J. Am. Chem. Soc. 1992, 114, 3021–3027

3.65–3.69 (br m, 1 H); ^{13}C NMR (δ, ppm, $CDCl_3$) 29.80 ($CH_2CH_2CH_2$), 38.18 (SCH_2), 63.36 ($S(O)CH_2$); IR (NaCl, cm^{-1}) 2950, 1440, 1260, 1070 [lit.[50] ^{13}C NMR δ 29.98, 38.28, 63.65; IR (CCl_4) ν (SO)= 1090, 1070 cm^{-1}].

Preparation of 1,2-Dithiolane 1,1-Dioxide. Hydrogen peroxide (0.9 mL, 30%, 8 mmol) in 3 mL of acetic acid was added dropwise to the 1,2-dithiolane 1-oxide (1.0 g, 8 mmol) in 100 mL of acetic acid. After the reaction was stirred at room temperature for 24 h, the solvent was removed under reduced pressure. The residue was first washed with hexane and then extracted with three portions of 5 mL of ether. Evaporation left 0.43 g of 1,2-dithiolane 1,1-dioxide: mp 24–26 °C; ^1H NMR (δ, ppm, $CDCl_3$) 2.61 (br m, 2 H), 3.42 (t, J = 7.0 Hz, 2 H), 3.72 (t, J = 6.6 Hz, 2 H) [lit.[51] ^1H NMR ($CDCl_3$) δ 2.54 (m, 2 H), 3.47 (t, J = 7.0 Hz, 2 H), 3.75 (t, J = 6.5 Hz, 2 H); ^{13}C NMR (δ, ppm, $CDCl_3$) 23.91 ($CH_2CH_2CH_2$), 35.71 (SCH_2), 57.19 ($S(O_2)CH_2$) [lit.[52] ^{13}C NMR δ 24.87, 36.69, 58.17].

Preparation of 2,2,8,8-Tetradeuterio-1,5-dithiacyclooctane 1-Oxide. A solution of 1,5-dithiacyclooctane (50 mg, 0.3 mmol) in 0.5 mL of deuterium oxide was added to a 40% solution of sodium deuterioxide in 1 mL of deuterium oxide (99.8%). After the solution was stirred under a nitrogen atmosphere at 100 °C for 24 h, the solvent was removed under reduced pressure. The mixture was then extracted three times with 2 mL of chloroform. The combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by alumina column chromatography using chloroform as eluent, affording 43 mg of 2,2,8,8-tetradeuterio-1,5-dithiacyclooctane 1-oxide. The deuterium content was more than 95 atom % as determined by ^1H NMR spectroscopy.

Acknowledgment. The authors thank Dr. S. I. Khan for X-ray structure determination. This work was supported by NSF Grant No. CHE89-11916.

Supplementary Material Available: Tables of crystal data, fractional atomic coordinates, isotropic and anisotropic parameters, and bond distances and angles for **3** (5 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Comparison of the Photooxidations of 1,5-Dithiacyclooctane, 1,4-Dithiane, and Pentamethylene Sulfide. Another Example of Remote Participation during Photooxidation at Sulfur?

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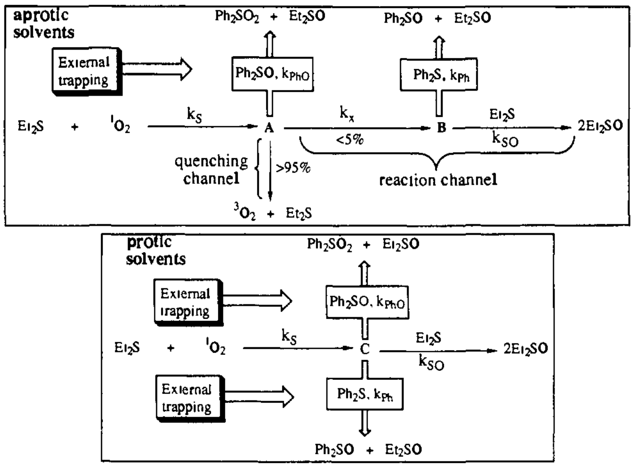
Abstract: The photooxidations of 1,5-dithiacyclooctane (1,5-DTCO), 1,4-dithiane, and pentamethylene sulfide have been compared. The photooxidation of 1,5-DTCO differs significantly from the other substrates in several respects: (1) the ratio of chemical quenching to total quenching of singlet oxygen during photooxidation of 1,5-DTCO is 70%, in comparison to 5% for 1,4-dithiane and 2.9% for pentamethylene sulfide; (2) a sulfone is produced in all of the photooxidations except in that of 1,5-DTCO; and (3) the value of k_T is larger for 1,5-DTCO than for any previously reported sulfide. A novel sulfur–sulfur interaction during photooxidation of 1,5-DTCO is utilized in order to explain these results. A *cis*-bissulfoxide was isolated from the photooxidation of 1,5-DTCO. It crystallizes in space group $P\bar{1}$ of the triclinic system with two molecules in a cell of the following dimensions: a = 5.348 (3), b = 6.755 (5), c = 11.677 (7) Å, α = 90.46 (6), β = 97.04 (5), γ = 101.88 (6)°. The structure has been refined to a final value of 0.0477 for the conventional R factor on the basis of 951 independent observed intensities.

The photooxidations of dialkyl sulfides were first reported nearly 30 years ago.[1] In 1983, mechanisms for sulfide photooxidations in protic and aprotic media were suggested that provided explanations for the diverse experimental observations which had been made in this complex system during the previous 21 years.[2] In aprotic solvents, sulfides remove singlet oxygen from solution by both physical and chemical processes (Scheme I). In contrast, in methanol the physical quenching processes are suppressed and the chemical reactions of the sulfides become efficient (Scheme I).

In 1990, Clennan and Yang[3] reported that photooxidations of γ-hydroxy sulfides resulted in the formation of sulfone olefins by migration of the hydroxy group to sulfur. The formations of these unusual oxidative elimination products were rationalized by invoking remote participation of a hydroxy group via a sulfurane intermediate. This suggestion has recently been supported by the observation that hydroxy groups which participate to form the most stable sulfuranes are also the most effective at promoting chemical reactions of the sulfide.[4] These results imply that

Scheme I



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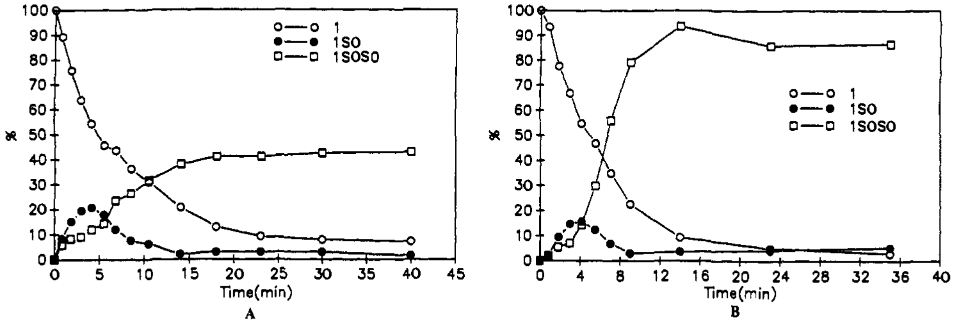
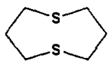


Figure 1. Photooxidation of **1** in acetone with 5% pyridine. A: [**1**] = 2 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, 20 °C. B: [**1**] = 2.9 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, -80 °C.

sulfuranes are also pivotal intermediates formed during photooxidations in methanol.

In order to examine the ability of other heteroatoms to participate during photooxidations at sulfur, we have studied the photooxidation of 1,5-dithiacyclooctane (1,5-DTCO) (**1**) and have compared it to the photooxidations of 1,4-dithiane (**2**) and pentamethylene sulfide (**3**). The choice of 1,5-DTCO as a substrate



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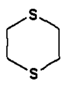

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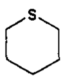
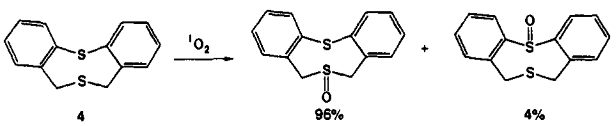


3

to search for sulfur participation was dictated by the well-established propensity of **1** to exhibit sulfur–sulfur interactions during both chemical[5-11] and electrochemical reactions.[12] Akasaka and Ando reported the only other example of the photooxidation of an 8-membered ring bissulfide.[13] Dithiocin **4** was shown to react to produce two sulfoxides; however, no evidence of sulfur participation was presented.



Results

Product Studies. Product evolution and starting materials disappearance during photooxidations of **1**, **2**, and **3** were followed by gas chromatography (GC).[14] The reaction profiles for photooxidations of **1** in acetone with 5% pyridine at both 20 and -80 °C are presented in Figure 1. The pyridine acts to retard the bleaching of the sensitizer. Reaction profiles in the absence of pyridine were nearly identical to those presented in Figure 1 but required the addition of rose bengal at frequent intervals. The formation of the products sulfoxide **1SO** and bissulfoxide **1SOSO** was suppressed in the presence of the quencher 3,3,7,7-tetramethyl-1,5-diazabicyclo[3.3.0]octane, as anticipated for $^1O_2$ reactions.[15]

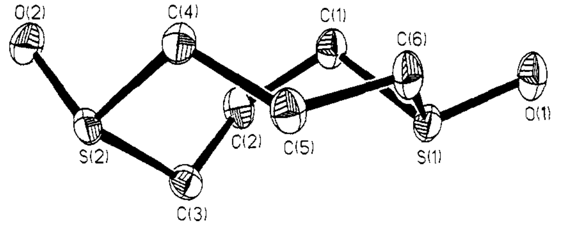


Figure 2. View of the molecule showing the cis disposition of the oxygen atoms. Hydrogen atoms are omitted for clarity.

The "GC concentration" of the sulfoxide, **1SO**, is a sensitive function of the GC helium flow rate indicative of its slow decomposition under the analysis conditions. The reaction profiles in Figure 1 were generated using the most rapid analysis experimentally reasonable in order to minimize this decomposition, and as a result the peak for **1SO** only exhibited a slight asymmetry. In contrast to **1SO**, **1** and **1SOSO** appear to be stable under a wide variety of GC conditions. Two separate peaks for the **1SOSO** isomers, however, were never observed.

The GC product balance in the room-temperature reaction of Figure 1 decreased from 100, at the beginning of the reaction, to 52%, at the end of the reaction (40 min). Concomitant with the decreasing product balance was the appearance of small peaks which were not analyzed. The monosulfoxide, **1SO**, was not present at the end of the reaction, and the small mass balance (52%) was therefore most likely due to formation of the sulfoxide oxidation products which were identified by Sheu, Foote, and Gu.[16] In contrast, at -80 °C the GC product balance at the end of the reaction was 100%, suggesting that the Foote sulfoxide oxidation products did not form or formed much slower at low temperatures.

Two bissulfoxides, A and B, were formed in the photooxidation of **1** at 20 °C in a 72/28 ratio, respectively, as demonstrated by the cutting and weighing of ^{13}C NMR peaks from four different reactions. In contrast, at -80 °C A was the only bissulfoxide observed in the photooxidation mixtures. Bissulfoxide A was also the major product formed during oxidations of **1** with 2 equiv of MCPBA in CH_2Cl_2 (88/12) and $CHCl_3$ (92/8). A has subsequently been isolated, crystallized, and identified as the *cis*-bissulfoxide by X-ray crystallography (Figure 2).

The structure of *cis*-**1SOSO** consists of molecules that are well separated from each other with no significant intermolecular interactions in the crystal. The sulfur–sulfur distance is 4.182 Å, significantly longer than the values of 3.175, 3.135, 3.259, and 3.143 Å reported for 3-methoxy-1,5-dithiacyclooctane 1-oxide,[17]

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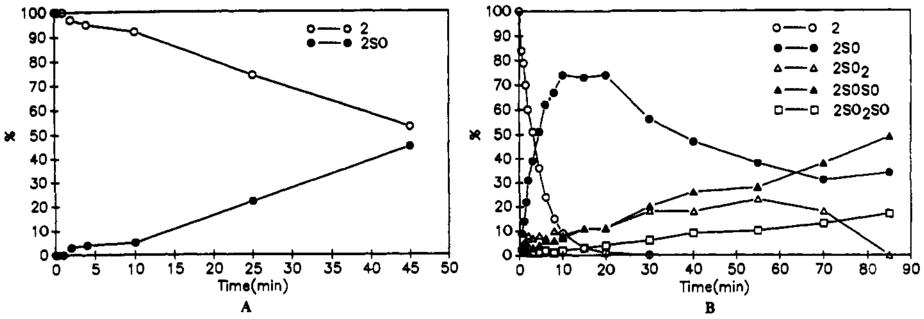


Figure 3. Photooxidation of **2** in acetone. A: [**2**] = 1.6 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, 0 °C. B: [**2**] = 1.5 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, −80 °C.

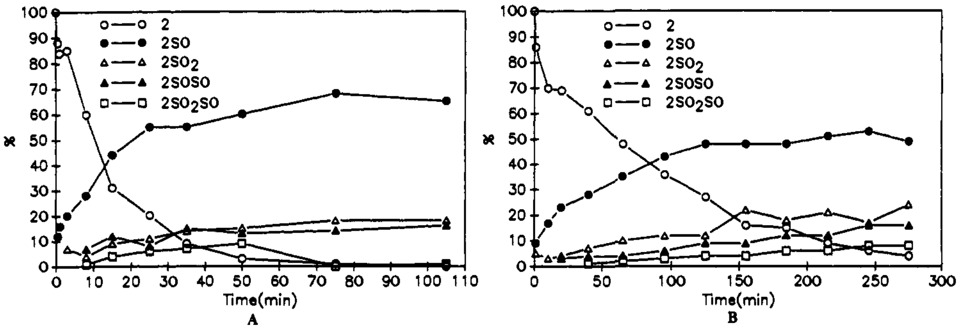


Figure 4. Photooxidation of **2** in 2-propanol. A: [**2**] = 1.6 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, 0 °C. B: [**2**] = 1.7 × 10^{-2} M, [rose bengal] = 2 × 10^{-5} M, −80 °C.

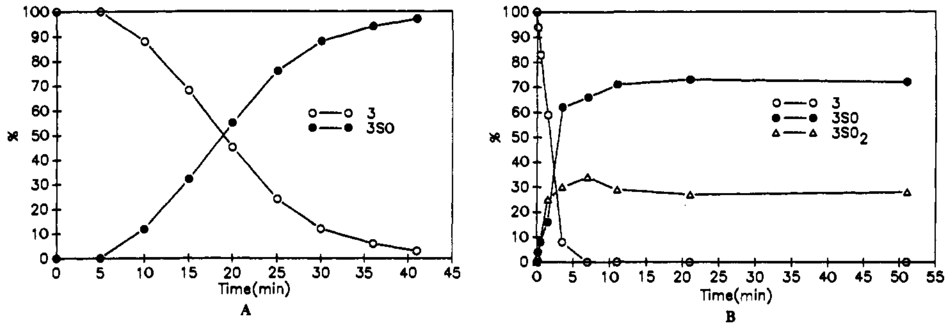


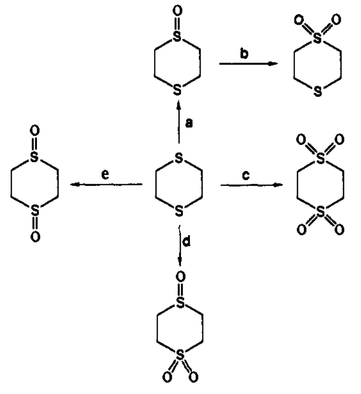
Figure 5. Photooxidation of **3** in acetone. A: [**3**] = 3.8 × 10^{-3} M, [rose bengal] = 2 × 10^{-5} M, 25 °C. B: [**3**] = 6.9 × 10^{-3} M, [rose bengal] = 2 × 10^{-5} M, −80 °C.

3-hydroxy-1,5-dithiacyclooctane 1-oxide,[17] 1-methyl-5-thia-1-thioniacyclooctane iodide,[18] and 1-(tosylimino)-1,5-dithiacyclooctane,[19] respectively. The S_1–O_1 distance of 1.498 ± 0.004 Å and the S_2–O_2 distance of 1.502 ± 0.004 Å are also shorter than the S–O distance of 1.519 Å reported for 3-hydroxy-1,5-dithiacyclooctane 1-oxide[17a] but longer than the S–O bond length of 1.477 Å in dimethyl sulfoxide.[17b] These structural parameters strongly suggest the absence of sulfur–sulfur interactions in ***cis*-1SOSO**. A complete list of interatomic distances and angles in the structure are available as supplementary material.

The GC reaction profiles for the photooxidations of **2** in acetone at 0 and −80 °C are significantly more complex than for **1** and are presented in Figure 3. The progress of the reaction in $CDCl_3$ was also followed at room temperature by ^{13}C NMR spectroscopy and gave very similar results. The formation of a small amount of bissulfone **$2SO_2SO_2$** is observed at long irradiation times but is not indicated in the figure. The structures of the products were verified by independent synthesis (Scheme II) and by comparison to the ^{13}C NMR spectrum of the reaction mixture.

The ^{13}C NMR spectrum of the reaction mixture reveals that only the *trans*-bissulfoxide formed when the concentration of **2** was 10^{-2} M. A single resonance of the ^{13}C spectrum of a purified sample of **2SOSO** (33.2 ppm) at room temperature split into two resonances (32.7 and 32.3 ppm) of unequal intensity at −80 °C as anticipated for the trans configuration. Foote and Peters, however, have reported that **2** reacts to form the *cis*-bissulfoxide but only when its concentration is 10^{-3} M or lower.[20] This is

Scheme II[a]



[a] (a) 1 equiv of MCPBA, CH_2Cl_2, 0 °C → room temperature. (b) 0.67 equiv of $KMnO_4/MgSO_4$, acetone, −30 °C. (c) >5 equiv of MCPBA, CH_2Cl_2, 0 °C → room temperature. (d) 3 equiv of MCPBA, CH_2Cl_2, 0 °C → room temperature. (e) 2 equiv of MCPBA, CH_2Cl_2, 0 °C → room temperature.

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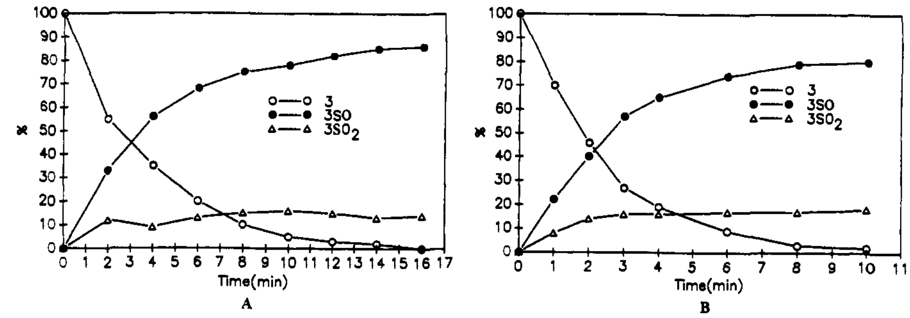

Figure 6. Photooxidation of 3 in 2-propanol. A: [3] = 6.6 × 10^{-3} M, [rose bengal] = 2 × 10^{-5} M, 25 °C. B: [3] = 5.7 × 10^{-3} M, [rose bengal] = 2 × 10^{-5} M, −80 °C.

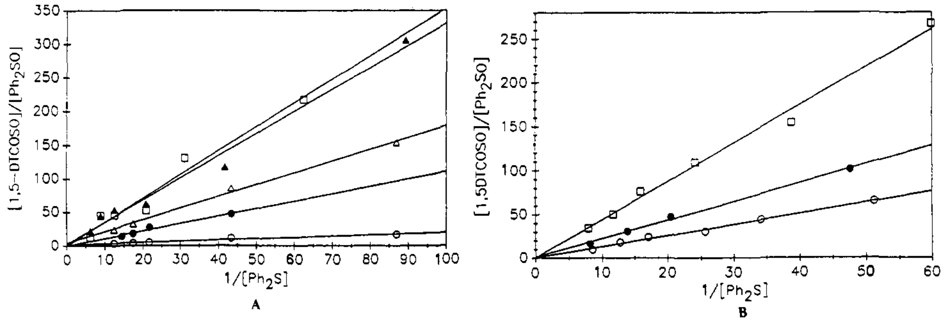

Figure 7. Diphenyl sulfide trapping. A: In acetone; ○, [1,5-DTCO] = 0.003 M, slope = 0.187, r = 0.9825; ●, [1,5-DTCO] = 0.008 M, slope = 1.112, r = 0.9879; △, [1,5-DTCO] = 0.016 M, slope = 1.748, r = 0.9978; ▲, [1,5-DTCO] = 0.059 M, slope = 3.287, r = 0.9917; □, [1,5-DTCO] = 0.076 M, slope = 3.541, r = 0.9800. B: In 2-propanol; ○, [1,5-DTCO] = 0.032 M, slope = 1.26, r = 0.9963; ●, [1,5-DTCO] = 0.053 M, slope = 2.11, r = 0.9984; □, [1,5-DTCO] = 0.132 M, slope = 4.34, r = 0.9956.

consistent with an intramolecular transfer of an oxygen atom in a persulfoxide intermediate at low concentrations. The photooxidation of **2** was also followed in 2-propanol at 0 and −80 °C; the GC reaction profiles are presented in Figure 4.

The GC reaction profiles for the photooxidations of **3** at 25 and −80 °C in acetone and 2-propanol are presented in Figures 5 and 6, respectively. Sensitizer bleaching was not as severe a problem in the photooxidations of **2** and **3** as in the photooxidation of **1**, and as a result no pyridine was used in these reactions.

Kinetic Studies. The total rate constants of sulfide-induced removal of singlet oxygen from solution, k_T, for **1**, **2**, **3**, and **1SO** (the monosulfoxide of **1**) were measured by irradiation of a series of samples containing different concentrations of the sulfide at 532 nm with a Nd:YAG laser (Table I). The singlet oxygen phosphorescence intensities were monitored at 1270 nm for each sulfide concentration as a function of time. Each of the resulting exponential decays is pseudo-first-order and adequately described by eq 1. The values of k_T are extracted by plotting the pseudo-first-order rate constant, k_{obsd}, versus the concentration of sulfide used to collect the data (eq 2). The k_T values represent the sum of the rate constants for all of the sulfide-induced chemical, k_r, and physical, k_q, processes that remove singlet oxygen from solution.

$$\frac{d[^1O_2]}{dt} = k_{obsd}[^1O_2] \qquad (1)$$

$$k_{obsd} = k_T[\text{sulfide}] + k_d \qquad (2)$$

The chemical rate constants, k_r, were measured using the competition method of Higgins, Foote, and Cheng.[21] The chemical rate constants for the reactions of **1** and **3** were measured relative to tetramethylethylene (k_r = 2.7 × 10^7 M^{-1} s^{-1})[22] and for the reactions of **2** relative to 2,5-dimethyl-2,4-hexadiene (k_r = 7.4 × 10^5 M^{-1} s^{-1}).[23,24] They are listed in Table I along with the k_q values, which are determined by difference.

Table I. Kinetic Data for the Reactions of **1**, **2**, **3**, and **1SO** with $^1O_2$[a]

compd	solvent	k_T × 10^{-6} (M^{-1} s^{-1})	k_r × 10^{-6} (M^{-1} s^{-1})	k_q × 10^{-6} (M^{-1} s^{-1})	k_r/k_T × 100
1	acetone[b]	53	37.3	15.7	70
	toluene[c]	16.9			
	2-propanol[b]	24			
2	acetone[b]	4.83	0.24	4.59	5
	toluene[c]	1.98			
	2-propanol[b]	2.13			
3	acetone[b,d]	16.1	0.47	15.6	2.9
	toluene[c]	13.0			
	2-propanol[b]	14.1			
1SO	acetone	3.28			

[a] At 25 °C except where noted. [b] [rose bengal] = (1–3) × 10^{-5} M. [c] [TPP] = (1–3) × 10^{-5} M. [d] At 20 °C.

Table II. Diphenyl Sulfide and Sulfoxide Trapping during Photooxidations of **1** and Et_2S

compd	solvent	k_{SO}/k_{Ph}	k_{SO}/k_{PhO}	k_X/k_{PhO}
1	acetone	20.81		1.16[a]
	2-propanol	15.04	2.96	
Et_2S	methanol	4.81	2.77	
	benzene	17.63		0.023
	CH_3CN	36.5		0.082

[a] Slope of the least-squares line in Figure 8A.

Trapping Experiments. Several years ago it was demonstrated that diphenyl sulfide[20] and diphenyl sulfoxide[25] were effective trapping agents in sulfide photooxidations. They are essentially inert to singlet oxygen, yet when cophotooxidized with a reactive sulfide substantial amounts of diphenyl sulfoxide and diphenyl

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(21) The k_r values were all determined by following product appearance except for the reaction of **1** which was followed by starting material disappearance. This protocol eliminates any problems associated with sulfoxide instability. Higgins, R.; Foote, C. S.; Cheng, H. In *Advances in Chemistry Series*; Gould, R. F., Ed.; American Chemical Society: Washington D.C., 1968; Vol. 77, pp 102–117.

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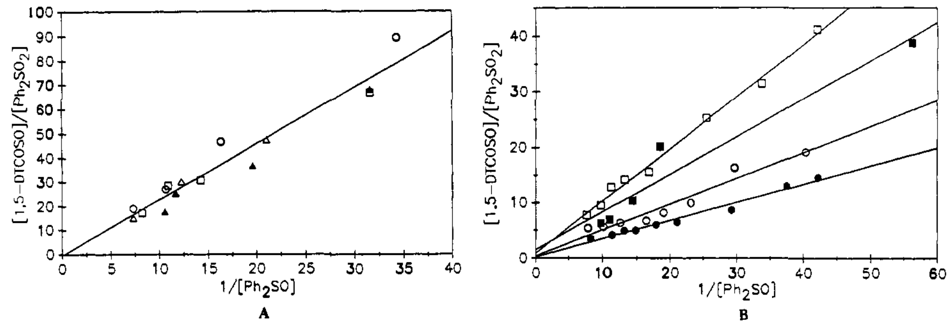


Figure 8. Diphenyl sulfoxide trapping. A: In acetone; ○, [1,5-DTCO] = 0.012 M; △, [1,5-DTCO] = 0.38 M; ▲, [1,5-DTCO] = 0.095 M; □, [1,5-DTCO] = 0.15 M, slope = 2.32, r = 0.9691. B: In 2-propanol; ●, [1,5-DTCO] = 0.024 M, slope = 0.33, r = 0.9886; ○, [1,5-DTCO] = 0.06 M, slope = 0.47, r = 0.9709; ■, [1,5-DTCO] = 0.083 M, slope = 0.68, r = 0.9676; □, [1,5-DTCO] = 0.13 M, slope = 0.94, r = 0.9968.

sulfone are observed. Diphenyl sulfide and sulfoxide also function as trapping agents during the photooxidation of **1** as shown in Figures 7 and 8, respectively.

The slopes of plots of [1,5-DTCOSO]/[Ph_2SO] versus 1/[Ph_2S] in acetone and 2-propanol and the slope of the plot of [1,5-DTCOSO]/[Ph_2SO_2] versus 1/[Ph_2SO] in 2-propanol are dependent on the concentration of **1**, as anticipated if Ph_2S and Ph_2SO are competing with **1** for a common intermediate. In contrast, Ph_2SO in acetone does not appear to compete with **1** for a common intermediate, and the slope of the plot of [1,5-DTCOSO]/[Ph_2SO_2] versus 1/[Ph_2SO] is independent of the concentration of **1**. These observations are very similar to those made in the Et_2S photooxidation for which the mechanisms in Scheme I are suggested.[2] If the same mechanisms operate in the reactions of **1**, eq 3 can be derived to describe Ph_2S trapping in acetone and 2-propanol, eq 4 for Ph_2SO trapping in 2-propanol, and eq 5 for Ph_2SO trapping in acetone.[2] The kinetic parameters in Table II were derived for the Ph_2S trapping and for the Ph_2SO trapping in 2-propanol by plotting the slopes of the lines in Figures 7 and 8 (eqs 3 and 4) versus the concentration of **1** used to collect the data.

$$\frac{[\text{1,5-DTCOSO}]}{[\text{Ph}_2\text{SO}]} = 1 + \frac{2k_{\text{SO}}[\text{1,5-DTCO}]}{k_{\text{Ph}}[\text{Ph}_2\text{S}]} \tag{3}$$

$$\frac{[\text{1,5-DTCOSO}]}{[\text{Ph}_2\text{SO}_2]} = 1 + \frac{2k_{\text{SO}}[\text{1,5-DTCO}]}{k_{\text{PhO}}[\text{Ph}_2\text{SO}]} \tag{4}$$

$$\frac{[\text{1,5-DTCOSO}]}{[\text{Ph}_2\text{SO}_2]} = 1 + \frac{2k_{\text{X}}}{k_{\text{PhO}}[\text{Ph}_2\text{SO}]} \tag{5}$$

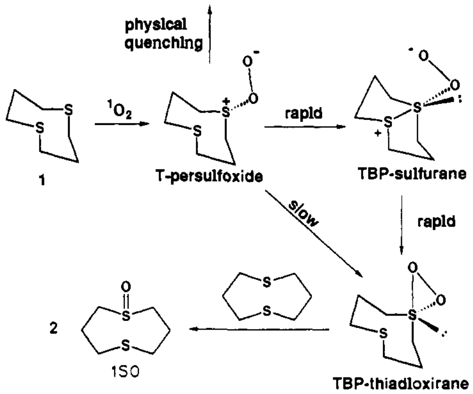
Discussion

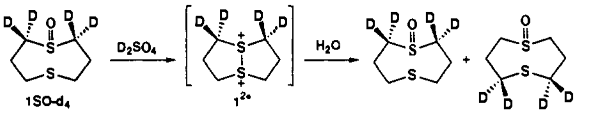
The photooxidation of **1** is very different from the photooxidations of **2** and **3** or diethyl sulfide in two important respects: (1) The formation of products during the photooxidation of **1** at room temperature is much more efficient because of the decreased importance of physical quenching (Table I) than the reactions of **2** or **3** at room temperature (Figures 3A and 5A). At −80 °C, physical quenching is suppressed (Figures 3B and 5B), and the reactions of **2** and **3** become comparable in efficiency to **1**. This temperature-dependent efficiency has been noted previously during the photooxidation of diethyl sulfide,[2] and its absence during the photooxidation of **1** (see Figure 1) is unusual. (2) Photooxidation of **1** does not produce a sulfone at either high or low temperatures, while photooxidation of **2** and **3** produces as much as 20% sulfone at −80 °C and very complex reaction mixtures.

A mechanism which provides an explanation for these differences and which also takes advantage of the ubiquitous sulfur–sulfur interaction which occurs in **1** is depicted in Scheme III. In this mechanism, addition of singlet oxygen to **1** produces an intermediate similar to that formed in diethyl sulfide photooxidation: a tetrahedral (T) sulfonium ion, the persulfoxide. This intermediate collapses rapidly to a trigonal bipyramidal (TBP) sulfurane as a result of the proximity of the remote sulfur.

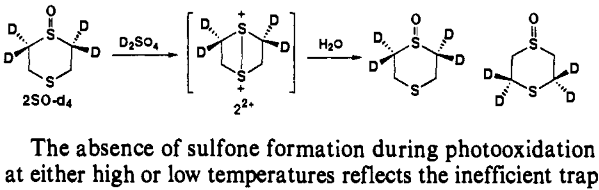
Scheme III suggests that decomposition of the persulfoxide is responsible for physical quenching. We have no direct evidence for this step. However, extensive kinetic studies have shown that decomposition of its analogue, diethyl persulfoxide, does lead to physical quenching. The more efficient chemical reaction of **1** in comparison to either **2** or **3** (Table I) is therefore consistent with the mechanism in Scheme III since rapid formation of the sulfurane competes with physical quenching. Competitive formation of a sulfurane is impossible in **3** and geometrically difficult in **2**, and as a result physical quenching during their photooxidations is more prevalent than in **1**. The geometric difficulty of achieving stabilizing sulfur–sulfur interactions in **2** is consistent with the observation that deuterium scrambling occurs in both **1SO**-d_4 and **2SO**-d_4 (eqs 6 and 7)[26] but that attempts to isolate the dication salts, $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, are only successful in the reaction of **1SO**-d_4.

Scheme III





(6)



(7)

The absence of sulfone formation during photooxidation of **1** at either high or low temperatures reflects the inefficient trapping of the nucleophilic persulfoxide and/or trigonal bipyramidal sulfurane by **1SO** and is consistent with their very low steady-state concentrations and rapid interconversions to the thiadioxirane (Scheme III). The rapid interconversion of these peroxy anions to the thiadioxirane is also supported by the trapping data in Table II. Since diphenyl sulfoxide trapping of diethyl persulfoxide and **1**-persulfoxide and/or the trigonal bipyramidal sulfurane (Scheme III) are likely to occur with similar rate constants, k_{PhO} in Scheme

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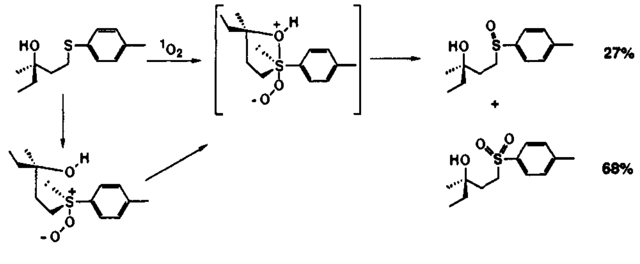
[26] Fuijhara, H.; Kawada, A.; Furukawa, N. *J. Org. Chem.* **1987**, *52*, 4254–4257.

Scheme IV



I, relative k_X/k_{PhO} values are a measure of relative rates of thiadioxirane formation. The thiadioxirane in the reaction of **1** in acetone forms 50 times faster than diethylthiadioxirane in benzene and 14 times faster than diethylthiadioxirane in acetonitrile.[27]

The remote sulfur in **1** catalyzes the formation of the thiadioxirane by providing an energetically favorable pathway to a trigonal bipyramidal sulfurane which is closer in geometry to the thiadioxirane than the tetrahedral persulfoxide.[28] As a result of this similar geometry, the collapse of the sulfurane to the thiadioxirane is not impeded by an unfavorable internal reorganization energy. We believe this same phenomenon is responsible for the unexpected high yield of sulfone formed during photooxidations of γ-hydroxy sulfides[29] (Scheme IV). The γ-hydroxy sulfides, however, are not as potent as **1** as nucleophiles, and unimolecular decomposition of the thiadioxirane to give the sulfone competes effectively with nucleophilic attack to give two sulfoxides.

Conclusion

The photooxidation of 1,5-dithiacyclooctane (**1**) has been compared to the photooxidations of 1,4-dithiane (**2**) and pentamethylene sulfide (**3**). A tentative mechanism which invokes remote participation by sulfur has been proposed in order to rationalize the unusual photooxidation of **1**. The diphenyl sulfoxide trapping results demand at least two intermediates in acetone. A thiadioxirane which has recently been criticized as a viable precursor of sulfoxides[30] was suggested as one of these intermediates because of the absence of sulfone even after extended irradiation times. A persulfoxide has also been suggested as an intermediate in Scheme III; however, it is conceivable that its formation is bypassed and the TBP sulfurane forms directly.

Experimental Section

Analytical gas chromatographic measurements were carried out on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector and an HP 10 m × 0.53 mm cross-linked FFAP capillary column. Chromatographic separations were also carried out on a Harrison Research Model 7624T chromatotron using plates coated with EM Science 7749 silica gel 60PF254. Proton and carbon NMR spectra were obtained on a JEOL FX270 at 269.7 and 67.8 MHz, respectively, and on a JEOL GX 400 at 399.78 and 100.59 MHz, respectively. The proton and carbon spectra are referenced to TMS. Toluene was distilled from P_2O_5 prior to use, and Baker "photrex" grade acetone, methanol, 2-propanol, and ethyl acetate were used as received.

Pentamethylene sulfide, *m*-chloroperbenzoic acid, 1,3-dibromopropane, sodium periodate, sodium metabisulfite, and 1,3-propanedithiol were obtained from Aldrich and used without purification. 1,4-Dithiane was obtained from Aldrich and recrystallized from ethanol before use. Sodium bisulfite was obtained from Baker and used without purification.

1,5-Dithiacyclooctane (1,5-DTCO) (1).[5] 1,3-Propanedithiol disodium salt (94.2 mmol) and 94.2 mmol of 1,3-dibromopropane each in 400 mL of 100% ethanol were placed in two different 500-mL round-bottom flasks and stirred. Nitrogen pressure was used to slowly (30–40 drops per minute) push these two solutions through small connecting tubes into a 3-L 3-neck round-bottom flask containing 1000 mL of vigorously stirred 100% refluxing ethanol. After the addition was complete, the mixture was refluxed for 24 h. The mixture was then cooled and the ethanol removed. The residue was washed 6–8 times with dichloromethane (150 mL each), and the washings were combined. The dichloromethane was then removed, and vacuum distillation gave 5.34 g (38.3% yield) of 1,5-DTCO as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.08 (m, 4 H), 2.80 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 29.9, 30.4.

1,5-Dithiacyclooctane 1-Oxide (1SO).[31] A solution of 1.46 g (6.82 mmol) of sodium periodate in 15 mL of water was added to a solution of 1.01 g (6.82 mmol) of 1,5-DTCO in 20 mL of methanol at room temperature over a 10-min period. This mixture was stirred for 20 h and filtered, and the solvent was removed. Water was added to the residue and then extracted three times with chloroform. The combined chloroform extracts were washed with sodium bisulfite ($Na_2S_2O_3$) and then dried over anhydrous sodium sulfate. Removal of the solvent gave a 62% yield of 1,5-dithiacyclooctane 1-oxide as an oil. Recrystallization from ethyl acetate gave a low-melting white solid: ^{1}H NMR ($CDCl_3$) δ 2.1–2.3 (m, 4 H), 2.5–2.7 (m, 4 H), 3.0–3.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) 52.8, 30.8, 23.8.

1,5-Dithiacyclooctane 1,5-dioxide (1SOSO) was synthesized by slow addition of 5.586 g (13.8 mmol) of 85% *m*-chloroperbenzoic acid in 100 mL of dichloromethane to a rapidly stirred solution of 2.037 g (13.8 mmol) of 1,5-DTCO in 75 mL of dichloromethane maintained at −20 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, treated with ammonia for a second time, and filtered. The filtrate was concentrated under reduced pressure to give a mixture of 1,5-DTCO 1-oxide and 1,5-DTCO 1,5-dioxide. Final purification was carried out by flash column chromatography by increasing the eluent polarity from 50% acetonitrile in dichloromethane to 90% acetonitrile in dichloromethane: mp 151–152 °C; ^{1}H NMR ($CDCl_3$) δ 2.1–2.2 (m, 2 H), 2.5–2.7 (m, 2 H), 3.0–3.1 (m, 4 H), 3.2–3.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 49.5, 13.7.

1,4-Dithiane 1-oxide (2SO) was synthesized by slow addition of 47.6 mg (0.23 mmol) of 85% *m*-chloroperbenzoic acid in 1.5 mL of chloroform to a rapidly stirred solution of 25.2 mg (0.21 mmol) of 1,4-dithiane in 2.0 mL of chloroform maintained at −20 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, treated with ammonia a second time, and filtered. The filtrate was concentrated under reduced pressure to give 1,4-dithiane 1-oxide as a white solid. Final purification was carried out by sublimation: ^{1}H NMR ($CDCl_3$) δ 2.45–2.55 (m, 2 H), 2.90–3.15 (m, 4 H), 3.49–3.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 46.9, 18.7.

1,4-Dithiane 1,1-dioxide ($2SO_2$) was synthesized by a modified procedure of Henbest.[32-34] A solution of 200 mg (1.47 mmol) of 1,4-dithiane 1-oxide, 500 mg of $MgSO_4$, and 15 mL of acetone in a 100-mL round-bottom flask was cooled to −30 °C in a dry ice/acetone bath. Acetone (25 mL) containing 155.7 mg of $KMnO_4$ was added slowly with constant stirring. After the addition was complete, the reaction mixture was kept at −30 °C for another 90 min and then warmed to room temperature. Excess sodium metabisulfite ($Na_2S_2O_5$) was then added and the mixture stirred for a few minutes. The solution was filtered and the product purified by flash column chromatography (4/1 dichloromethane/ethyl acetate): ^{1}H NMR ($CDCl_3$) δ 3.24–3.29 (m, 2 H), 3.13–3.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 54.1, 27.7.

1,4-Dithiane 1,4-dioxide (2SOSO) was synthesized by slow addition of 95.2 mg (0.46 mmol) of 85% *m*-chloroperbenzoic acid in 2 mL of chloroform to a rapidly stirring solution of 25.2 mg (0.21 mmol) of 1,4-dithiane in 2.0 mL of chloroform maintained at −20 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, treated with ammonia a second time, and filtered. The filtrate was concentrated under reduced pressure to give 1,4-dithiane 1,4-dioxide as a white solid. Final purification was carried out by recrystallization from 90% ethanol: mp 261–262 °C dec; ^{1}H

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(27) If a small amount of decomposition of **1SO** is occurring during the GC measurement, 1.16 (Table II) represents a lower limit and the real k_X/k_{PhO} would even be larger.

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Table III. Crystallographic and Data Collection Parameters

formula	$C_6H_{12}S_2O_2$	Z	2
color	colorless	$F(000)$	192
system	triclinic	μ, mm^{-1}	0.565
space group	$P1$	index ranges	$0 \leq h \leq 6$
a, Å	5.348 (3)		$-8 \leq k \leq 8$
b, Å	6.755 (5)		$-15 \leq l \leq 15$
c, Å	11.677 (7)	no. reflns	2062
α, deg	90.46 (6)	obsd reflns	951
β, deg	97.04 (5)	R	0.0477
γ, deg	101.88 (6)	R_w	0.0587
vol, Å^3	409.5 (5)		

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$)[a]

	x	y	z	U(eq)
S(1)	3456 (3)	7386 (2)	6080 (1)	41 (1)
S(2)	7766 (3)	7121 (2)	9295 (1)	36 (1)
O(2)	10650 (7)	7549 (6)	9353 (3)	52 (1)
C(2)	7882 (11)	9660 (8)	7384 (4)	45 (2)
C(5)	3761 (10)	4524 (8)	7855 (4)	39 (2)
C(1)	6927 (10)	8265 (8)	6321 (4)	42 (2)
C(4)	6635 (10)	4926 (7)	8339 (4)	37 (2)
O(1)	2759 (8)	7123 (6)	4798 (3)	55 (2)
C(6)	3145 (10)	4829 (8)	6564 (4)	43 (2)
C(3)	6659 (11)	9099 (8)	8475 (4)	40 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

NMR ($CDCl_3$) δ 2.90 (m, 2 H), 3.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.1.

1,4-Dithiane 1,1,4-trioxide ($2SOSO_2$) and 1,4-dithiane 1,1,4,4-tetraoxide ($2SO_2SO_2$) were synthesized by slow addition of 190.5 mg (0.92 mmol) of 85% *m*-chloroperbenzoic acid in 2 mL of chloroform to a rapidly stirred solution of 25.2 mg (0.21 mmol) of 1,4-dithiane in 2.0 mL of chloroform maintained at −20 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, treated a second time with ammonia, and filtered. The filtrate was concentrated under reduced pressure to give a mixture of 1,4-dithiane 1,1,4-trioxide and 1,4-dithiane 1,1,4,4-tetraoxide as a white solid. Final purification was carried out by sublimation. 1,4-Dithiane 1,1,4-trioxide: ^1H NMR ($CDCl_3$) δ 2.05 (m, 2 H), 2.19–2.42 (m, 4 H), 2.90–3.15 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 42.0, 45.4. 1,4-Dithiane 1,1,4,4-tetraoxide: ^{13}C NMR ($CDCl_3$) δ 42.1.

Pentamethylene sulfoxide (3SO)[35] was synthesized by slow addition of 0.99 g (9.7 mmol) of 85% *m*-chloroperbenzoic acid in 15 mL of dichloromethane to a rapidly stirred solution of 2.08 g (0.01 mol) of pentamethylene sulfide in 15 mL of dichloromethane maintained at −20 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, ammonia was bubbled through the solution for a second time, and the mixture was filtered. The solvent was removed to give 0.40 g (yield 35%) of pentamethylene sulfoxide: ^{13}C NMR ($CDCl_3$) δ 47.6, 23.6, 18.0.

Pentamethylene sulfone ($3SO_2$) was synthesized by slow addition of 0.99 g (9.7 mmol) of 85% *m*-chloroperbenzoic acid in 15 mL of dichloromethane to a rapidly stirred solution of 4.16 g (0.02 mol) of pentamethylene sulfide in 15 mL of dichloromethane maintained at −10 °C in an acetone/dry ice bath under a nitrogen atmosphere. The solution was stirred for 1.5 h and then allowed to warm to room temperature (20 °C) for an additional 2 h. Anhydrous ammonia was bubbled into the reaction mixture, and a white precipitate, ammonium *m*-chlorobenzoate, was formed. The mixture was filtered, treated with ammonia a second time, and filtered. The solvent was removed to give 0.45 g (yield 35%) of pentamethylene sulfone: mp 96–97 °C; ^{13}C NMR ($CDCl_3$) δ 51.4, 23.7, 23.0.

Photolysis Conditions. The singlet oxygen reactions were conducted in 5-mm NMR tubes or in cylindrical 3-mL vessels approximately 3 cm high. The temperatures were maintained by submersion in a methanol bath held at the desired temperature by the use of a refrigerator probe (FTS Systems Inc. Flexicool). Prior to photolysis, the samples were saturated with oxygen for 20 min. The irradiations were conducted under continuous oxygen bubbling by using a 750-W, 120-V tungsten halogen lamp and by filtering out the high-energy light with a 1-cm 0.5% $K_2Cr_2O_7$ filter solution. The lamp was turned on for 30 s prior to irradiation of the sample.

k_T Measurements. The k_T measurements were carried out as previously described.[15]

X-ray Structure Determination. The structure was determined at room temperature on a Nicolet R3m/V diffractometer equipped with a graphite monochromator and a molybdenum tube ($\lambda K\alpha_1$ = 0.709 26 Å, $\lambda K\alpha_2$ = 0.713 54 Å). Crystal data and experimental parameters are given in Table III. The data were corrected for Lorentz polarization effects but not for absorption. The structure was solved by direct methods and refined by least-squares techniques; the programs used were from the SHELXTL system.

The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules in the cell. Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and allowed to ride on the heavy atom to which they were attached with fixed temperature factors. The final values of the conventional R factors were $R = 0.0477$ and $R_w = 0.0577$, based on 951 independent observed [$F > 6.0\sigma(F)$] intensities. The final values of the atomic parameters, along with their standard deviation as estimated from the inverse matrix, are presented in Table IV. Listings of observed and calculated structure factor amplitudes are available as supplementary material.

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Supplementary Material Available: Plot of the competitive photooxidation of **1** with TME and tables of bond lengths and angles, hydrogen atom coordinates, and anisotropic thermal parameters (5 pages); listings of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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