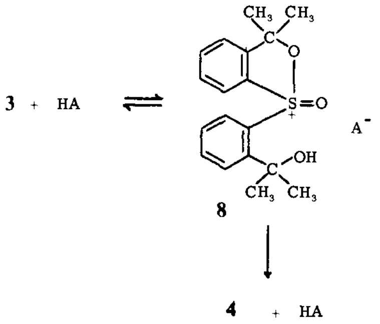
5 **6**



7

Sulfurane oxide **3** is formed in 70% yield when **6**, dissolved in a minimum amount of dry methylene chloride, is treated with excess ozone at 78 °C. After 1 h **3** precipitates and is collected at −20 °C. This material was recrystallized from ether–THF containing one drop of pyridine (mp 153 °C).[13] The ^1H NMR spectrum of **3** in pyridine-d_5 shows diastereotopic methyl singlets at δ 1.65 and 1.87 which is consistent with a postulated chiral trigonal-bipyramidal geometry about sulfur like that shown for **6**,[10,14] in close analogy to the x-ray structure determined for **2**.[4c]

Scheme I



The first step in the acid catalyzed fragmentation (Scheme I) may be the reversible protonation of an apical oxygen on **3** giving oxysulfoxonium cation **8**. Postulated intermediate **8** is an O-alkylated sulfone which is expected to be very reactive,[15] rapidly losing a proton to base to give sulfone-olefin **4**.[17] A fragmentation pathway similar to the one postulated for **3** in Scheme I is not available to sulfurane oxide **2**.

Further work is underway to establish the generality and the detailed mechanism of this sort of fragmentation to generate sulfones.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (MPS-75-17742).

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(5) Calculated from data tabulated by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970, pp 376, 384, 388.

(6) The reaction was followed by NMR spectroscopy either by the disappearance of the two diastereomeric methyl singlets on **3** or by the appearance of the α-methyl group of the olefin. Compound **4** was prepared independently by the reaction of **3** with *m*-chloroperbenzoic acid.

(7) The reaction in benzonitrile solvent, with 0.5 M pyridine, is first order in **3** for at least two half-lives.

(8) 2,2′-Dicarboxydiphenyl sulfide was prepared by a modification of Protiva's method for the synthesis of the monoacid sulfide; J. Jilek, V. Seidlova, E. Svatek, and M. Protiva, *Monatsh. Chem.*, **96** (1), 182 (1965). The diacid was treated with thionyl chloride forming the diacid chloride which was treated with ethanol and pyridine to form the diester. The diester was then converted to diol **5** by reaction with methylmagnesium bromide in ether.

(9) A satisfactory elemental analysis, infrared spectrum, and mass spectrum were obtained for **6**.

(10) Evidence for the chirality of **6** was seen when the addition of (*S*)-(+)-2,2,2-trifluoro-1-(10-methyl-9-anthryl)ethanol to a CCl_4 solution of **6** showed four resolved methyl singlets in the 220-MHz NMR spectrum. W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Am. Chem. Soc.*, **93,** 2817 (1971). We thank Dr. Pirkle and Dr. D. Sikkenga for supplying a sample of the optically pure reagent.

(11) The protons ortho to sulfur were found at very low field (δ 8.62) which is characteristic for sulfuranes of this type.[4b] For the selenium analogue of **6** see H. J. Reich, *J. Am. Chem. Soc.*, **95,** 965 (1973).

(12) Sulfurane **6** will also react with strong acids (HCl, HBr, $HOSO_2CF_3$, HBF_4) to form stable, isolable halosulfuranes or sulfonium salts.

(13) Elemental analyses and mass spectrum were consistent with the postulated structure for **3**.

(14) The downfield shift of the ortho proton of **3** places it at δ 8.66. See ref 4b for a similar shift seen in **2**.

(15) Intermediates similar to **8** have been postulated in reactions involving chlorination of sulfoxides.[4b] Whiting[16] has prepared isolable O-arylated

sulfones from the reaction of aryldiazonium salts with sulfones.

(16) G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(17) ^1H NMR (CD_2Cl_2) δ 1.62 (s, 6 H), 1.92 (m, 3 H), 4.47 (m, 1 H), 4.73 (broad s, 1 H), 5.04 (m, 1 H), 7.20–8.10 (m, 8 H). Elemental analyses, infrared and mass spectra were also consistent with sulfone **4**.

L. J. Adzima, J. C. Martin*
Department of Chemisty, Roger Adams Laboratory
University of Illinois
Urbana, Illinois 61801

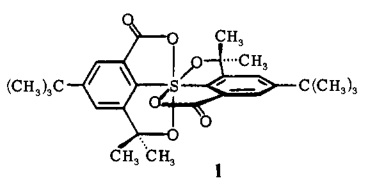
Received November 22, 1976

A Diaryldiacyloxydialkoxypersulfurane.[1] The First Example of a Hexacoordinated Organosulfur Derivative Lacking Fluorine Ligands, a Sulfone Bisketal

Sir:

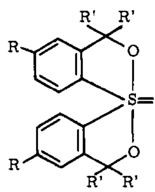
Derivatives of SF_6 in which one or two of the fluorine ligands have been replaced by aryl, vinyl, ethynyl, or perfluoroalkyl groups have been known[2] for many years. The first persulfuranes with two simple alkyl or aryl ligands and four fluorines bound to sulfur were only recently prepared, and found to be stable at −78 °C, by Denney et al.[3]

We now report the isolation and characterization of the first[4] persulfurane[5] lacking fluorine ligands, diaryldiacyloxydialkoxypersulfurane (**1**), a compound of surprising stability.



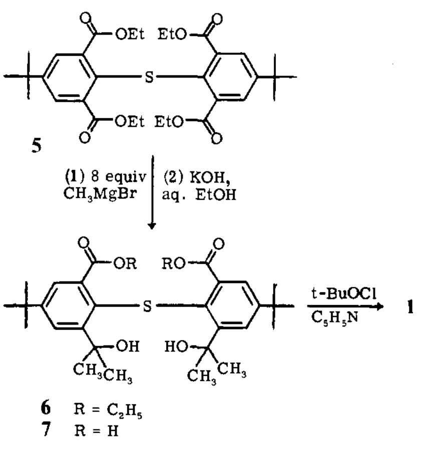
1

By analogy to the spirobicyclicsulfurane oxide **4a**,[6] the first reported monoketal analogue of a sulfone, persulfurane **1**, can be considered the first bisketal analogue of a sulfone.



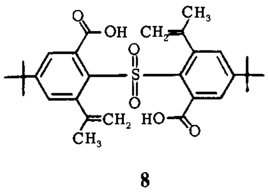
4a R = $(CH_3)_3C$; R' = CF_3
4b R = H; R' = CH_3

Reaction of tetraester **5**[7] with methyl Grignard (8 equiv, 3 h) in ether gave diester diol **6** in 86% yield (mp 154–156 °C). Saponification of **6** with 15% KOH in aqueous ethanol (1:1) gave diacid diol **7** (mp 268–270 °C). Treatment of a CCl_4 suspension of **7** and pyridine (2 equiv) with *tert*-butyl hypochlorite (5 equiv) at 0 °C afforded white powdery **1** in 90–95% yield. The product, **1**, was recrystallized from ether–pentane or THF–pentane, mp 166–170 °C dec.[8] The crystalline **1** is stable indefinitely at room temperature. The two peaks at δ 1.799 and 1.782 in its ^1H NMR spectrum[8] clearly indicate the diasterotopic nature of the two geminal methyl groups on the five-membered heterocyclic ring, as expected for the pictured octahedral structure of **1**.



6 R = C_2H_5
7 R = H

The solid persulfurane **1** is stable and unreactive toward atmospheric moisture. However, **1** was found to decompose completely at room temperature (<30 min) in ordinary $CDCl_3$ and (3 days) in pyridine-d_5 solvent, as evidenced by the ^1H NMR spectra. The product from decomposition of **1** was identified as the isomeric sulfone diene diacid (**8**) by elemental analysis, infrared, NMR, and mass spectrometry.[9] The decomposition of persulfurane **1** to give **8** is analogous to the acid-catalyzed fragmentation[10] of spirobicyclicsulfurane oxide **4b**, to give **9**, another fragmentation deriving its driving force from the formation of the stable sulfone functional group. In the case of persulfurane **1**, fragmentation is catalyzed either by a trace of HCl present in ordinary chloroform or by a trace of water present in the pyridine-d_5. When a drop of D_2O was added to a sample of **1** in pyridine-d_5, the rate of fragmentation was greatly enhanced (complete reaction within minutes at room temperature).



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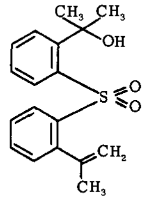

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The spectroscopic and chemical evidence presented here provides a compelling case for the proposed structure for persulfurane **1**. Further work on the structure and reactivity of persulfuranes is underway in our laboratory.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, MPS 75-17742.

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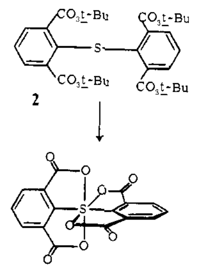
(4) It has been reported by M. M. Chau, Ph.D. Thesis, University of Illinois, 1975 (manuscript, with J. C. Martin, in preparation), that decomposition of tetraperester **2** gave a compound for which structure **3**, a persulfurane, was proposed. Evidence for its structure was, however, incomplete.



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(7) Prepared from the corresponding tetraacid, which was synthesized from 2,6-dimethyl-4-*tert*-butylbromobenzene by a procedure similar to that described[4] for the preparation of bis(2,6-dicarboxyphenyl) sulfide. The elemental analyses and infrared and NMR spectra are all consistent with the structures proposed for compounds used in the preparation of **1**.