

1731 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 213.6, 175.4, 170.6, 127.7, 127.2, 52.5, 51.5, 39.8, 39.3, 38.8, 28.8, 28.0, 27.7, 26.7, 19.6; exact mass calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5$ 280.1305, found 280.1309.

Dimethyl Methylmalonate with Sodium Hydride as Base. Dimethyl methylmalonate (0.146 g, 1.0 mmol) was added dropwise to a suspension of sodium hydride (0.0432 g, 0.9 mmol) (washed with 1 mL of hexane) in toluene (4 mL). The solution was warmed to 100 °C and stirred for 15 min. Then *cis*-3-acetoxy-1-carbomethoxycyclohex-4-ene (0.100 g, 0.5 mmol) and molybdenum hexacarbonyl (0.013 g, 0.05 mmol) were added, and the solution was heated at reflux for 24 h. As TLC indicated remaining starting material, a second portion of molybdenum hexacarbonyl (0.013 g, 0.05 mmol) was added, and reflux was continued another 12 h. The mixture was added to ether (30 mL) and washed with 10% aqueous potassium hydroxide solution (2 \times 20 mL) and saturated aqueous sodium chloride solution (20 mL). The ether solution was dried (MgSO_4) and chromatographed (80:20 hexane:ethyl acetate) to yield 0.112 g (79%) of the product as a colorless oil. Gas chromatography (12 m \times 0.32 mm, SE-30, 100–200 °C via 10 deg/min intervals) showed a 89:11 *cis*:*trans* ratio of alkylated products: IR (CHCl_3) 1730 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 5.85–5.75 (1 H, m), 5.57–5.48 (1 H, m), 3.73 (6 H, s), 3.69 (3 H, s), 3.20–3.10 (1 H, m), 2.73–2.58 (1 H, m), 2.36–2.10 (2 H, m), 1.97–1.88 (1 H, m), 1.43 (1 H, q, $J = 12.3$ Hz), 1.35 (3 H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 175.4, 171.5, 171.3, 127.3, 127.1, 56.6, 52.3 (2), 51.5, 40.3, 39.5, 27.6, 26.8, 16.0; exact mass calcd for $\text{C}_{14}\text{H}_{20}\text{O}_6$ 284.1260 found 284.1253.

Preparation of Dimethyl (4-*tert*-Butyl-1-vinylcyclohex-1-yl)malonate (33). Alkylation of Allylic Acetate 30 with Dimethyl Malonate. Following general procedure B,⁴ allylic acetate 30 (330 mg, 1.47 mmol), dimethyl malonate (306 mg, 2.5 mmol), BSA (445 mg, 2.2 mmol), and $\text{Mo}(\text{CO})_6$ (40 mg, 10 mol %) in toluene (4 mL) were heated at reflux for 1.75 h. Standard workup and bulb-to-bulb distillation (100 °C at 0.01 mmHg) provided a clear oil, 388 mg (89%). The product exhibited identical spectral characteristics with those derived from alkylation of allylic acetate 31 (see below). Furthermore, the ratio of stereoisomers was also identical as determined by integration of signals at δ 6.38 and 5.80 (i.e., 1:5).

Alkylation of Allylic Acetate 31 with Dimethyl Malonate. Following general procedure B,⁴ allylic acetate 31 (330 mg, 1.47 mmol), dimethyl malonate (306 mg, 2.5 mmol), BSA (445 mg, 2.2 mmol), and $\text{Mo}(\text{CO})_6$ (40 mg, 10 mol %) in toluene (4 mL) were heated at reflux for 2.5 h. Purification via bulb-to-bulb distillation (100 °C at 0.01 mmHg) provided a clear oil, 301 mg (69%). Integration of signals in the ^1H NMR spectrum at δ 6.38 and 5.80 provides the ratio of isomers (1:5): ^1H NMR (200 MHz, CDCl_3) δ 6.38 (0.13 H, dd, $J = 19, 11$ Hz), 5.80 (0.87 H, dd, $J = 18, 11$ Hz), 5.28 (0.87 H, d, $J = 11$ Hz), 5.08 (0.87 H, d, $J = 18$ Hz), 3.92 (0.13 H, s), 3.70 (5.2 H, s), 3.32 (0.87 H, s), 2.10 (0.87 H, br d, 11 Hz), 1.8–1.0 (8 H, m), 0.89 (1.18 H, s), 0.80 (7.83 H, s); ^{13}C NMR (CDCl_3) δ 168.2, 167.6, 144.5 (minor), 141.6, 116.0, 112.5 (minor), 62.7, 51.5, 47.6, 41.9, 33.5, 32.0, 27.2, 22.8; IR (neat) 1755, 1735, 1635 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4$: C, 68.89; H, 9.52. Found: C, 68.71; H, 9.40.

Alkylation of Allyl Acetate 31 with Di-*tert*-butyl Malonate. Following general procedure B,⁴ allylic acetate 31 (228 mg, 1.0 mmol), toluene (3 mL), BSA (375 mg, 1.8 mmol), di-*tert*-butyl malonate (432 mg, 2.0

mmol), and $\text{Mo}(\text{CO})_6$ (25 mg, 10 mol %) were heated at reflux for 1.5 h. Flash chromatography (10:1 hexane:ether) yielded 311 mg (81.4%) of a clear viscous oil. A 1:4 ratio of isomers was observed in the alkylation reaction, which was measured by integration of signals in the ^1H NMR spectrum at δ 6.40 and 5.82: ^1H NMR (200 MHz, CDCl_3) δ 6.40 (0.2 H, dd, $J = 18, 12$ Hz), 5.82 (0.8 H, dd, $J = 18, 10$ Hz), 5.25 (0.8 H, d, $J = 10$ Hz), 5.05 (0.8 H, d, $J = 18$ Hz), 3.64 (0.2 H, s), 3.08 (0.8 H, s), 2.10 (1.6 H, br d, $J = 12$ Hz), 1.6–1.0 (9 H, m), 1.45 (1.8 H, s), 0.86 (1.8 H, s), 0.82 (5.6 H, s); ^{13}C NMR (CDCl_3) δ 167.2, 166.8, 144.2 (minor), 141.5, 115.5 (minor), 112.0, 80.5, 77.1, 64.5, 47.7, 41.6, 33.4, 31.9, 27.7, 22.7; IR (neat) 1755, 1730, 1648 cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{O}_4$: C, 72.59; H, 10.59. Found: C, 72.77; H, 10.68.

Preparation of 3 β -Acetoxy-3 α -ethenyl-5 α -cholestane (34). To a solution of the allylic alcohol²¹ derived from addition of vinylmagnesium bromide to cholestanone (1.33 mg, 3.22 mmol) in methylene chloride (15 mL) was added DMAP (65 mg, 0.53 mmol) and pyridine (550 mL, 6.8 mmol). The reaction mixture was cooled to 0 °C, and then acetyl chloride (1.2 mL, 16.9 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C, warmed to room temperature, and stirred for 24 h. The crude reaction mixture was then poured into ether and washed with saturated aqueous sodium bicarbonate. After the mixture was dried over magnesium sulfate, the solvent was removed under reduced pressure to yield a solid which was recrystallized from acetone: 1.1 g, 71%; mp 75.5–77.0 °C; ^1H NMR (200 MHz, CDCl_3) δ 6.10 (1 H, dd, $J = 17, 11$ Hz), 5.12 (1 H, d, $J = 17$ Hz), 5.06 (1 H, d, $J = 11$ Hz), 2.20 (1 H, d, $J = 15$ Hz), 1.02 (3 H, s), 1.00–2.00 (29 H, m), 0.91 (3 H, d, $J = 7$ Hz), 0.88 (6 H, d, $J = 6$ Hz), 0.81 (3 H, s), 0.68 (3 H, s); IR (CDCl_3) 1738, 1550 cm^{-1} ; exact mass calcd for $\text{C}_{31}\text{H}_{52}\text{O}_2$ 456.3959, found 456.3969.

Preparation of 3 β -Ethenyl-3 α -(bis(carbomethoxy)methyl)-5 α -cholestane (35). Following general procedure B,⁴ allylic acetate 34 (228 mg, 0.5 mmol), toluene (1 mL), BSA (190 mg, 0.95 mmol), dimethyl malonate (132 mg, 1.0 mmol), and $\text{Mo}(\text{CO})_6$ (13 mg, 10 mol %) were combined and heated at reflux for 3 h. Standard workup procedures followed by flash chromatography (5:1 hexane:ether) afforded 183 mg (69%) of a clear viscous oil which slowly solidified to a waxy solid. The ratio of stereoisomers was determined by measuring the signals in the ^1H NMR spectrum at δ 6.32 and 5.80 (ratio found = 1:4): ^1H NMR (200 MHz, CDCl_3) δ 6.32 (0.20 H, dd, $J = 17, 11$ Hz), 5.80 (0.80 H, dd, $J = 18, 11.5$ Hz), 5.25 (1 H, d, $J = 11.5$ Hz), 5.05 (1 H, d, $J = 18$ Hz), 3.70 (6 H, s), 3.34 (9 H, s), 1.00–1.80 (3 H, m), 0.89 (3 H, s), 0.84 (6 H, d), 0.80 (3 H, s), 0.68 (3 H, s); ^{13}C NMR (CDCl_3) δ 167.9, 142.1, 115.8, 62.8, 56.5, 56.3, 54.3, 51.8, 42.6, 41.7, 39.9, 39.5, 36.2, 35.9, 35.8, 34.4, 31.9, 28.7, 28.2, 27.9, 24.1, 23.9, 22.7, 22.5, 20.9, 18.7, 12.9; IR (neat) 1762, 1742 cm^{-1} ; exact mass calcd for $\text{C}_{34}\text{H}_{56}\text{O}_4$ 628.4164, found 528.4176.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. Mark Lautens thanks NSERC of Canada for a fellowship. We especially thank Craig Merlic for performing one of the alkylation reactions and Carol Carmichael and Brian Peterson for the preparation of some starting materials.

Chemistry of Singlet Oxygen. 49. Photooxidation of Thiiranes

Frank Jensen and Christopher S. Foote*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received September 26, 1986

Abstract: The reaction between thiiranes and singlet oxygen has been investigated. Diphenylthiirane is unreactive, but simple alkyl thiiranes react readily, even at low temperature. The products depend on solvent and substrate concentration. In nonnucleophilic solvents, the primary product is the thiirane oxide. In methanol, the primary products are sulfenic esters at low substrate concentration and thiirane oxide at high concentration. It is suggested that the reaction proceeds via an intermediate, for which we assign a peroxythiirane oxide structure. The structures of potential intermediates have been calculated at the *ab initio* level using a 3–21 G(*) basis set. The reaction mechanism is discussed on the basis of Frontier Molecular Orbital theory and *ab initio* calculations.

The reaction between organic sulfur compounds and singlet oxygen continues to yield intriguing results.^{1–6} The reactions of

simple organic sulfides have been extensively studied by Foote et al.^{2,5b,6b,14a,b} Recently Ando et al.³ have reported an interesting

effect of ring size on the products of photooxygenation of cyclic sulfides. The reaction of thioketenes with singlet oxygen has also been reported.⁴ An interesting rearranged product is obtained in the presence of methanol. In all cases, the proposed primary intermediate is a peroxy-sulfoxide ("persulfoxide"). The fate of this intermediate depends on solvent and, in some cases, also on temperature.⁵ Intermolecular trapping with unreacted starting material can compete with dissociation to sulfide and ground-state oxygen and with intramolecular rearrangement to the sulfone.⁶

We now report on the photooxygenation of the smallest cyclic sulfides, thiiranes. It is well-known that thiiranes are less stable than the corresponding epoxides. Thermal loss of elementary sulfur often occurs at or slightly above ambient temperature. A number of reagents, such as trivalent phosphorus compounds and certain organometallic compounds, also cause loss of sulfur to give the corresponding olefin.⁷ Thiirane oxides can be obtained by oxidation of thiiranes, but are generally unstable at room temperature unless there are bulky substituents on the ring. Although thiirane oxides can be generated at low temperature, they are very susceptible to acid-catalyzed ring opening.⁸ So far, all attempts at obtaining thiirane dioxides from oxidation of thiiranes or thiirane oxides have failed, although thiirane dioxides have been prepared by other methods.⁹

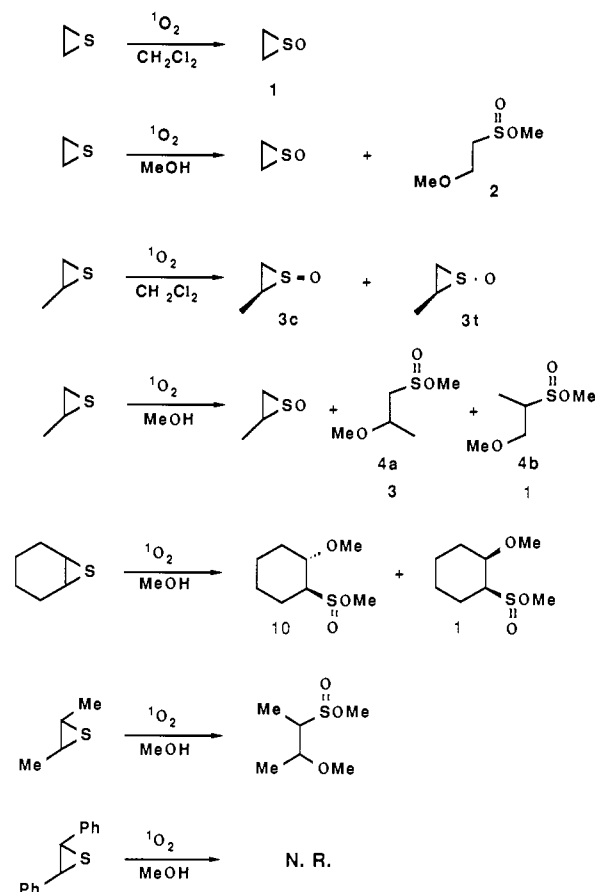
If thiiranes react similarly to simple alkyl sulfides, a peroxy-thiirane oxide should be the first intermediate. This compound should resemble a protonated thiirane oxide, and we were interested in whether it would spontaneously open the three-membered ring or show chemistry analogous to unstrained sulfides. Our results show that both modes of reaction are observed.

Results

Alkyl thiiranes react with oxygen in the presence of a sensitizer and light. Several sensitizers (rose bengal, methylene blue, tetraphenylporphine, and mesoporphyrin IX dimethyl ester) all give the same products at approximately the same reaction rate. If the photolysis is carried out under nitrogen or in the absence of a sensitizer, no reaction occurs. The oxygenation is inhibited by 1,4-diazabicyclooctane (DABCO), a known singlet oxygen quencher. Addition of a radical trap (2,6-di-*tert*-butyl-4-methylphenol) in concentrations up to 10^{-3} M does not have any influence. At higher concentration of the phenol, some quenching of singlet oxygen takes place¹⁰ and the reaction is slower, but the ratio of products remains the same. Products from the various reactions are shown in Scheme I.

Thiirane. In nonnucleophilic solvents such as acetone, acetonitrile, chloroform, and dichloromethane, the only product detected by GC and NMR is thiirane oxide (1). The thiirane oxide was identified by comparison of its GC retention time and NMR spectra with a sample prepared by an independent method.¹¹ In

Scheme I



MeOH, the only product observed at low thiirane concentration ($<10^{-2}$ M) is methyl 2-methoxyethanesulfinate (2), identified by its spectral properties. Above 0.5 M, extensive polymeric material forms.

2-Methylthiirane. In nonnucleophilic solvent, no major product can be observed by GC. However, low-temperature (-20 °C) NMR spectra show two products together with a small amount of polymeric material. Upon warming, these products give polymeric material. The same two compounds can be generated by *m*-chloroperoxybenzoic acid (MCPBA) oxidation of 2-methylthiirane at -20 °C. Based on the NMR spectra, they are *cis*- and *trans*-2-methylthiirane oxides (3c and 3t).

In MeOH at low thiirane concentration, two isomeric methoxy sulfonates 4a and 4b, in ratios approximately 3:1, are the only products as shown by NMR. At higher concentration, three isomeric methoxy disulfides 5a, 5b, and 5c (ratio 33:15:1) can be isolated by preparative GC (Scheme II). However, low-temperature NMR shows that the thiirane oxides are the primary products. The thiirane oxides react with unreacted starting material in the presence of small amounts of strong acid to give the observed disulfides at approximately -10 °C. The disulfides are also formed when the thiirane oxides are generated by MCPBA oxidation (0.5 equiv) in MeOH and a trace of H_2SO_4 is added. If sodium acetate is added to the photolyzed reaction mixture, no disulfides are formed. If the reaction is carried to completion at low temperature, again no disulfide is observed. The pH of the solution after photolysis was found to be 2–3.

Since no unidentified products are detected in the low-temperature NMR, the source of the acid remains uncertain. However, sulfinic acids have a pK_a around 2,¹² and it is likely that a small amount of a sulfinic or sulfonic acid is a minor product (see Discussion). If the thiirane oxides are generated at low tem-

(1) Ando, W.; Kabe, T.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191–194.

(2) (a) Foote, C. S.; Peters, J. W. In *XXIIIrd International Congress of Pure and Applied Chemistry, Special Lectures*; Butterworths: London, 1971; Vol. 4, pp 129–154. (b) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765–769.

(3) (a) Toshikazu, T.; Koshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767–4770. (b) Toshikazu, T.; Ishibashi, K.; Ando, W. *Ibid.* **1985**, *26*, 4609–4612.

(4) Rao, V. J.; Ramamurthy, V.; Schaumann, E.; Nimmesgern, H. *J. Org. Chem.* **1984**, *49*, 615–621.

(5) (a) Ando, W.; Watanabe, K.; Suzuki, J.; Migita, T. *J. Am. Chem. Soc.* **1974**, *96*, 6766–6768. (b) Gu, C.-L.; Foote, C. S. *Ibid.* **1982**, *104*, 6060–6063.

(6) (a) Cauzzo, G.; Gennari, G.; Re, F. D.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541–544. (b) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717–4721.

(7) (a) Lutz, E.; Biellmann, J.-F. *Tetrahedron Lett.* **1985**, *26*, 2789–2792. (b) Zoller, U. In *Heterocyclic Compounds. Small Ring Heterocycles*. Wiley-Interscience: New York, 1983; Vol. 42, Part 1, pp 403–410.

(8) (a) Manser, G. E.; Mesure, A. D.; Tillett, J. G. *Tetrahedron Lett.* **1968**, 3153–3156. (b) Kondo, K.; Negishi, A.; Tsuchihashi, G.-I. *Ibid.* **1969**, 3173–3174. (c) Kondo, K.; Negishi, A.; Ojima, I. *J. Am. Chem. Soc.* **1971**, *93*, 5786–5793.

(9) For review see ref 7b, pp 499–511.

(10) Thomas, M. J.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683–693.

(11) (a) Hartzell, G. E.; Paige, J. N. *J. Am. Chem. Soc.* **1966**, *88*, 2616–2617. (b) Hartzell, G. E.; Paige, J. N. *J. Org. Chem.* **1967**, *32*, 459–460.

(12) Oae, S.; Kunieda, N. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; p 612.

perature from methylthiirane using MCPBA in CDCl_3 , the initial *cis*-thiirane oxide undergoes ring opening to the sulfenic acid (overall analogy to the ene reaction) at approximately 0°C , while the *trans*-thiirane oxide is stable at temperatures above 60°C .¹³

The major isomer of the disulfide **5a** shows some interesting NMR properties. Since **5a** contains two chiral centers, there are *dl* and *meso* diastereomers. In the ^{13}C NMR, the CH_2 group appears as a "doublet" (chemical shift difference $\Delta\delta = 0.05$ ppm), and the ^1H NMR shows the CH_2 group as two overlapping AB subsystems (AB part of a ABX spin system) ($\Delta\delta = 0.01$ ppm). However, the chiral CH groups have identical ^{13}C chemical shifts within the resolution of the instrument (the ^1H spectrum of the CH group is too complex to analyze). Isomer **5b** shows the same pattern (splitting of the CH_2 but not the CH resonance in the ^{13}C NMR).

Other Thiiranes. 7-Thiabicyclo[4.1.0]heptane (cyclohexene sulfide) and *trans*-2,3-dimethylthiirane give reactions similar to those of 2-methylthiirane. Cyclohexene sulfide in methanol gives two isomers of methyl 2-methoxycyclohexanesulfinate in a ratio of approximately 1:10. The major isomer is assigned the *trans* stereochemistry based on ^1H NMR coupling constants. Analytical GC indicated a second product formed at higher concentration of cyclohexene sulfide, but we were unable to obtain it sufficiently pure for identification. Based on its spectra and the products from thiirane and 2-methylthiirane, it appears to be a mixture of isomeric disulfides. *trans*-2,3-Dimethylthiirane at low concentration gives methyl 2-methoxy-1-methylpropanesulfinate (stereochemistry unknown) as the only product. *trans*-2,3-Diphenylthiirane is inert toward reaction at 0°C and only starting material is observed even after hours of photolysis, whereas the alkyl thiiranes give detectable product in less than 30 s of photolysis under the same conditions.

Trapping Experiments. It is possible to trap one or more intermediates in the photooxygenation of simple sulfides using diphenyl sulfide and diphenyl sulfoxide,¹⁴ which are themselves very unreactive toward singlet oxygen. In the present case, addition of diphenyl sulfide or diphenyl sulfoxide does not have any effect on the oxygenation of the thiiranes, and no diphenyl sulfoxide or diphenyl sulfone is detected. Addition of methyl propiolate (which has been shown in some cases to trap sulfenic acids¹⁵) to a photolyzed solution of 2-methylthiirane in MeOH at -78°C followed by warming to room temperature, or carrying out the reaction in the presence of methyl propiolate, does not have any influence on the products and no new products are detected. Addition of Me_2S immediately after photolysis of a solution of 2-methylthiirane in MeOH at -78°C inhibits the production of disulfides, but no dimethyl sulfoxide or dimethyl sulfone can be detected. GC analysis does not show any new products. Low-temperature NMR shows that the thiirane oxides give only polymeric material upon warming in the presence of Me_2S . Addition of MeOH to a photolyzed solution of 2-methylthiirane in CFCl_3 at -130°C does not give any volatile products.

Discussion

The absence of a sensitizer effect and the inhibition by DABCO of the reactions makes it probable that singlet oxygen is the primary oxygenating species. The structure of the products can be rationalized by assuming that a reactive intermediate with a lifetime less than a few seconds at -130°C is formed from thiiranes and singlet oxygen. This intermediate can be trapped by 2 mol of MeOH to give the methoxy sulfinates, or, at higher concentrations, by starting material to give 2 mol of thiirane oxide.

(13) Baldwin, J. E.; Hofle, G.; Choi, S. C. *J. Am. Chem. Soc.* **1971**, *93*, 2810-2812.

(14) (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795-3796. (b) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *Ibid.* **1981**, *103*, 5949-5951. (c) Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, 4263-4266. (d) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203-1204. (e) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947-5948.

(15) Davis, F. A.; Jenkins, R. H.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467-3474.

Scheme II

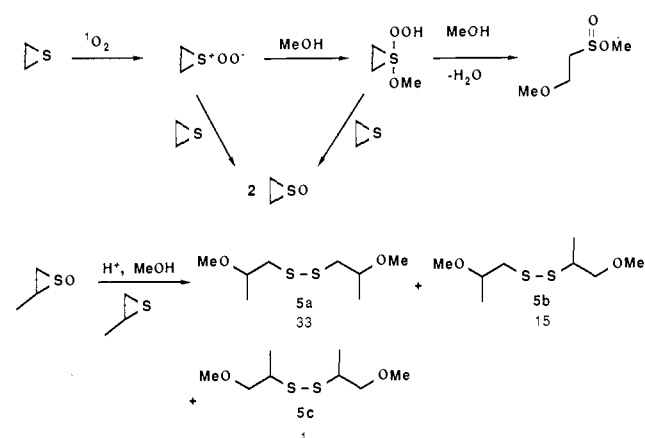


Table I. Rate Constants for Quenching of Singlet Oxygen in Freon 113

compound	$k_q, \text{M}^{-1} \text{s}^{-1}$
<i>trans</i> -diphenylthiirane	$4.3 \pm 0.4 \times 10^3$
<i>trans</i> -diphenyloxirane	$5.0 \pm 0.2 \times 10^3$
2-methylthiirane	$6.6 \pm 0.2 \times 10^4$
diethyl sulfide	$3.2 \pm 0.1 \times 10^6$

A peroxythiirane oxide would be a reasonable structure for an intermediate in this reaction; a possible second intermediate in the reaction with methanol would be a hydroperoxymethoxysulfuran. These intermediates are analogous to those previously proposed.¹⁴

Cyanoanthracenes (9,10-dicyanoanthracene and 9-cyanoanthracene) also act as sensitizers and give the same products in the same ratio. If these sensitizers cause oxygenation via an electron-transfer mechanism, the peroxythiirane oxide could come from the reaction of thiirane radical cation and superoxide radical anion.¹⁶ Products are still observed when β -carotene (which quenches singlet oxygen at a nearly diffusion-controlled rate) is present (10^{-3} M) and the reaction time is kept low (30 s). However, it has been demonstrated that 9,10-dicyanoanthracene generates large amounts of singlet oxygen,^{16c} because there is some destruction of β -carotene under the reaction conditions, we cannot be sure whether the reaction proceeds via singlet oxygen or by electron transfer, and this reaction was not investigated further.

Possible reactions leading to the observed products are shown in Scheme II. As shown by control experiments, acid is required for the reaction of the thiirane oxide with methanol. The nature of the acid in the photolyzed solution is unknown, but either trace amounts of water (reaction analogous to MeOH) or a small amount of opening of the thiirane sulfoxide (in the alkyl thiiranes: this reaction is analogous to the ene reaction¹³) could generate a trace of a sulfenic acid and thus account for the observed acidity. The difference in isolated products between thiirane itself and 2-methylthiirane is probably due to the lower stability of the thiirane oxide in the 2-methyl-substituted case.

The observed inertness of diphenylthiirane could be due to two factors: (1) it is unreactive toward singlet oxygen, or (2) the initially formed peroxythiirane oxide is so sterically hindered that attack of MeOH is slow and unimolecular decomposition to starting material and ground state oxygen is much faster than intermolecular trapping by starting material. To address this question we determined the total removal rate of singlet oxygen (i.e., reaction plus quenching) by *trans*-diphenylthiirane, *trans*-diphenyloxirane (diphenylstilbene oxide), 2-methylthiirane, and diethyl sulfide. The quenching rates were determined by observing the time-resolved phosphorescence of singlet oxygen at $1.27 \mu\text{m}$ in the presence of different concentrations of quencher.¹⁷ The

(16) (a) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455-6466. (b) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083-6088. (c) Manning, L. E.; Kramer, M. K.; Foote, C. S. *Tetrahedron Lett.* **1984**, *25*, 2523-2526. (d) Manning, L. E.; Gu, C.-L.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 40-44. (e) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221 (1985).

singlet oxygen was generated by excitation of dinaphthalene-thiophene with a short laser pulse (7 ns) at 355 nm using Freon 113 (1,1,2-trichlorotrifluoroethane) as solvent. The results are given in Table I. The quenching rate for diethyl sulfide is in good agreement with that obtained with Young's method in MeOH ($6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).¹⁸

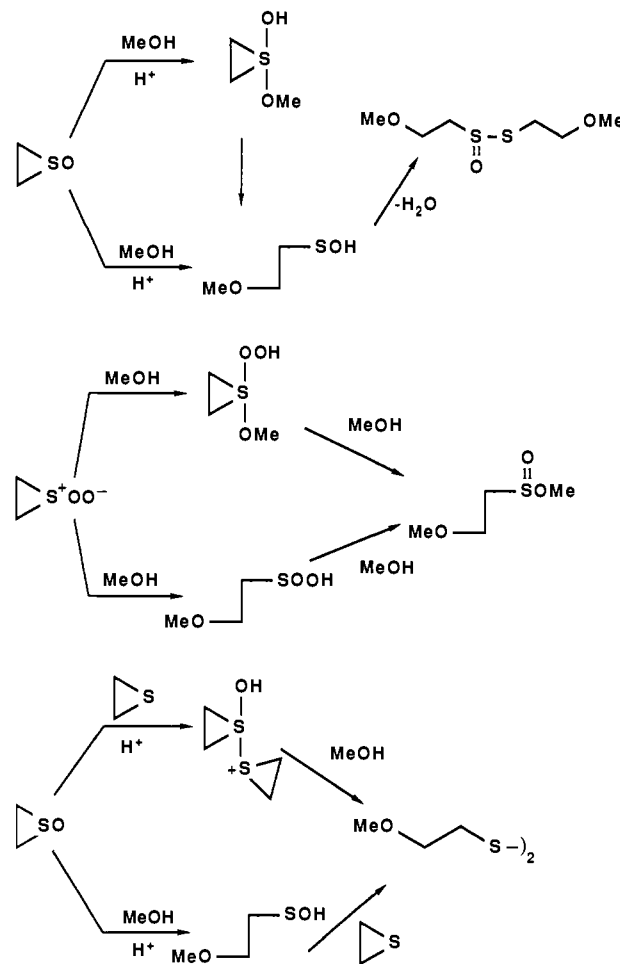
The quenching rate for 2-methylthiirane is slower by approximately a factor of 50 than for diethyl sulfide. Diphenylthiirane quenches singlet oxygen approximately a factor of 10 slower than 2-methylthiirane, but at the same rate as diphenylstilbene oxide; i.e., the sulfur atom is completely unreactive toward singlet oxygen. Since inspection of molecular models of *trans*-diphenylthiirane compared to *trans*-dimethylthiirane does not reveal any steric "shielding" of the sulfur atom, the inertness must be due to an electronic effect. Singlet oxygen is known to react as an electrophilic reagent,¹⁹ and we would expect that electron-rich thiiranes would react faster with singlet oxygen than electron-poor ones. It is well-known that phenyl groups are less electron-donating than alkyl groups (e.g., Hammett σ values for phenyl and methyl are -0.01 and -0.17 , respectively²⁰). We assign the low reactivity of diphenylthiirane to a lower electron density on the sulfur atom caused by the inductive effect of the phenyl groups. The lower reactivity of 2-methylthiirane vs. diethyl sulfide could be due to some delocalization of the sulfur lone pairs into the ring or to an increase in electronegativity of the sulfur because of the small ring. However, although thiiranes are less reactive than sulfides toward singlet oxygen, they are apparently better scavengers for the intermediate, since external scavengers such as diphenyl sulfide or sulfoxide do not compete effectively with the thiiranes, in contrast to the situation with simple sulfides.

It is known that thiirane oxides undergo nucleophilic ring opening in the presence of a strong acid.⁸ In the case where the nucleophile is MeOH, the product is a methoxy thiosulfinate.^{8b,c} Ethanethiol reacts similarly to MeOH and gives 2,2'-bis(ethylthiodiethyl)disulfide as product.^{8c} The products are generally believed to arise from dehydration of a sulfenic acid, which is assumed to be the primary product from the ring opening. The exact mechanism for the ring opening has not been established.

Formally, one can draw two reaction mechanisms leading from a protonated thiirane oxide to a sulfenic acid as shown in Scheme III. One involves backside attack by MeOH to form the sulfenic acid directly, whereas the other assumes the initial formation of a sulfurane followed by ring opening and elimination of MeOH. The formation of disulfides when thiirane is present can be rationalized similarly. Assuming that the peroxythiirane oxide is the primary intermediate in the sulfenic ester formation, the question is again whether the nucleophile attacks first on carbon or on sulfur. Attack on sulfur would lead to sulfuranes similar to those isolated by Martin et al.²¹ and Schomburg et al.,²¹ as shown in Scheme III.

The curious effect of Me₂S on the formation of the disulfide from the acid-catalyzed reaction of thiirane oxide with thiirane might offer a clue to whether a sulfurane is an intermediate. It is possible that the formation of disulfides is inhibited because

Scheme III

Table II. SCF Energies^a for Structures Shown in Figure 1

structure	HF/3-21G(*)	ϵ_{LUMO}	ϵ_{HOMO}
¹ O ₂ (¹ Δ_g)	-148.71220	0.04889	-0.50159
H ₂ O	-75.58596	0.26107	-0.47723
(CH ₂) ₂ S	-473.26795	0.16359	-0.34638
(CH ₂) ₂ SO	-547.65011	0.17864	-0.36862
(CH ₂) ₂ SH ⁺ O (8)	-547.91077		
(CH ₂) ₂ SOH ⁺ (9)	-548.00774	-0.07518	-0.65192
		-0.07116 ^b	
(CH ₂) ₂ S ⁺ OO ⁻	-621.96509	0.13663	-0.37016
(CH ₂) ₂ S(OH) ₂	-623.20043	0.15331	-0.33798
(CH ₂) ₂ S(OOH)OH	-697.55618	0.12982	-0.36467

^aEnergies in hartrees: 1 hartree = 627.71 kcal/mol. ^bSLUMO.

Me₂S coordinates to the peroxythiirane oxide more effectively than the thiirane and that the resulting sulfurane cannot undergo ring opening at the ligand, with the consequence that other reactions are favored. On the other hand, the Me₂S might simply react with the sulfenic acid and inhibit the formation of disulfides that way. Unfortunately, not much is known about the chemistry of sulfenic acids, and the difficulty in generating and handling them makes this suggestion hard to test.

Theoretical Calculations

Since it is very difficult to devise experiments that would distinguish between the two reaction modes, we hoped that a combination of Frontier Molecular Orbital theory and ab initio calculations could offer a clue to the reaction mechanism. Several structural calculations have been reported for thiirane itself,²² and a comparison between thiirane, thiirane oxide, and thiirane dioxide has been made using a medium-sized basis set.²³ However, for

(17) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423-3430.
 (18) See, e.g.; Gollnick, K. In *Singlet Oxygen Reaction with Organic Compounds and Polymers*; Rånby, B.; Rabek, J. F., Eds.; Wiley: New York, 1978; pp 111-134.

(19) See, e.g., ref 17.

(20) Hansch, C.; Leo, A. J. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley-Interscience: New York, 1979; p 3.

(21) For a review of sulfurane chemistry see: Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry*; Bernardi, F.; Csizmadia, I. G.; Mangini, A., Eds.; Elsevier: New York, 1985; pp 408-483. (a) Hodges, K. C.; Schomburg, D.; Weiss, J.-V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096-6097. (b) Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, *101*, 1155-1159. (c) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *Ibid.* **1972**, *94*, 5010-5017. (d) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *Ibid.* **1971**, *93*, 6674-6775. (e) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *Ibid.* **1974**, *96*, 6735-6744. (f) Schomburg, D.; Mir, Q.-C.; Shreeve, J. *Ibid.* **1981**, *103*, 406-409. (g) Mir, Q.-C.; Laurence, K. A.; Shreeve, R. W.; Babb, D. P.; Shreeve, J. M. *Ibid.* **1979**, *101*, 5949-5953. (h) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001-4005. (i) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127-135. (j) Kalman, A.; Sasvari, K.; Kapovits, I. *Acta Crystallogr., Sect. B. Found. Crystallogr.* **1973**, *29*, 355-357.

(22) Absar, I.; Lawrence, J. S.; Wazer, J. R. V. *Theor. Chim. Acta* **1973**, *29*, 173-181 and references cited therein.

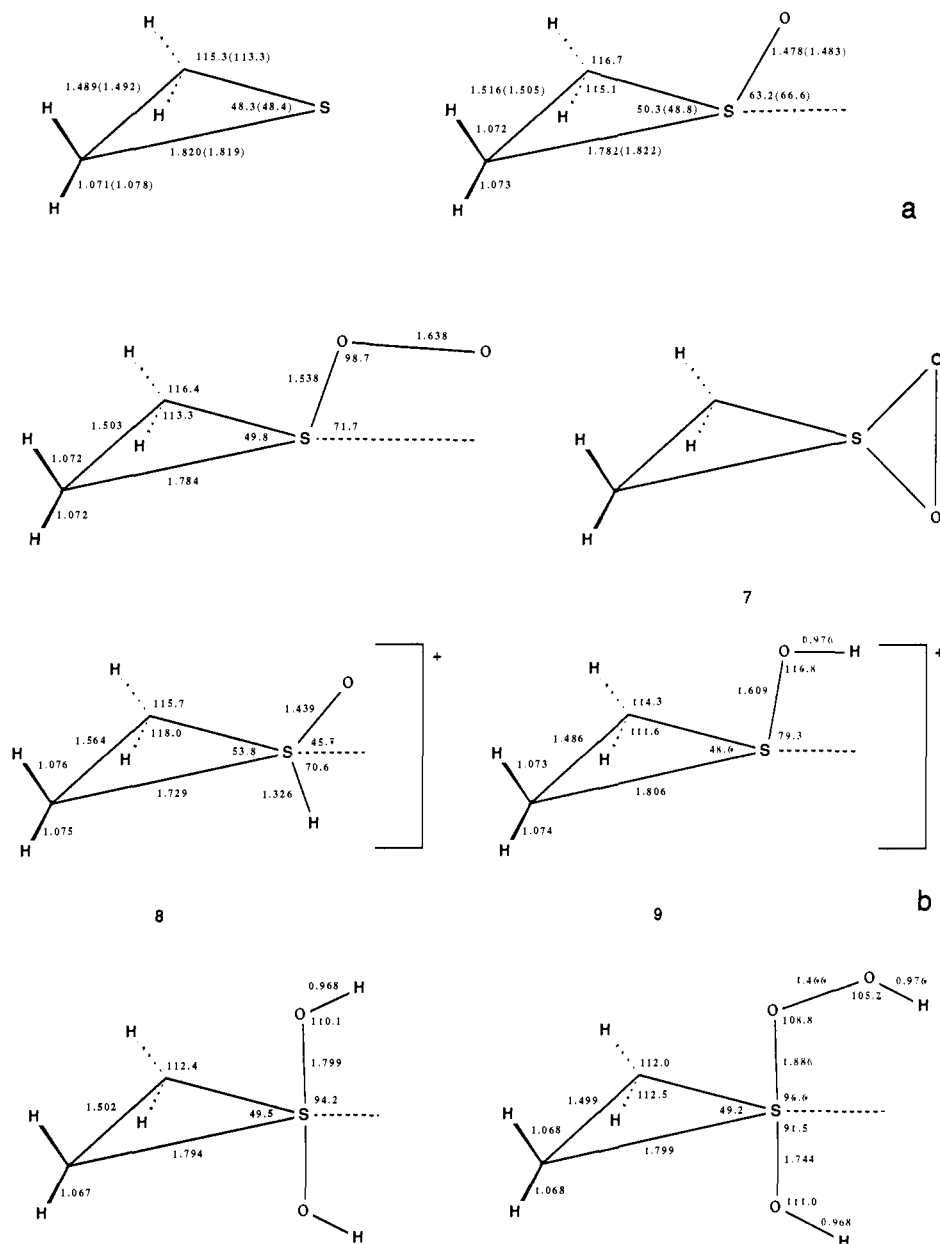


Figure 1.

consistency, we recalculated the structures of thiirane and thiirane oxide using a 3-21G(*) basis set (d orbitals on second-row elements only).²⁴ This basis set has been shown to give geometries in good agreement with experimental data, and the calculated structures are close to those obtained with larger basis sets. The inclusion of d orbitals on second-row elements is essential for "hypervalent" molecules.²⁴ The structures and relative energies of thiirane, thiirane oxide, protonated thiirane oxide, peroxythiirane oxide, dihydroxysulfurane, and hydroxyhydroperoxysulfurane were calculated at the Hartree-Fock level of theory using standard gradient techniques and the same basis set.

The structures of the calculated species are shown in Figure 1 (experimental values²⁵ in parentheses), and the energies are in Table II. An alternative cyclic structure for the peroxythiirane oxide was not considered as a stable intermediate, since in a similar case (H_2SO_2), a frequency calculation on the C_{2v} -symmetric op-

timized structure (HF/3-21G(*) corresponding to 7 has three imaginary frequencies,²⁶ indicating a maximum on the potential energy surface.

Olah and Szilagyí have reported²⁷ that thiirane oxide is actually protonated on sulfur instead of oxygen. Their assignment is based on the ^1H NMR spectrum in superacid media at low temperature. However, we optimized the two corresponding structures and found that the S-protonated thiirane oxide 8 is 60.9 kcal/mol less stable than the O-protonated thiirane oxide 9, in agreement with a priori expectations. That the somewhat unusual structure corresponding to the S-protonated thiirane oxide 8 indeed is a true minimum on the potential energy surface was proven by the fact that all the calculated frequencies for the optimized structure are real (e.g., no imaginary frequencies). The lowest frequency was calculated to be 348 cm^{-1} , ruling out a van der Waals type complex.

The calculated structures agree well with the experimentally determined values, where available. It should be noted that in the experimental determination of the thiirane oxide structure^{25b} the CH distances and angles were assumed to be the same as in thiirane. The relative energies at this level of theory should not

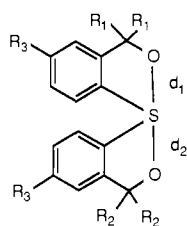
(23) Rohmer, M.-M.; Roos, B. O. *J. Am. Chem. Soc.* **1975**, *97*, 2025-2029.

(24) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048.

(25) (a) Cunningham, G. L., Jr.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; Le Van, W. I. *J. Chem. Phys.* **1951**, *19*, 676-685. (b) Saito, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 663-666.

(26) Jensen, F.; Foote, C. S., in progress.

(27) Olah, G. A.; Szilagyí, P. J. *J. Org. Chem.* **1971**, *36*, 1121-1126.



6

Figure 2.

be considered as quantitative but rather as guidelines. Unfortunately, the size of the system makes it prohibitively expensive to carry out the calculation at a higher level.

In order to reduce computational expenses we considered only structures with at least C_s symmetry. For the peroxythiirane oxide, several conformations of the outer oxygen relative to the CH_2 groups are possible. We have assumed them to be of the same energy (free rotations around the S–O bond) and optimized the structure for an anti- C_s symmetry (outer oxygen anti to the CH_2 groups). The dihydroxy- and hydroxyhydroperoxysulfuranes were assumed to have C_{2v} and C_s symmetry, with the oxygen ligands occupying the axial positions. There are several similar compounds reported in the literature for which X-ray crystal structures are available,²¹ and they all show that oxygen ligands prefer to occupy the axial positions (see also Figure 2).

It is possible that the C_s symmetries assumed for the above compounds do not represent true minima, in which case the calculated energies are an upper limit (at the HF/3-21G(*) level). It is very likely that the true minima for the peroxythiirane oxide and dihydroxy- and hydroxyhydroperoxysulfuranes will have the OH hydrogens and possibly also the peroxy oxygen out of the plane of symmetry. Since these S–O rotations will have very low barriers (model calculations on the peroxysulfoxide from $\text{H}_2\text{S} + {}^1\text{O}_2$ at the RHF/3-21G(*) give a rotational barrier of 4 kcal/mol), the energies of the C_s structures should not be more than a few kcal/mol above the true minima. The HOMO and LUMO are mainly located on the carbons and sulfur and they should not be significantly affected by breaking the symmetry.

One striking feature in the calculated structure of peroxythiirane oxide is the very long O–O bond (1.638 Å). Calculations on the carbon analogue of this peroxysulfoxide, carbonyl oxide, at different levels have shown that the O–O bond length is very sensitive to the level of theory used (i.e., 1.634 Å at HF/3-21G and 1.275 Å at CAS SCF/DZ + P).²⁸ We have some indication that this may also be true in this case. For a smaller system, H_2SO_2 , the O–O bond distance for the peroxysulfoxide changes from 1.615 Å at the HF/3-21G(*) level to 1.471 Å at the MP2/6-31G* level.²⁶ The S–O bond distance changes from 1.531 to 1.571 Å. However, the potential surface for the O–O bond strength in the carbonyl oxide is very flat, and consequently the energy does not vary much with O–O distance. The energy change for a 0.18-Å elongation of the O–O bond for formaldehyde oxide (from the equilibrium distance of 1.313 to 1.489 Å) has been reported to be only 0.24 kcal/mol (with a CAS SCF + PT CI/DZ + P wave function).²⁹

The hydroxyhydroperoxysulfurane has a very normal hydroperoxy O–O bond length of 1.466 Å (H_2O_2 has a O–O bond length of 1.473 Å at the same level). The S–O bond lengths for the sulfuranes (1.799 Å for the dihydroxy and 1.886 and 1.744 Å for the hydroxy hydroperoxy) are much longer than those found in sulfoxides or sulfones, but are very close to those found by X-ray crystallography in related compounds, some of which are shown in Figure 2. As for the O–O bond in the peroxythiirane oxide, it is likely that these S–O bonds will have a very flat potential energy surface for bond stretching as with the carbonyl oxides,³⁰

(28) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205 and references cited therein. (b) Karlstrom, G.; Engstrom, S.; Johnson, B. *Chem. Phys. Lett.* **1979**, *67*, 343–347.

(29) Karlstrom, G.; Roos, B. O. *Chem. Phys. Lett.* **1981**, *79*, 416–420.

	R ₁	R ₂	R ₃	d ₁	d ₂	< OSO	Ref.
a :	CH ₃	CH ₃	H	1.787(2)	1.814(2)	181.8(1)	20i
b :	CH ₃	CF ₃	H	1.713(2)	1.955(2)	182.7	20h
c :	CF ₃	CF ₃	t-butyl	1.819(5)	1.832(5)	182.9(2)	20e

Table III. Reaction Energies Calculated at HF/3-21G(*)

reaction	ΔE (kcal/mol)
(CH ₂) ₂ S + ¹ O ₂ → (CH ₂) ₂ S ⁺ OO ⁻	9.5
2(CH ₂) ₂ S + ¹ O ₂ → 2(CH ₂) ₂ SO	-32.7
(CH ₂) ₂ SO + H ₂ O → (CH ₂) ₂ S(OH) ₂	22.4
(CH ₂) ₂ S ⁺ OO ⁻ + H ₂ O → (CH ₂) ₂ S(OOH)OH	-3.2

Table IV. Net Charges^a for Structures Shown in Figure 1

structure	q _s	q _c	q _{H(C)}	q _{O(S)}	q _{O(O)}	q _{O(S)}
H ₂ O				-0.74		
(CH ₂) ₂ S	0.10	-0.57	0.26			
(CH ₂) ₂ SO	0.98	-0.70	0.27	-0.67		
(CH ₂) ₂ SH ⁺ O (8)	1.07	-0.68	0.37	-0.42		
(CH ₂) ₂ SOH ⁺ (9)	1.00	-0.62	0.36	-0.69		
(CH ₂) ₂ S ⁺ OO ⁻	1.06	-0.68	0.30	-0.59	-0.30	
(CH ₂) ₂ S(OH) ₂	0.91	-0.56	0.30	-0.83		
(CH ₂) ₂ S(OOH)OH	0.90	-0.57	0.31	-0.50	-0.43	-0.81

^a Mulliken population analysis.

Table V. HOMO Coefficients for Structures Shown in Figure 1

structure	C _s	C _c	C _{H(C)}	C _{O(S)}	C _{O(O)}	C _{O(S)}
H ₂ O				1.00		
(CH ₂) ₂ S	0.93	0.01	0.01			
(CH ₂) ₂ SO	0.26	0.14	0.00	0.46		
(CH ₂) ₂ SOH ⁺	0.37	0.14	0.02	0.30		
(CH ₂) ₂ S ⁺ OO ⁻	0.03	0.02	0.00	0.24	0.68	
(CH ₂) ₂ S(OH) ₂	0.27	0.00	0.00	0.36		
(CH ₂) ₂ S(OOH)OH	0.22	0.00	0.00	0.47	0.03	0.26

making the calculated S–O distances dependent on the level of theory used. Indeed, it is gratifying to see how well this small basis set performs. The large difference in calculated S–O bond distances for the hydroxy hydroperoxy sulfurane is what would be expected based on the X-ray structures of the symmetrical (6a, 6c) and unsymmetrical (6b) sulfuranes shown in Figure 2.

Although this level of theory cannot be expected to give quantitative results for relative energies, it is instructive to take a look at calculated energies of reactions (Table III). (In the following, H₂O serves as a model for MeOH.) The formation of the peroxythiirane oxide from thiirane and singlet oxygen is predicted to be a few kcal/mol endothermic. The overall reaction of singlet oxygen with 2 mol of thiirane to give 2 mol of thiirane oxide is 32.7 kcal exothermic. The addition of H₂O to the peroxythiirane oxide to give the hydroxyhydroperoxysulfurane is calculated to be slightly exothermic, while the addition of H₂O to the thiirane oxide is found to be 22 kcal/mol endothermic.

The polyelectronic perturbation approach to chemical reactivity, as developed by Klopman and Salem,³¹ should be well-suited for the present problem. We wish to determine whether nucleophilic attack on protonated thiirane oxide and peroxythiirane oxide occurs on sulfur or carbon (Scheme III). The perturbation ap-

(30) An indication of the weak S–O bond can be found in the X-ray structure of compound 6a. Although formally of C_2 symmetry, the X-ray structures show significant difference in the two S–O bond distances probably due to crystal packing forces. See also ref 21c and 21d for a similar case.

(31) (a) Klopman, G.; Hudson, R. F. *Theor. Chim. Acta* **1967**, *8*, 165–174. (b) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234. (c) Salem, L. *Ibid.* **1969**, *91*, 543–552. (d) Salem, L. *Ibid.* **1969**, *91*, 552–566.

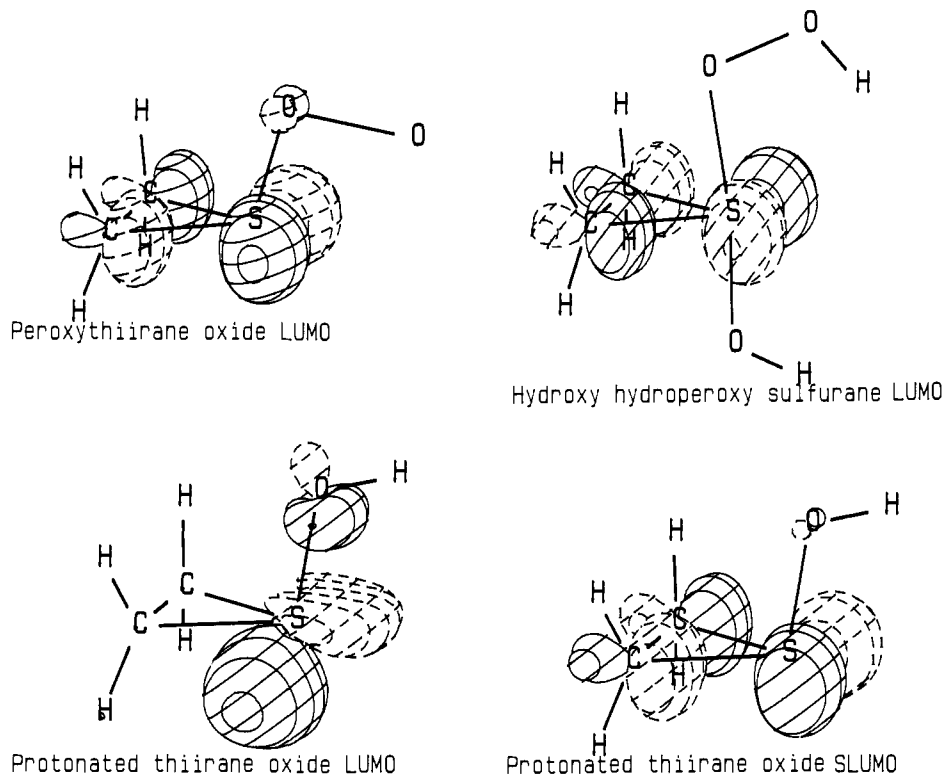


Figure 3.

Table VI. LUMO Coefficients for Structures Shown in Figure 1

structure	C^2_S	C^2_C	$C^2_{H(C)}$	$C^2_{O(S)}$	$C^2_{O(O)}$	$C^2_{O(S)}$
H ₂ O				0.08		
(CH ₂) ₂ S	0.51	0.23	0.01			
(CH ₂) ₂ SO	0.53	0.18	0.01	0.09		
(CH ₂) ₂ SOH ⁺	0.73	0.02	0.01	0.12		
	0.44 ^a	0.26 ^a	0.01 ^a	0.02 ^a		
(CH ₂) ₂ S ⁺ OO ⁻	0.52	0.20	0.01	0.05	0.00	
(CH ₂) ₂ S(OH) ₂	0.48	0.24	0.00	0.02		
(CH ₂) ₂ S(OOH)OH	0.47	0.25	0.00	0.01	0.00	0.01

^aSLUMO.

proach uses the stabilization during the first part of the reaction as a measure of the favored reaction mode (an initial state approach). According to theory, there are two parameters that play an important role.³² One is the repulsion (or attraction) between net charges on the atom in the molecule, the other the mixing of orbitals. Since only orbitals close in energy cause a large interaction, we will only consider the frontier molecular orbitals (HOMO-LUMO).

The net charges and the HOMO-LUMO coefficients for the 3-21G(*) wave functions are given in Tables IV-VI. For the protonated thiirane oxide, there are two nearly degenerate LUMO's (orbital energy difference = 4 mhartrees) and both are listed. Orbital pictures of the LUMO's for protonated thiirane oxide, peroxythiirane oxide, and hydroxyhydroperoxysulfurane are shown in Figure 3.

Let us first examine the reaction of peroxythiirane oxide with H₂O. As mentioned above, the calculations show that the formation of the H₂O adduct (hydroxyhydroperoxysulfurane) is probably energetically accessible. The sulfur atom in the peroxythiirane oxide has a net charge of 1.06 while the carbons have a net charge of -0.68. Furthermore, the LUMO is mainly located on the sulfur, with only 20% on the carbons. This makes it likely that an incoming nucleophile will attack at the sulfur atom to form a sulfurane. The second step should then be attack on the carbon of the sulfurane. Relative to the peroxythiirane oxide, the sulfurane has less charge on the carbons, lower LUMO energy, and

higher LUMO coefficient on the carbons, making nucleophilic attack easier.

Let us now turn to the ring opening of protonated thiirane oxide. The calculations show that addition of H₂O and elimination of H⁺ from the protonated thiirane oxide (which is the same as addition of H₂O to thiirane oxide) should be highly endothermic, as expected. However, it is very likely that a protonated thiirane oxide will be solvent-coordinated. Inspection of the atomic net charges and the LUMO of protonated thiirane oxide shows that coordination of a nucleophile should occur at the sulfur. We tried to optimize (HF/3-21G*) the structure of the protonated thiirane oxide with one molecule of H₂O coordinated to the axial position of sulfur, e.g., protonated dihydroxysulfurane **10**, but within the constrained C_s symmetry used, the optimization showed the structure to be a separated protonated thiirane oxide and H₂O. It is possible that relaxation of the symmetry could lead to a stable adduct, but calculation without symmetry with this large a molecule is very time-consuming.

Conclusion

We have investigated the reaction of singlet oxygen with thiiranes. The primary products in alcoholic solvents are thiirane oxides and sulfinic esters. In aprotic solvents, they are thiirane oxides. These products can be rationalized by assuming that a reactive intermediate, a peroxythiirane oxide, is formed from singlet oxygen and thiirane. This intermediate can undergo trapping by the thiirane itself or by nucleophilic solvents. The structure of the peroxythiirane oxide has been investigated by ab initio calculations. Based on frontier molecular orbital theory and ab initio calculations, it is suggested that the formation of the observed sulfinic esters might go through a hydroperoxymethoxysulfurane. It is possible that the acid-catalyzed ring opening of thiirane oxide occurs via a similar mechanism.

After this paper was submitted, Ando et al. reported the photooxidation of biadamantylidene thiirane.⁴⁰ Their results are similar to ours although they propose a mechanism that differs slightly from the one proposed in this paper.

Experimental Section

Thiirane (ethylene sulfide), 2-methylthiirane (propylene sulfide), and 7-thiabicyclo[4.1.0]heptane (cyclohexene sulfide) were obtained from Aldrich. Thiirane and 2-methylthiirane were used as received. Cyclo-

(32) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976; pp 27-32.

hexene sulfide as delivered contains approximately 5% cyclohexene and 10% cyclohexene oxide. It can be purified to approximately 97% by evaporating half the solution at room temperature with a stream of nitrogen. However, there was no difference in reactivity between the purified and unpurified materials. *trans*-Dimethylthiirane was a gift from Michael Orfanopoulos, UCLA. *trans*-Diphenylthiirane was synthesized by the method of Ketcham and Shah.³³ Rose bengal, methylene blue, tetraphenylporphine, mesoporphyrin IX dimethyl ester, 9,10-dicyanoanthracene, and 9-cyanoanthracene were obtained from Aldrich. DCA and CNA were recrystallized from toluene; the other sensitizers were used as received.

The photolysis was carried out in Pyrex test tubes inside a temperature-controlled cell described previously¹⁷ with a Varian-Eimac 300W xenon-mercury lamp as the light source. No difference in products or reaction rate was noticed if a Corning 3-70 glass filter (cutoff 500 nm) was placed in front of the light source.

Analytical gas chromatography was done using a Hewlett-Packard Model 5800 equipped with a 25-m 50% phenyl-50% methyl-silicone capillary column and FID detector. Preparative GLC was done on a Aerograph A 90-P3 using a 6 × 1/4 in. column packed with 20% UCON WS on Chromosorb W. IR was done on a Perkin-Elmer instrument Model 137, and mass spectra on a Kratos MS 902 instrument. ¹H and ¹³C NMR data were obtained on a Bruker WP-200 operating at 200 MHz for ¹H and 50 MHz for ¹³C. Deuterated chloroform was used as the solvent unless otherwise specified. Chemical shift values are reported in δ (ppm) relative to internal tetramethylsilane standard. The number of hydrogens directly bonded to carbons were assigned with a DND experiment.³⁴

Quenching rates were determined as follows. A 1.5-mL solution of Freon 113 (1,1,2-trichlorotrifluoroethane) containing 1×10^{-4} M diphthalenethiophene and a known concentration of the quencher was excited with a 7-ns pulse at 355 nm using a frequency tripled Nd-YAG laser. The phosphorescence of singlet oxygen was detected at 1.27 μ m using a germanium diode and digitized on a DATA-6000 (Data Precision Corp.). An average of 512 pulses was taken for each point. The decay rate of singlet oxygen (k_{obsd}) was calculated with the method of Guggenheim³⁵ and obeyed first-order kinetics in all cases. All points were done in triplicate and quenching rates were calculated from a plot of k_{obsd} vs. quencher concentration. For *trans*-diphenylthiirane and *trans*-diphenyloxirane, three different concentrations were used, while five different concentrations were used for diethyl sulfide and 2-methylthiirane.

Theoretical calculations were carried out on DEC VAX 11/780 and VAX 11/750 computers using the GAUSSIAN 80³⁶ and GAUSSIAN 82³⁷ program systems. Wave functions were calculated within the SCF MO-LCAO framework using Roothaan's equations.³⁸ The structures were optimized using standard gradient techniques with a 3-21G(*) basis set.²⁴ Net atomic charges were calculated via the Mulliken population analysis.³⁹ Orbital coefficients as given in Tables V and VI were calculated by normalizing the MO's from the ab initio wave function as follows. The j th MO, φ_j , can be written as $\varphi_j = \sum a_{ij} \chi_i$, where χ_i are the AO's and the sum is over $i = 1, N$, where N is the number of AO's. The contribution C_{kj}^2 to the j th MO from the k th AO can be written as $C_{kj}^2 = a_{kj} \sum a_{ik} S_{ik}$, where S_{ik} is the overlap integral between the k th and i th AO, and the sum again over i . The C_{kj}^2 coefficient calculated by this procedure is equivalent to a Mulliken population of one electron in the j th MO.

(33) Ketcham, R.; Shah, V. P. *J. Org. Chem.* **1963**, *28*, 229-230.

(34) Anet, F. A. L.; Jaffer, N.; Strouse, J. 21st Experimental NMR Conference, Poster Session, Tallahassee, Fla., 1980.

(35) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley-Interscience: New York, 1981; pp 70-72. The authors thank Richard C. Kanner, UCLA, for writing the computer program.

(36) Singh, U. C.; Kollman, p.; Binkley, J. S.; Whiteside, R. A.; Krishan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80 (UCSF), Quantum Chemistry Program Exchange (Program 446), Indiana University, Bloomington, IN.

(37) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82 Carnegie-Mellon University, Pittsburgh, PA.

(38) Roothaan, C. C. *J. Rev. Mod. Phys.* **1951**, *23*, 69-89.

(39) Mulliken, R. S. *J. Chem. Phys.* **1955**, *22*, 1833-1840; **1955**, *22*, 1841-1846; **1955**, *22*, 2338-2342; **1955**, *22*, 2343-2346.

(40) Ando, W.; Sonebe, H.; Akasaka, T. *Tetrahedron Lett.* **1986**, *27*, 4473-4476.

Photolysis. General Procedures. A 0.1 M solution of the thiirane in MeOH containing methylene blue as sensitizer was photolyzed to approximately 50% conversion at -78 °C. The solvent was removed under reduced pressure and the resulting oil was subjected to preparative GLC at 160 °C. All products were isolated as slightly yellow oils.

Thiirane. Thiirane oxide is not stable under preparative GC conditions, and only methyl 2-methoxyethanesulfinate (**2**) could be isolated together with a small amount of 2-methoxyethane disulfide. Methyl 2-methoxyethanesulfinate had ¹H NMR 3.77 (s, 3 H), 3.72 (m, 2 H), 3.35 (s, 3 H), 2.95 (m, 2 H). 2-Methoxyethane disulfide had ¹H NMR 3.63 (t, $J = 7$ Hz, 2 H), 3.36 (s, 3 H), 2.87 (t, $J = 7$ Hz, 2 H). Thiirane oxide was identified in the crude reaction mixture by comparison of ¹H NMR and GC retention time with that of an authentic sample prepared according to Hartzell and Paige.¹¹ The ¹H NMR showed an AA'BB' spin system centered at 2.21 ppm.

2-Methylthiirane. The first fraction from preparative GLC was shown by analytical GC to consist of two compounds in a ratio of 3:1. The major isomer was methyl 2-methoxypropanesulfinate (**4a**): ¹H NMR 3.73 (s, 3 H), 3.7 (m, ¹H), 3.27 (s, 3 H), 2.9 (m, 2 H), 1.20 (d, $J = 6$ Hz, 3 H); ¹³C NMR 71.7, 64.3, 56.3, 54.5, 19.2. The minor isomer (**4b**) was methyl 2-methoxy-1-methylethanesulfinate: ¹H NMR 3.71 (s, 3 H), 3.28 (s, 3 H), 1.19 (d, $J = 6$ Hz, 3 H). Other resonances were obscured by those of the major isomer: ¹³C NMR 71.4, 64.0, 56.4, 54.8, 18.6; IR (of isomeric mixture, neat) 1130, 1085, 999 cm^{-1} . HRMS (of isomeric mixture): exact mass calculated for $\text{C}_5\text{H}_{12}\text{SO}_3$, 152.0518; found, 152.0507. The second fraction was shown to consist of three components in approximate ratios 33:15:1 by analytical GC. The major component was 2,7-dimethoxy-4,5-dithiaoctane (**5a**): ¹H NMR 3.5 (m, 1 H), 3.32 (s, 3 H), 2.80 (AB of ABX system, 2 H), 1.20 (d, $J = 6$ Hz, 3 H, X of ABX). Diastereomer one (dl or meso): AB part of ABX system, 2.791 ppm, $\Delta\delta = 0.182$ ppm; $J_{AB} = 13.39$ Hz, $J_{AX} = J_{BX} = 6.15$ Hz. Diastereomer two: 2.801 ppm, $\Delta\delta = 0.178$ ppm; $J_{AB} = 13.41$ Hz, $J_{AX} = J_{BX} = 5.86$ Hz; ¹³C NMR 75.8 (CH), 56.3 (CH₃), 45.6 (CH₂), 18.6 (CH₃). Diastereomer one: 45.63 (CH₂). Diastereomer two: 45.58 (CH₂). The second major isomer was 2-methyl-1,6-dimethoxy-3,4-dithiaheptane (**5b**): ¹H NMR 1.27 (d, $J = 7$ Hz). Other resonances were obscured by the major component: ¹³C NMR 75.9 (CH), 58.8 (CH₃), 46.6 (CH₂), 17.4 (CH₃). Additional peaks are assumed buried under the resonances from the major component. The CH₂ consists of two resonances at 46.65 and 46.54; IR (of isomeric mixture) (neat) 1125, 1085 cm^{-1} ; UV (of isomeric mixture) (ether) 249 and 217 nm. HRMS (of isomeric mixture): exact mass calculated for $\text{C}_8\text{H}_{18}\text{S}_2\text{O}_2$, 210.0774; found, 210.0745. Because of the amount of the minor isomer it was not possible to obtain any spectral data, but the analytical GC trace had a retention time very close to that of the major isomers.

***trans*-2,3-Dimethylthiirane.** Photolysis was run at a concentration of 0.02 M. The only product detected was methyl 2-methoxy-1-methylpropanesulfinate (stereochemistry unknown): ¹H NMR 3.92 (d, q, $J_1 = 6$ Hz, $J_2 = 3$ Hz, 1 H), 3.78 (s, 3 H), 3.31 (s, 3 H), 2.53 (d, q, $J_1 = 7$ Hz, $J_2 = 3$ Hz, 1 H), 1.21 (d, $J = 7$ Hz, 3 H), 1.18 (d, $J = 6$ Hz, 3 H).

7-Thiabicyclo[4.1.0]heptane. Photolysis was run at a concentration of 0.1 M. The fraction isolated by preparative GC was shown to consist of two isomers in a 10:1 ratio by analytical GC. The major isomer was methyl *trans*-2-methoxycyclohexanesulfinate: ¹H NMR 3.80 (s, 3 H), 3.33 (s, 3 H), 3.32 (m, 1 H), 2.6 (d, d, $J_1 = 11$ Hz, $J_2 = 10$ Hz, $J_3 = 4$ Hz, 1 H), 2.2 (m, 2 H), 1.8 (m, 2 H), 1.2-1.5 (m, 4 H); ¹³C NMR 78.5 (CH), 68.8 (CH), 56.1 (CH₃), 55.6 (CH₃), 30.4 (CH₂), 24.5 (CH₂), 23.5 (CH₂), 19.0 (CH₂). The minor isomer was methyl *cis*-2-methoxycyclohexanesulfinate: ¹H NMR 3.78 (s, 3 H), 3.36 (s, 3 H), other resonances obscured by major isomer; ¹³C NMR 77.8 (CH), 68.0 (CH), 56.3 (CH₃), 55.7 (CH₃), 32.0 (CH₂), 24.2 (CH₂), 24.1 (CH₂), 18.7 (CH₂); IR of neat isomeric mixture 1190, 1130, 1115, 1095, 995 cm^{-1} .

***trans*-Diphenylthiirane** was photolyzed in a 1:1 mixture of MeOH and acetone at 0 °C. After 3 h of photolysis, only starting material was observed by NMR and TLC.

Acknowledgment. This work was supported by NSF Grant No. CHE-83-11804. F. J. thanks UCLA for a Graduate Division Research grant supporting some of the computational work. C. S. F. thanks the Alexander von Humboldtstiftung for a Senior Scientist Award, and the Hahn-Meitner Institut, Berlin, for hospitality.