solution (500 mL), 0.1 M 2-ME in 0.01 M HCl (200 mL), and then 0.1 M 2-ME in 0.05 M HCl. Analysis by HPLC showed 90% recovery of tetrahydrofolic acid along with a small amount of 7,8-dihydrofolic acid. Eluant was removed after addition of 5 mL DMF by evaporation to a volume less than 5 mL and precipitation of product with Et_2O. The chromatographic elution and mass spectra of this material were found to be identical to authentic tetrahydrofolic acid. A sample was purified further by precipitation from aqueous solution by adjustment to pH 3.4 with NaOH, followed by recrystallization from distilled water: UV λ_{max} (ϵ) (1.0 M HCl) 269 nm (25100), 292 nm (20600); (0.05 M KPO_4, pH 7.0) 218 nm (31900), 297 nm (30100). Anal. Calcd for $C_{19}H_{23}N_7O_6 \cdot 1.3H_2O$: C, 48.67; H, 5.50; N, 20.91. Found: C, 48.71; H, 5.52; N, 20.89.

(6*R*)-Tetrahydrofolic Acid. The above series of experiments was repeated starting with D-serine methyl ester with similar results yielding the unnatural (6*R*)-epimer of tetrahydrofolic acid (97.5 ± 0.5% enantiomeric purity).

N^5-Formyl-(6*S*)-tetrahydrofolic Acid. A crude reaction mixture containing 0.056 mmol of (6*S*)-tetrahydrofolic acid was evaporated together with 40 mL of DMF to a final volume of 10.4 mL. The resulting slurry was mostly solubilized by addition of 1% v/v of 98% formic acid. After centrifugation, the supernate was found to contain 0.042 mmol of **1a**, the remainder being associated with the undissolved salts. The clear supernate was sparged with argon and 13.6 mg (0.084 mmol) CDI dissolved in dry DMF added in two aliquots with vigorous stirring. Analysis by HPLC (Spherisorb ODS2, 5 mM Bu_4NPO_4, pH 5.7/MeOH (7:3), 1.0, 285, +0.5) showed 0.035 mmol of N^5-formyl-(6*S*)-tetrahydrofolic acid with 8% of starting material remaining. The chromatographic properties and UV spectra were identical to authentic material.

Enantiomeric purity was established after an initial HPLC purification (as for **1a** above, but without electrochemical detection). The collected fraction was then analyzed by HPLC (Nucleosil-HSA,[37] 50 mM KPO_4, pH 7.1/2-PrOH (24:1), 30 °C, 0.7, 285, +0.8), which showed 97.0–97.5% enantiomeric purity, identical to the starting **1c**.

Pure tetrahydrofolic acid can be similarly formylated, but in 91% initial yield. In this case only 5 mol of formic acid is required per mole of **1c**. No 7,8-dihydrofolate or N^5,N^{10}-methylenetetrahydrofolate was detected, and N^5,N^{10}-methenyl- and N^{10}-formyltetrahydrofolate were both less than 1% of the total absorbance of the chromatogram.

Acknowledgment. This investigation was supported by Grant NS-26662 awarded by the National Institute of Neurological Disorders and Stroke, and Grant GM-30368 awarded by the National Institute of General Medical Sciences. Mass spectra were performed at the University of South Alabama Mass Spectrometry Center, supported by NIH Grant RR 02973.

(37) Domenici, E.; Bertucci, C.; Salvadori, P.; Félix, G.; Cahagne, I.; Motellier, S.; Wainer, I. W. *Chromatographia* **1990**, *29*, 170.

Remote Participation during Photooxidation at Sulfur. Evidence for Sulfurane Intermediates

E. L. Clennan* and Kang Yang

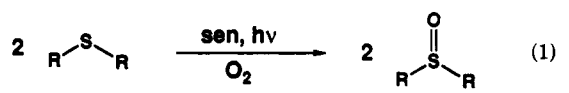
Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Received March 12, 1992

The photooxidations of geminally substituted γ-hydroxy sulfides results in formation of unusual oxidative elimination products. Detailed spectral data and the independent synthesis of a close analogue provide compelling evidence for the structures of these olefins. The formation of the olefins is attributed to decomposition of sulfurane intermediates. This conclusion is supported by a detailed kinetic study which separated the chemical, k_r, and physical, k_q, components to the overall deactivation of singlet oxygen. Those sulfides with the best geometry for sulfide–hydroxyl interaction are also the substrates which react most rapidly with singlet oxygen to give oxidation products. In addition, sulfone yields are in excess of 50% for the hydroxy-substituted sulfides but less than 5% for their hydrocarbon analogues. Several mechanisms that provide explanations for these unusually high sulfone yields are presented.

Sulfides (R_2S) are ubiquitous in the biosphere, and as a result their chemistry has been extensively investigated. Oxidation reactions, in particular, have been thoroughly examined with the realization that sulfides act as antioxidants and are also easily converted into the more highly oxidized sulfoxides (R_2SO) and sulfones (R_2SO_2). Both chemical and photosensitized oxidations are effective in these interconversions. For example, photodynamic destruction of the enzyme α-chymotrypsin occurs by oxidation of methonine-192,[1] and sodium metaperiodate chemically converts penicillin into its *S*-oxide.[2]

The photosensitized oxidations of simple dialkyl sulfides (eq 1) were first reported by Schenck and Krausch[3] in 1962 as a new synthetic method for the formation of sulfoxides. Sulfones (R_2SO_2) are formed in appreciable quantities in



(1)

these reactions only at very low (10^{-3} M) sulfide concentrations and at very low (−78 °C) temperatures. Photooxidation of the sulfoxide product is a very slow reaction and can be eliminated as a viable mechanism for sulfone formation under these reaction conditions.

Foote and co-workers[4] examined the photooxidative formation of diethyl sulfoxide in detail in both aprotic and protic solvents. A mechanism for sulfoxide formation which summarized a large amount of experimental work

(1) Gennari, G.; Jori, G.; Galiazzo, G.; Scoffone, E. *J. Am. Chem. Soc.* **1970**, *92*, 4140–4141.
(2) Cooper, R. D. G.; Hatfield, L. D.; Spry, D. O. *Acc. Chem. Res.* **1973**, *6*, 32–40.
(3) Schenck, G. O.; Krausch, C. H. *Angew. Chem.* **1962**, *74*, 510.
(4) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717–4721.

0022-3263/92/1957-4477$03.00/0

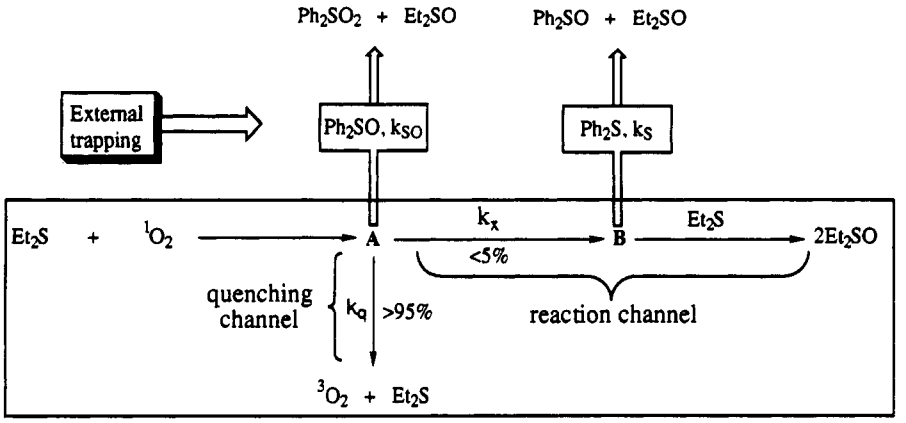
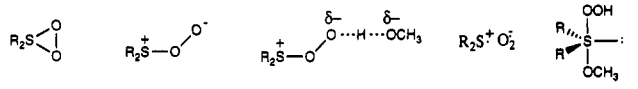


Figure 1.

in benzene and acetonitrile was suggested and is reproduced here in Figure 1. Also included in this figure are the external trapping reactions with diphenyl sulfoxide and diphenyl sulfide[4] which were critical in establishing the existance of two reactive intermediates **A** and **B**. Diphenyl sulfoxide did not react with singlet oxygen under the reaction conditions but did competitively inhibit physical quenching (quenching channel) by trapping a nucleophilic intermediate.[5] Diphenyl sulfide on the other hand was unreactive toward singlet oxygen but competed with diethyl sulfide for an electrophilic intermediate[6] and did not competitively inhibit physical quenching.

In contrast to photooxidations in aprotic solvents, in methanol only one intermediate, **C**, is required kinetically. In addition, physical quenching is suppressed and the formation of diethyl sulfoxide (reaction channel in Figure 1) becomes 100% rather than 5% efficient.

The inability to spectroscopically detect intermediates **A**, **B**, and **C** has hampered their conclusive structural assignments. A variety of structures including thiadioxirane, **1**,[7] persulfoxide, **2**,[8] hydrogen-bonded persulfoxide, **3**,[8] ion pair, **4**,[9] and sulfurane, **5**,[10-12] have been suggested based primarily on circumstantial evidence.

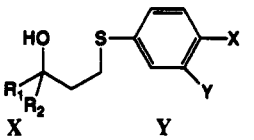


1 **2** **3** **4** **5**

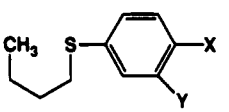
Sawaki and co-workers[13] have examined the photooxidation of several dialkyl and aryl alkyl sulfides. They discovered that in the initial stage of the photooxidation (<4% conversion) that both the sulfoxide and sulfone are formed as major products. ^{18}O tracer studies[13] conducted with *n*-octyl methyl sulfide indicated that the two oxygens in the sulfone product formed in this early stage of the reaction were from the same oxygen molecule, implicating thiadioxirane[7] (**1**) as an intermediate in sulfone formation.[13]

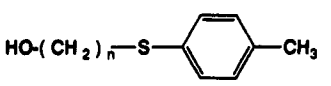
We report here the results of a study specifically designed to provide experimental evidence that intermediate **C** formed in protic solvents is sulfurane (**5**). Our approach has been to study the photooxidations of a series of compounds (Chart I) in which a hydroxy group is intramolecularly tethered to the sulfide.[14] This functional group arrangement has allowed us to exert geometric control over the accessibility of the hydroxy group to the sulfide. Product and kinetic studies for these hydroxy sulfides, and for comparison sulfides without a hydroxy group, are reported in detail and provide a compelling case that at least in these reactions the sulfurane is an authentic intermediate.

Chart I



Compound	X	Y	R_1	R_2
6	Me	H	H	H
7	Me	H	H	Me
8	Me	H	H	tBu
9	Me	H	Me	Et
10	Me	H	Me	iPr
11	Me	H	Me	tBu
12	OMe	H	Me	iPr
13	H	H	Me	iPr
14	F	H	Me	iPr
15	Cl	H	Me	iPr
16	H	Cl	H	H
17	F	H	H	H
18	Cl	H	H	H
19	H	H	H	H
20	OMe	H	H	H





Compound	X	Y	Compound	n
21	OMe	H	27	2
22	Me	H	6	3
23	H	H	28	4
24	F	H	29	5
25	Cl	H	30	6
26	H	Cl		

Results

Product Studies. Photooxidations of hydroxy sulfides **6**–**15** and **27**–**30** and sulfide **22** were conducted at −80 °C by irradiation of acetone-d_6 solutions (2–4) × 10^{-2} M in the sulfide and (1.3–1.6) × 10^{-5} M in the sensitizer Rose Bengal. In the following discussion suffixes **SO**, **SO_2**, **O1**,

(5) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191–194.
(6) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947–5948.
(7) For a critical discussion of the stability of a thiadioxirane, see: Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 2368–2375.
(8) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795–3796.
(9) Inoue, K.; Matsuura, T.; Saito, I. *Tetrahedron* **1985**, *41*, 2177–2181.
(10) Gu, C.-L.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 6060–6063.
(11) Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581–3584.
(12) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787–5792.
(13) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677–2682.

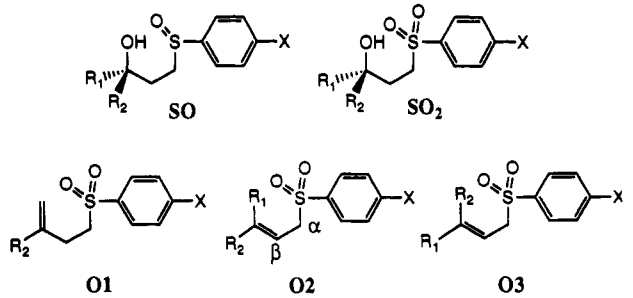
(14) For preliminary accounts of this work see: (a) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044–4046. (b) Clennan, E. L.; Yang, K.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5251–5252.

Table I. NMR Product Yields from Photooxidations of Sulfides[a,b]

compd	% unreacted sulfide	% SO	% SO_2	% O1	% O2	% O3
6	1	43	56			
7		45	55			
8	1	40	59		trace	
9	5	27	68			
10		30	48	15	6.5	0.5
11	5	39	17	21	19	
12		32	56	10	2	
13		28	59	10	3	
14		28	64	6	2	
15		28	67	4	1	trace
22	5	95	1			
27		57	43			
28		48	52			
29		79	21			
30[c]	61	39				

[a] All reactions run in acetone-d_6 at −80 °C using Rose Bengal as the sensitizer unless otherwise noted. [b] Product ratios determined by repetitive cutting and weighing of expanded portions of the NMR spectra, see text for details. [c] Reaction run at −35 °C for 75 min because of solubility problems at −80 °C.

O2, and **O3** are appended to the number used to identify the sulfide in order to designate the corresponding, sulfoxide, sulfone, and olefin (see below) product derived from it by oxidation. A 1-cm 0.5% $K_2Cr_2O_7$ filter solution was used in all the photooxidations in order to prevent absorption of light by either starting materials or products. Product formation during the photooxidations of **6** and **10** in the presence of (3.5–4) × 10^{-3} M 1,4-diazabicyclo-[2.2.2]octane (DABCO) was completely quenched, verifying that singlet oxygen was the oxidative intermediate.



Photooxidations of **6**, **7**, **9**, **22**, and **27–30** led exclusively to the formation of sulfoxides (**SO**) and sulfones (SO_2). The sulfoxides **7SO** and **9SO** which were formed during the photooxidations of **7** and **9** exhibited a doubling of some of the peaks in the ^1H NMR spectra indicative of diastereomer formation. Cutting and weighing of these "doublets" allowed determination of diastereomer ratios of 4/1 and 1.1/1 for **7SO** and **9SO**, respectively. All of the sulfoxides and sulfones except **28SO_2** and **29SO_2** were either isolated chromatographically from the reaction mixtures or synthesized independently by treating the sulfides with 1 or 2 equivalents of *m*-chloroperbenzoic acid (MCPBA). In many cases the submilligram quantities of isolated materials required extended ^{13}C NMR collection times and in some cases completely prevented collection of the ^{13}C NMR spectral data. However, the kinetic behavior (vide infra) and an internal comparison of spectral data in several closely related series (e.g. **10**, **12**, **13**, **14**, **15**, and **6**, **16**, **17**, **18**, **19**, **20**, and their sulfoxides and sulfones) provide compelling evidence for the structures of the products. The yields reported in Table I were determined by cutting and weighing peaks in the expanded aromatic region of the proton NMR spectra. The downfield "doublets" of the aromatic AA′XX′ spin systems for the

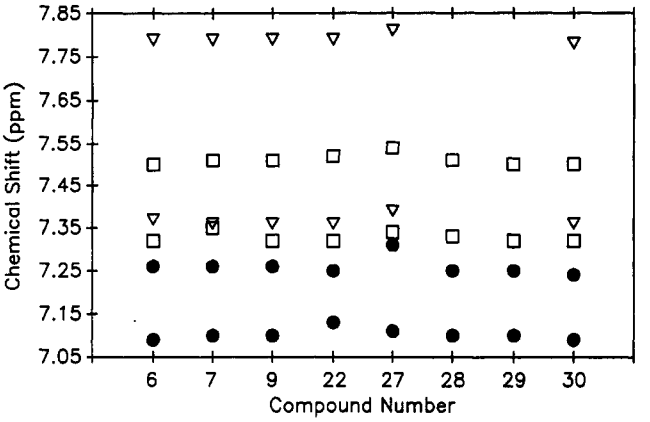


Figure 2. Chemical shifts of the downfield aromatic AA′XX′ "doublets" for sulfides (●), sulfoxides (□), and sulfones (▽).

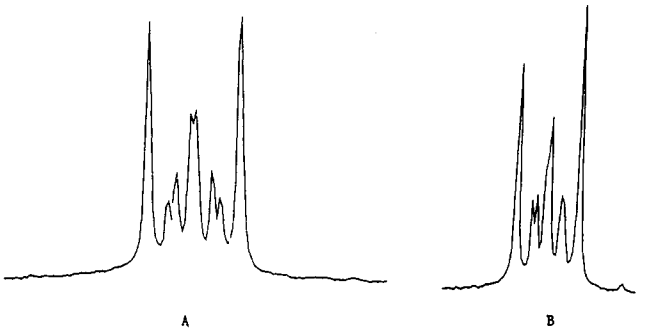


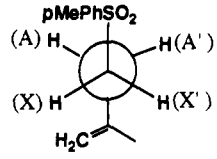
Figure 3. Downfield portion of the ethylene AA′XX′ multiplet for **10O1** (A) and **31** (B).

sulfoxides and sulfones formed in the reactions of **6**, **7**, **9**, **22**, and **27–30** are clearly discernible, as shown diagramatically in Figure 2, and were conveniently used for this analysis.

Photooxidations of **8** and **10–15** resulted in the formation of the unusual olefins **O1**, **O2**, and **O3** in addition to the anticipated sulfoxide diastereomers and sulfones, **SO** and **SO_2**. The diastereomer ratios for **8SO**, **10SO**, and **11SO** were 4.3/1, 1.2/1, and 2.0/1, respectively. Small peaks possibly due to formation of minor amounts of hydroperoxides or aldehydes were also observed between 9.7 and 10 ppm in the proton spectra. Hydroperoxides could arise by ene reactions of the trisubstituted olefins, **O2** and/or **O3**, or by oxidation α to sulfur.[15] Aldehydes have previously been observed in sulfide photooxidations and their formations attributed to reduction and cleavage of transient α-hydroperoxy sulfides.[16] These minor NMR peaks were only observed in the photooxidations that generated olefins, but their small quantities precluded isolation and definitive verification of origin. The product ratios of the photooxidations of **7–10** as a function of solvent are reported in Table II. Hydroxy sulfide **10** gave the olefins in all the solvents examined including methanol.

Olefins **O1** exhibit two slightly broadened singlets in the vinyl region of the proton NMR indicative of a vinyl methylene. These vinyl protons appear at 4.65 and 4.76 ppm in both **10O1** and in the independently synthesized olefin **31**. In addition, the striking similarity of the ethylene AA′XX′ spin systems (downfield portions shown in Figure 3) in these two olefins provide corroborating evidence for the structure of **10O1**. The ethylene AA′XX′ spin system for **10O1** was successfully simulated using δ_A

(15) Takata, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767–4770.
(16) Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, 4263–4266.



31

$= \delta_{A'} = 2.45$ ppm, $\delta_X = \delta_{X'} = 3.19$ ppm, $J_{AA'} = 13$ Hz, $J_{AX} = J_{A'X'} = 3$ Hz, $J_{A'X} = J_{AX'} = 8.75$ Hz, and $J_{XX'} = 14$ Hz (protons labeled as in **31**). The vinyl carbons in **10O1** appear at 108.2 (CH_2) and 151.8 ppm (CR_2) and in **31** at 111.8 (CH_2) and 141.5 ppm (CR_2). The downfield shift (141.8 → 151.8) of the disubstituted vinyl carbon in **10O1** in comparison to **31** is the anticipated effect of two additional β carbon atoms.[17]

Olefins **O2** exhibit characteristic triplets in the vinyl region for the β hydrogens and associated doublets between 3.7 and 3.9 ppm for the methylene α to the sulfonyl sulfur. The only disubstituted olefin that was observed, **8O2**, exhibited a doublet at 5.43 ppm (J = 15.7 Hz) and a doublet of triplets at 5.32 ppm (J = 15.7 and 7.0 Hz) and is clearly trans. The double bond stereochemistry in the trisubstituted olefin **10O2**[18] was conveniently established with a difference NOE experiment (Figure 4). Low-power irradiation of the allylic methylene protons (d) adjacent to the sulfonyl group resulted in intensity enhancements at methyl (b), double-bond hydrogen (c), and aromatic protons ortho to the sulfonyl substituent (e). Irradiation of the methyl protons (b) resulted in intensity enhancements at the isopropyl methyl (a) and allylic methylene (d) protons.

The fate of the hydroxy group in these oxidative elimination reactions was explored by photooxidation of a sample of **10** labeled with ^{17}O (δ ^{17}O, 46.5 ppm relative to H_2O). Examination of the reaction mixture after complete disappearance of **10** revealed both a hydroxyl peak at 46 ppm and a new peak at 141 ppm in the ^{17}O NMR spectrum in an 81/19 ratio, respectively. No ^{17}O NMR peaks were observed in unlabeled **10**, **10O1**, **10O2**, or **10O3** with the same number of scans under identical reaction conditions. The ^{17}O peak at 141 ppm is in the range (δ 120–183 ppm) anticipated for sulfonyl (R_2SO_2) oxygen and substantially downfield of that expected for sulfinyl (R_2SO) oxygen (δ −20 to +20 ppm). The ratio of the areas under the peaks at 46 and 141 ppm in the ^{17}O NMR spectrum of the photooxidized reaction mixture is very similar to the ratio [**10SO** + **10SO$_2$**]/[**10O1** + **10O2** + **10O3**], obtained from analysis of the ^1H NMR spectrum of the crude reaction mixture. Indeed, chromatographic separation of the products followed by ^{17}O NMR revealed that only the hydroxyl oxygens in **10SO** and **10SO$_2$** and the sulfonyl oxygens in **10O1**, **10O2**, and **10O3** were labeled. The absence of detectable levels of oxygen-17 in either **10SO** or **10SO$_2$** demands that the hydroxy transfer be completely intramolecular within experimental error.

Kinetic Studies. In addition to chemically reacting with singlet oxygen to give isolable products, the sulfides in Chart I also act as catalysts for the radiationless interconversion of singlet oxygen ($^1\Delta_g$) to its electronic ground state ($^3\Sigma_g$).[19] It is the contribution from this latter process, often referred to as physical quenching (k_q in Figure 1), which is responsible for the low efficiencies of sulfide photooxidations. The reaction efficiency [$(k_r/k_T) \times 100$] can be conveniently determined by measuring the total rate constant for sulfide induced singlet oxygen disappearance, k_T, and the rate constant for the appearance of product, k_r. The chemical rate constant, k_r, will be smaller than k_T to the extent that physical quenching, k_q, contributes to the overall deactivation of singlet oxygen (eq 2).

$$k_T = k_r + k_q \tag{2}$$

The total rate constants for sulfide-induced deactivation of singlet oxygen, k_T, were measured for sulfides **6**, **10**, and **16–30** by irradiating oxygen-saturated solutions of the sulfides and Rose Bengal at 532 nm with a Nd:YAG laser and by monitoring the decrease in the $^1O_2$ phosphorescence intensities as a function of time at 1270 nm.[11,20] A family of five to seven exponentially decaying curves were collected representing the disappearance of singlet oxygen in the absence and in the presence of variable amounts of sulfide. The experimental conditions (see the Experimental Section) were adjusted so that each exponential decay was first order and adequately described by eq 3.

$$-\frac{d[^1O_2]}{dt} = k_{obsd}[^1O_2] \tag{3}$$

$$k_{obsd} = k_d + k_T[\text{sulfide}]$$

The rate constant k_d represents the solvent-induced deactivation of singlet oxygen[21–25] and can be determined along with k_T by plotting k_{obsd} versus the concentration of the sulfide used to collect the exponential decay. Two to three independent measurements were used in every case in order to determine the total rate constants (k_T) listed in Table III. The k_T values for **21–26** and for **6** and **16–20** are linearly related to the Hammett substituent constants[26] (σ_p and σ_m) with reaction constants (ρ) of −1.42 (r = −0.997) and −1.23 (r = −0.988), respectively. These values are very similar to the reaction constant (ρ) of −1.6 reported for the photooxidations of substituted thioanisoles.[27,28]

The chemical rate constants for reaction, k_r, of **6**, **10**, **27**, and **28** in acetone were determined in competition with limonene and for **19**, **23**, **29**, and **30** in competition with (1*R*)-(+)-α-pinene (see supplementary material). The concentrations of the sulfides, [**S**], and the competing olefins were monitored by capillary gas chromatography at a variety of different conversions and the relative rate constants determined from a plot of ln ($[S]_f/[S]_o$) versus ln ($[\text{olefin}]_f/[\text{olefin}]_o$) according to eq 4 where f and o refer to the final and initial concentrations of the substrates.

$$\ln\left(\frac{[S]_f}{[S]_o}\right) = \frac{k_r(S)}{k_r(\text{olefin})} \ln\left(\frac{[\text{olefin}]_f}{[\text{olefin}]_o}\right) \tag{4}$$

The chemical rate constants, k_r(**S**), were found by multiplying the slope of the kinetic plot by k_r for the olefins. The chemical rates of reaction of limonene [(1.74 ± 0.13)

(17) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons, Inc.: New York, 1991.
(18) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, England, 1987.
(19) Foote, C. S. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Vol. 40, pp 139–171.
(20) Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080–5085.
(21) Schmidt, R. *J. Am. Chem. Soc.* **1989**, *111*, 6983–6987.
(22) Schmidt, R.; Brauer, H.-D. *J. Am. Chem. Soc.* **1987**, *109*, 6976–6981.
(23) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760.
(24) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.
(25) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201–6205.
(26) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987.
(27) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761–764.
(28) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765–769.

Table II. Solvent Effects on Product Distributions[a]

compd	solvent	T (°C)	% S	% SO	% SO_2	% O1	% O2	% O3
7	$CDCl_3$	−56		83	17			
	CD_3OD	−56		69	31			
8	$CDCl_3$	−56		64	31		5	
	$(CD_3)_2CO$	−56		42	57		1	
	CD_3OD	−56		52	48			
9	$CDCl_3$	−56		60	40			
	$(CD_3)_2CO$	−56	8	25	66			
	CD_3OD	−56	2	90	8			
10	$(CD_3)_2CO$	−45		30	50	15	5	
	CD_3CN	−45		33	64	2	1	
	$CDCl_3$	−56		53	30	2	3	
	$(CD_3)_2CO$	−56		29	52	14	5	
	CD_3OD	−56		91	5	3	1	

[a] Product yields determined by cutting and weighing appropriate peaks in the proton NMR spectra.

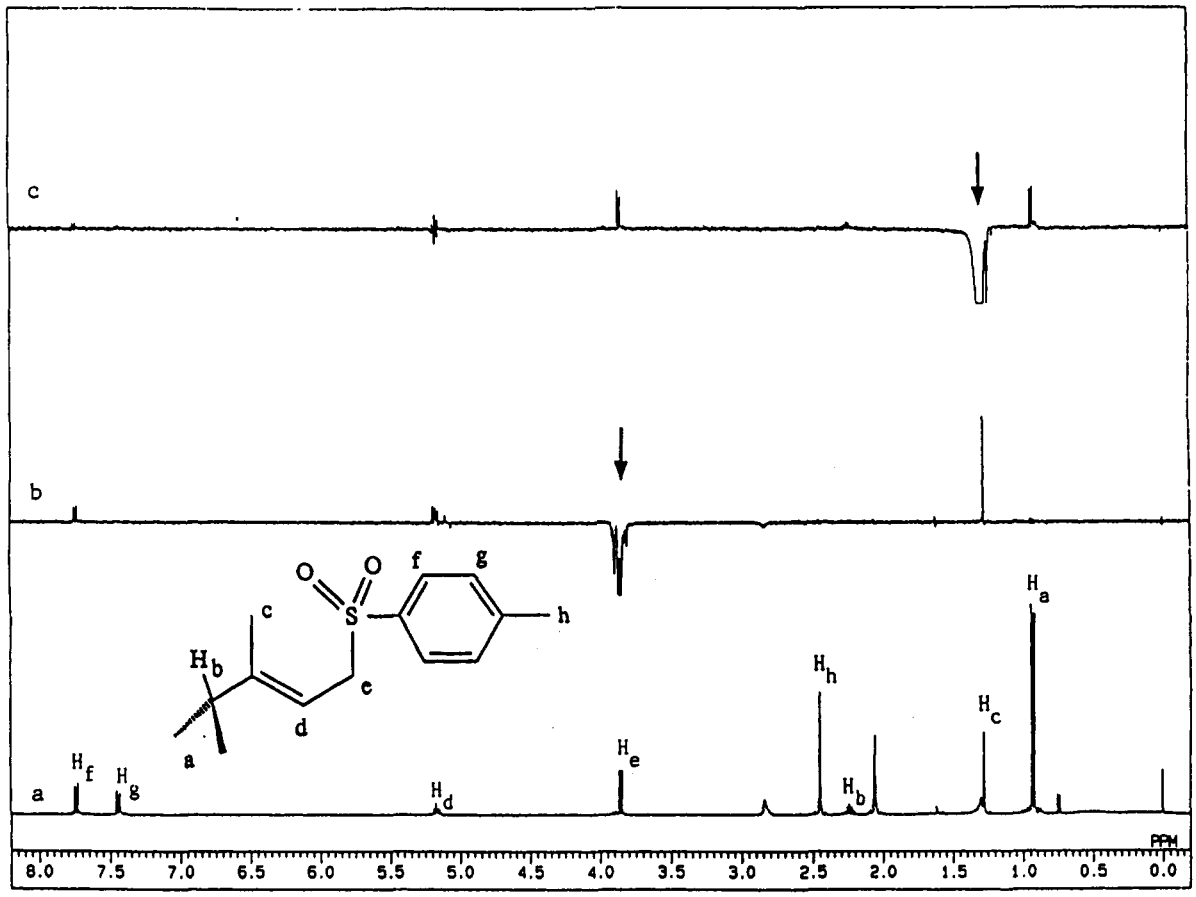


Figure 4. (a) Proton NMR spectrum for **10O2**. (b) NOE difference spectrum of **10O2** generated by irradiation of H_e. (c) NOE difference spectrum of **10O2** generated by irradiation of H_c.

$\times 10^5$ M^{-1} s^{-1}][29] and (1*R*)-(+)-α-pinene [$(4.3 \pm 0.1) \times 10^4$ M^{-1} s^{-1}][29] with singlet oxygen in acetone were determined using the previously described laser phosphorescence apparatus and by assuming that $k_T = k_r$.[30]

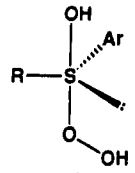
The disappearance of the sulfides were monitored for these experiments because we were unable to prevent extensive decompositions of sulfoxides **29SO** and **30SO** and minor decomposition of sulfoxide **28SO** on the capillary GC column. In contrast, the smaller sulfoxides with two or three carbon alkyl chains were well behaved, and both disappearance of sulfide and appearance of products could be used for relative rate determinations.

Discussion

The formation of olefins during the photooxidations of sulfides **8** and **10–15** can be most easily rationalized by invoking the intermediacy of diastereomeric sulfuranes as depicted in Figure 5 for the reaction of **10**. Examination of molecular models demonstrates that intramolecular hydrogen abstraction by the peroxy anion is geometrically feasible. The hydrogen abstractions lead initially to novel hydroperoxysulfuranes **32** which lose H_2O to form **O1**, **O2**, and **O3**. This mechanism is consistent with the absence of any olefinic sulfoxide and with the ^{17}O NMR tracer experiment which demonstrated that the hydroxy oxygen migrates to sulfur. An intramolecular reaction is also consistent with the observation that no ^{17}O was found in **10SO_2**.

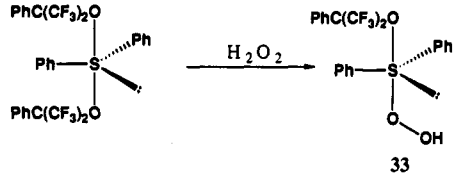
(29) The chemical rate constants for reaction of limonene and α-pinene in MeOH were reported to be 5.9×10^4 and $(1.2\text{–}3.6) \times 10^4$ M^{-1} s^{-1}, respectively. Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809–999.

(30) The following reference reports that simple olefins like 2-methyl-2-pentene react only chemically in contrast to dienes like 2,5-dimethyl-2,4-hexadiene which react both chemically and physically with singlet oxygen. Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4710–4717.

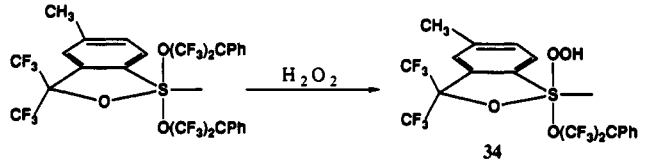


32

The diastereomeric sulfuranes **A** and **B** in Figure 5 are drawn with the two electronegative oxygen ligands occupying apical positions on the trigonal bipyramidal (TBP) framework as anticipated for their most stable conformations.[31] The viability of these elusive hydroperoxysulfurane as intermediates is supported by the report that ligand exchange reactions with hydrogen peroxide produce **33** and **34** which rapidly decompose to give sulfones as the major products.[32]



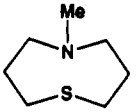
33



34

Only the γ-hydroxy sulfides bearing *gem*-dialkyl groups reacted to give appreciable amounts of olefinic products. This phenomena can be attributed to either (1) Thorpe–Ingold stabilization of the sulfurane allowing hydrogen abstraction to compete with decomposition to sulfone or sulfoxide, (2) steric enforcement of a sulfurane conformation which places the peroxy anion in close proximity to the abstractable hydrogen, or (3) back strain which facilitates transfer of oxygen to sulfur by increasing the ground-state energy of the sulfuranes **A** and/or **B** and decreasing the ground state–transition state energy gap. However, the absence of the olefin formed by loss of the isopropyl methine hydrogen during the photooxidation of **10** appears to rule out complete transfer of the hydroxy group and formation of a carbocation intermediate.

The increase in k_r (Table III) in the series **30** < **29** < **28** ≈ **27** ≪ **6** ≈ **10** parallels the anticipated effect of ring size on sulfurane stability (8 < 7 < 6 ≈ 4 < 5)[31] and further supports the intermediacy of a sulfurane. Martin and co-workers in particular have taken advantage of the stabilizing effect of 5-membered rings in order to synthesize a plethora of stable sulfuranes.[31] The rate enhancing effect of a γ-hydroxy group is also evident in a comparison of sulfides **19** and **23**. Sulfide **19** with a γ-hydroxy group reacts to form products 3 times faster than sulfide **23** in which the γ-hydroxy group has been replaced by a methyl group. A similar 2–5-fold rate enhancement has been observed during a comparison of the oxidations of para- and ortho-substituted thioanisoles with H_2O_2[33] and $NaIO_4$.[34] These rate enhancements are small compared to the rate enhancement of 10^5 reported for the aqueous iodine oxidation of **35** in comparison to thiocane[35] or to the rate



35

enhancements observed when thioether groups participate during solvolysis at carbon.[36] Neighboring group participation in these reactions, however, are entropically favored in comparison to neighboring group participation during photooxidations of the sulfides depicted in Chart I.

Examination of the Foote mechanism in Figure 1 suggests that the increase in k_r in compounds with favorably disposed hydroxy groups could be accompanied by an increase in k_T (anchimeric assistance) or alternatively by an inhibition of physical quenching k_q. Unfortunately, the change in k_r in the series **30**, **29**, **28**, **27**, **6**, **10** (fastest – slowest = 6.49×10^4) is small in comparison to the magnitude of $k_T[(1.5–3.7) \times 10^6]$ or $k_q[(1.46–3.63) \times 10^6]$ and its effect on these rate constants is experimentally undetectable.

The total sulfone yields ([**SO**$_2$] + [**O1**] + [**O2**] + [**O3**]) from photooxidations of all the hydroxy sulfides except **27**, **28**, and **29** (Table I) exceed 50% at 100% conversion to product. Photooxidations of **13**, **14**, and **15** lead to a remarkable 72% yield of sulfone even after complete conversion to product. This is unusual since photooxidation of typical sulfides result in formation of less than 5% sulfone except at low conversions (<4%)[13] when they can account for as much as 30% of the product mass balance. The hydroxy sulfoxide products are unreactive under the reaction conditions and their photooxidations cannot account for these exceptionally high yields of sulfone.

The sulfone yield is sensitive to the identity of the reaction solvent (Table II). For example, methanol dramatically suppresses and acetone slightly accelerates sulfone formation during photooxidations of **9** and **10** in comparison to other solvents. It is tempting to suggest that acetone induces sulfone formation by trapping the persulfoxide intermediates as shown in Figure 6. The presence of a hydroxy group, however, appears to be required; photooxidation of **22** in acetone (Table I) resulted in only a 1% yield of sulfone. Akasaka and Ando[37] have also ruled out the mechanism in Figure 6 by showing the absence of ^{18}O incorporation into dimethyl sulfone during photooxidation of dimethyl sulfide in ^{18}O-labeled acetone-d_6.

Two mechanisms, however, which could potentially account for the large sulfone yields are the following: (1) The hydrogen-bonded hydroxy-substituted sulfoxides[38] produced in the reactions are excellent trapping agents (k_{SO} in Figure 1) as a result of their increased electrophilicity. (2) The hydroxy group promotes formation of a thiadioxirane which subsequently collapses to sulfone.

The viability of mechanism 1 has been explored by examining the ability of **6SO** and **22SO** to trap the intermediate formed in the photooxidation of diethyl sulfide in acetone.[39] Plots of [Et_2SO]/[**6SO2**] versus 1/[**6SO**]

(31) Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, The Netherlands, 1985; Vol. 19, pp 408–483.
(32) Martin, L. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511–3513.
(33) Ruff, F.; Kucsman, A. *Gazz. Chim. Ital.* **1990**, *120*, 241–246.
(34) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1123.
(35) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1981**, *103*, 1159–1163.
(36) Glass, R. S. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990; Vol. 197, pp 213–226.
(37) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203–1204.
(38) Kingsbury, C. A.; Auerbach, R. A. *J. Org. Chem.* **1971**, *36*, 1737–1742.
(39) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909–1910.

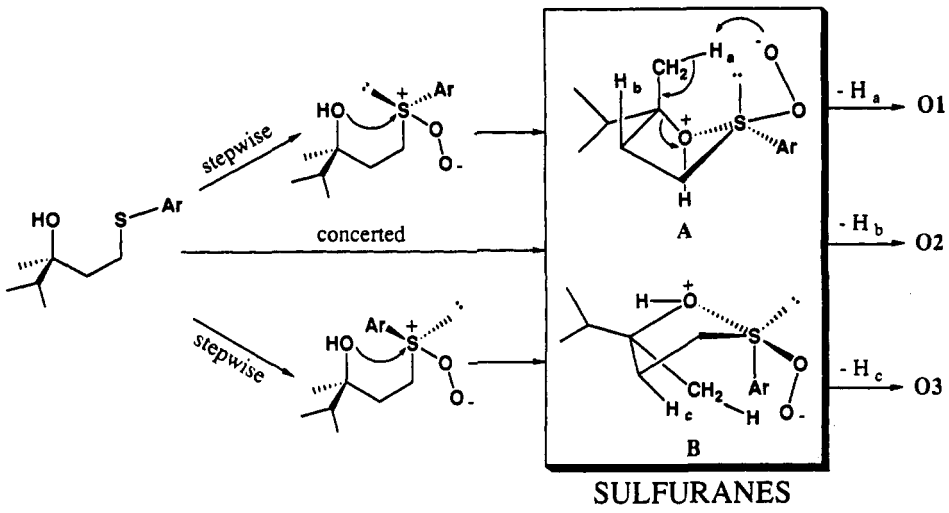


Figure 5.

Table III. Kinetic Data for the Reactions of Singlet Oxygen with Aryl Alkyl Sulfides[a]

compd	σ[b]	$k_T \times 10^{-6}$ (M^{-1} s^{-1})[c]	$k_r \times 10^{-4}$ (M^{-1} s^{-1})[c]	$k_q \times 10^{-6}$ (M^{-1} s^{-1})	k_q/k_r
6	−0.17	2.29 ± 0.2 (1.5)	7.1 ± 0.3 (11.6)	2.22	31.3
10		3.7 (2.4)	7.1 ± 0.5 (11.6)	3.63	51.1
16	0.37	0.60			
17	0.06	1.26			
18	0.23	0.86			
19	0	1.51	3.27 ± 0.03		
20	−0.27	4.07			
21	−0.27	4.28			
22	−0.17	2.83			
23	0	1.63	1.06 ± 0.03	1.62	153
24	0.06	1.25			
25	0.23	0.77			
26	0.37	0.53			
27		1.5 ± 0.1 (1.0)	4.2 ± 0.3 (6.9)	1.46	34.8
28		2.7 ± 0.1 (1.8)	4.1 ± 0.2 (6.7)	2.66	64.9
29		2.9 ± 0.1 (1.9)	1.5 ± 0.1 (2.5)	2.88	192
30		2.2 ± 0.1 (1.5)	0.61 ± 0.02 (1)	2.19	359

[a] All rate constants measured in acetone at room temperature. [b] Errors were determined by the methods reported by Bevington,[56] and Gorond and Ford[57] and are listed at the 95% confidence level. [c] Relative rates in parentheses.

Table IV. Relative Trapping Efficiencies

quencher	k_X/k_{SO}	k_{SO} (rel)
Ph_2SO[a]	0.082	1
$P(OMe)_3$[a]	0.0029	28
22SO[b]	0.111	0.74
6SO[b]	0.012	6.8

[a] In acetonitrile, ref 39. [b] In acetone at room temperature, this work.

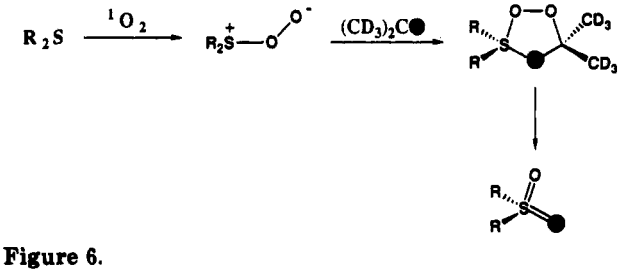


Figure 6.

and of $[Et_2SO]/[22SO2]$ versus $1/[22SO]$ are linear (Figure 7) in acetone with slopes of 0.024 and 0.22, respectively. The slopes are independent of sulfide concentration and obey eq 5 which was derived previously by Foote and co-workers[4] for the mechanism depicted in Figure 1. The values of k_X/k_{SO} were determined from the

$$[Et_2SO]/[(6 \text{ or } 22SO_2)] = 1 + (2k_X/k_{SO})(1/[(6 \text{ or } 22SO)]) \quad (5)$$

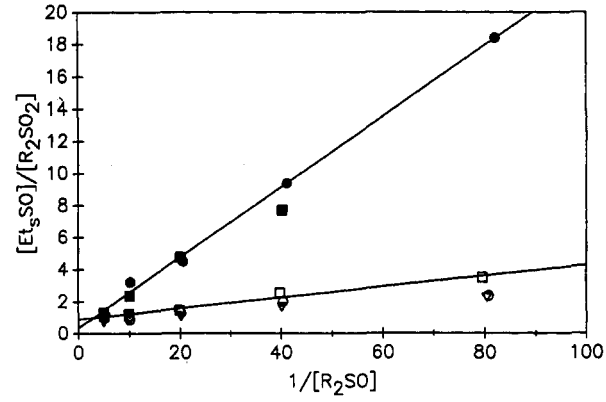


Figure 7. Trapping of the intermediate in diethyl sulfide photooxidation with 6 and 22. Trapping with 22: $[Et_2S]$ (●) 0.1 M, (■) 0.56 M, (▼) 0.01 M. Trapping with 6: $[Et_2S]$ (○) 0.099 M, (□) 0.056 M, (tdo) 0.022 M.

Table V. Trimethyl Phosphite Trapping Experiments[a]

compd	[SO][b,c]	$[SO_2]$[b,c]	[O1][b,c]	[O2][b,c]
7	90 (45)	10 (55)		
8	88 (40)	12 (59)		
9	78 (27)	22 (68)		
10	69 (30)	22 (48)	2 (15)	7 (7)
11	72 (39)	15 (17)	6 (21)	8 (19)

[a] $[P(OMe)_3] = (6–7) \times 10^{-2}$ M; [sulfide] = (5–6) × 10^{-2} M in acetone at room temperature. [b] moles/liter. [c] Values in parentheses are yields in the absence of $P(OMe)_3$.

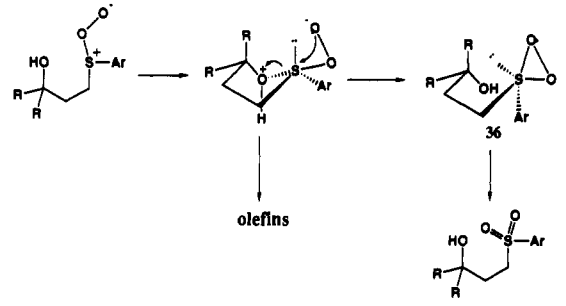


Figure 8.

slopes of the plots in Figure 7 and are listed in Table IV along with previously determined values for comparison. *n*-Butyl *p*-tolyl sulfoxide, **22SO**, is approximately as effective, and hydroxy-substituted sulfoxide, **6**, is 7–9 times better than Ph_2SO in their ability to trap an intermediate in the photooxidation of diethylsulfide. Trimethyl phosphite dramatically reduces the sulfone yields (Table V) during photooxidations of **7–11** as anticipated if it were competing with the hydroxy sulfoxide for a reactive intermediate. There are, however, other potential mechanisms for the trimethyl phosphite suppression of sulfone formation and a more detailed kinetic examination will be required in order to determine the extent, if at all, sulfoxide trapping occurs.

Mechanism 2 is depicted in Figure 8. In this mechanism the hydroxy group acts as a catalyst for the formation of the sulfone by converting a tetrahedral sulfonium ion (persulfoxide) into a trigonal-bipyramidal sulfurane which is closer in geometry to **36** and, consequently, energetically more likely to collapse to the thiadioxirane (Figure 8). This mechanism is supported by the observation that the total sulfone yield increases (0%, 21%, 43%, 52%, 56%, 70%) along the same series, **30 < 29 < 27 < 28 < 6 < 10**, that we previously argued represented increasing hydroxy group participation and by the report that **33** and **34** collapse to give sulfones as the major products. In addition, the increase in olefin formation, **O1**, **O2**, and **O3**, at the expense of hydroxy sulfone, **SO_2**, in the series **9**, **10**, and **11** is consistent with a common intermediate in the two processes (Figure 8).

Methanol in comparison to acetone suppresses sulfone formation during photooxidations of **8**, **9**, and **10** (Table II). The contrasting ability of intramolecular and intermolecular hydroxyl groups to promote sulfone formation is surprising but could be related to the reduction of the nucleophilicity of the apical hydroperoxy anion in the sulfurane intermediate by hydrogen bonding to methanol. The different magnitudes of sulfone suppression, however, reveals that the effect of methanol is complex.

Conclusion

The reactions of $^1O_2$ with a series of hydroxy-substituted sulfides has been presented. The important discoveries include (1) the formation of sulfone olefins concomitant with the transfer of the hydroxy oxygen to sulfur during photooxidations of γ-tertiary hydroxy sulfides, (2) the ability of hydroxy groups to influence the rate of product formation, and (3) unusually high yields of sulfones from photooxidations of hydroxy sulfides.

The formation of olefins and the ability of γ-hydroxy groups to enhance the rate of product formation has been attributed to formation of sulfurane intermediates. The enhanced sulfone yields have been attributed to either efficient trapping of persulfoxide intermediates by the γ-hydroxy sulfoxides formed in the reactions or to the collapse of sulfurane intermediates.

Experimental Section

Analytical gas chromatographic measurements were carried out on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector and a HP 10-m × 0.53-mm cross-linked HP-1 capillary column. Preparative chromatographic separations were carried out on a Harrison Research Model 7624T Chromatotron using plates coated with EM Science 7749 silica gel 60PF254. Proton and carbon NMR were obtained on a JEOL GX270 at 269.7 and 67.8 MHz, respectively, and proton, carbon, and oxygen on a JEOL GX400 at 399.78, 100.53, and 54.21 MHz, respectively. The proton and carbon NMR are referenced to internal TMS and the oxygen-17 NMR to external H_2O.

Methyl vinyl ketone, *p*-thiocresol, sodium methoxide, *p*-methoxythiophenol, thiophenol, *p*-fluorothiophenol, *p*-chlorothiophenol, lithium aluminum hydride, isopropyl bromide, magnesium monoperoxyphthalate hexahydrate, *tert*-butyllithium (1.7 M in pentane), 1-bromobutane, 6-chloro-1-hexanol, and 4-chloro-1-butanol were obtained from Aldrich as used without purification. 3-Bromopropanol was obtained from Aldrich and was purified by distillation. MCPBA and 5-acetoxyamyl chloride were used as received from Sigma. Oxygen-17-labeled water (21.72 atom % ^{17}O, 62.23 atom % ^{18}O) was obtained from Ventron. Hexanes, which were distilled, and ethyl acetate and CH_2Cl_2, which were used as received, were obtained from J. T. Baker. 3-Oxobutyl *p*-tolyl sulfide,[40] 3-oxobutyl *p*-methoxyphenyl sulfide,[40] 3-oxobutyl *p*-chlorophenyl sulfide,[40] 3-oxobutyl *p*-tolyl sulfone,[41] **6**,[42a] **18**,[43] **20**,[44] **21**,[45] **22**,[45] **23**,[45] **25**,[45] **28**,[46] **29**,[42b] **30**,[42b] **31**,[47] **6SO**,[46] **22SO**,[45] **27SO**,[48] **28SO**,[46] **6SO_2**,[49] **7SO_2**,[50] **22SO_2**,[45] and **27SO_2**[51] have previously been reported. The purity of all title compounds was judged to be ≥95% by ^{13}C or ^1H NMR spectral determinations.

Photolysis Conditions. The singlet-oxygen reactions were conducted as previously described.[52]

3-Oxobutyl-^{17}O *p*-tolyl sulfide was synthesized by addition of 0.5 mL of ^{17}O-labeled H_2O (21.72 atom % ^{17}O, 62.23 atom % ^{18}O) and 10 μL of 10% aqueous HCl to a solution of 201 mg (1.04 mmol) of 3-oxobutyl *p*-tolyl sulfide in 5 mL of dry ether. The ether layer was separated after 24 h of stirring at room temperature dried with $MgSO_4$ and removed by rotovap to give the product. ^{17}O NMR ($CDCl_3$) δ (relative to H_2O) 570 ± 2 ppm (line width 550 Hz).

3-Oxobutyl phenyl sulfide was synthesized by addition of 0.85 g (12.1 mmol) of methyl vinyl ketone to a 35-mL absolute ethanol solution of 12.1 mmol of *p*-thiophenol and 0.67 g (12.4 mmol) of $NaOCH_3$ which had been refluxing for 4 h. The resulting mixture was refluxed for an additional 4 h and then the ethanol removed by rotovap and the residue extracted with diethyl ether. The ether layer was washed with aqueous saturated sodium chloride and dried with $MgSO_4$. The product was purified by chromatotron using hexane/ethyl acetate as the eluting solvent and was obtained in 61% yield: ^1H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 2.76 (t, J = 7.2 Hz, 2 H), 3.13 (t, J = 7.2 Hz, 2 H), 7.15–7.4 (m, 5 H).

3-Oxobutyl *p*-fluorophenyl sulfide was synthesized via Michael addition as described for the synthesis of 3-oxobutyl

(40) Tilak, B. D.; Desai, H. S.; Deshpande, C. V.; Jain, S. K.; Vaidya, V. M. *Tetrahedron* **1966**, *22*, 7–23.
(41) Gopalan, A. S.; Jacobs, H. K. *Tetrahedron Lett.* **1990**, *31*, 5575–5578.
(42) (a) Truce, W. E.; Lindy, L. B. *J. Org. Chem.* **1961**, *26*, 1463–1467. (b) Nambara, T.; Matsuhisa, N. *Yakugaku Zasshi* **1963**, *83*, 642–647; *Chem. Abstr.* **1963**, *59*, 7411f.
(43) *Chem. Abstr.* **1988**, *108*, 55838h.
(44) Casalini, C.; Cesarano, G.; Mascellani, G. *Anal. Chem.* **1977**, *49*, 1002–1004.
(45) Galliani, G.; Rindone, B. *J. Chem. Res.* (*S*) **1981**, 74–75.
(46) Harpp, D. N.; Vines, S. M.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* **1976**, *41*, 3987–3992.
(47) Gaoni, Y. *J. Org. Chem.* **1982**, *47*, 2564–2571.
(48) McCormick, J. E.; McElhinney, R. S. *J. Chem. Res.* (*S*) **1983**, 176–177.
(49) Moreau, R.; Adam, Y.; Loiseau, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1978**, *287*, 39–42.
(50) Chinchilla, R.; Najera, C.; Pardo, J.; Yus, M. *Tetrahedron: Asymmetry* **1990**, *1*, 575–578.
(51) Biwas, G. K.; Bhattacharyya, P. *Synth. Commun.* **1991**, *21*, 569–573.
(52) Clennan, E. L.; Chen, X.; Koola, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 5193–5199.

phenyl sulfide and was obtained in 46% yield: ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3 H), 2.72 (t, J = 7.3 Hz, 2 H), 3.07 (t, J = 7.3 Hz, 2 H), 6.97–7.04 (m, 2 H), 7.33–7.38 (m, 2 H).

3-Methyl-3-butenyl *p*-tolyl sulfone, 31,[47] was synthesized by addition of a 10-mL anhydrous diethyl ether solution of 3-oxobutyl *p*-tolyl sulfone (250 mg, 1.1 mmol) to 10 mL of diethyl ether 1.4 mM in Ph_3PCH_2. The ylide Ph_3PCH_2 was synthesized by addition of 0.9 mL of 1.7 M $(CH_3)_3CLi$ in hexane to 566 mg (1.4 mmol) of triphenylmethylphosphonium iodide in 10 mL of diethyl ether followed by stirring for 3 h. The solution containing the sulfone and ylide was allowed to stir for 6 h and the precipitate removed by filtration. The ether layer was washed with water and dried with $MgSO_4$. The product was obtained in a very low 1% yield after purification by TLC using 4/1 hexane/ethyl acetate as the eluting solvent: ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 2.39 (m, 2 H), 2.46 (s, 3 H), 3.19 (m, 2 H), 4.65 (s, 1 H), 4.76 (s, 1 H), 7.37 (d, J = 7.8 Hz, 2 H), 7.79 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 22.4, 30.4, 54.8, 111.8, 128.1, 129.9, 136.1, 141.5, 144.7.

3-Hydroxypropyl *p*-tolyl sulfide, 6,[42a] was synthesized by a modified method of Nambara and Matsuhisa[42b] using sodium methoxide rather than KOH as the base. The product was obtained in 60% yield after purification on the chromatotron: ^{1}H NMR ($CDCl_3$) δ 1.7–1.8 (bs, 1 H), 1.89 (pent, J = 7 Hz, 2 H), 2.30 (s, 3 H), 3.00 (t, J = 7 Hz, 2 H), 3.76 (m, 2 H), 7.10 (d, J = 7.9 Hz, 2 H), 7.27 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.93 (q, J = 126 Hz), 31.02 (t, J = 135 Hz), 31.76 (t, J = 129 Hz), 61.39 (t, J = 142 Hz), 129.67 (d, J = 153 Hz), 130.11 (d, J = 162 Hz), 132.34 (s), 136.21 (s).

3-Hydroxybutyl *p*-Tolyl Sulfide, 7. An 800-mg portion of 3-oxobutyl *p*-tolyl sulfide was added to 165 mg of $LiAlH_4$ in 15 mL of diethyl ether and allowed to stir at 0 °C for 3 h. This solution was warmed to room temperature and worked up using the procedure of Fieser and Fieser;[53] 676 mg of the alcohol (84% yield) was obtained: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 6.2 Hz, 3 H), 1.54 (bd, 1 H), 1.74 (dt, J = 6.8, 7.3 Hz, 2 H), 2.31 (s, 3 H), 2.9–3.1 (m, 2 H), 3.9–4.0 (m, 1 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.26 (m, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{11}H_{16}SO$: C, 67.29; H, 8.23. Found: C, 67.40; H, 8.27.

3-Hydroxybutyl *p*-tolyl sulfoxide, 7SO: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 6.2 Hz, 3 H), 1.67 (bs, 1 H), 1.68–2.0 (m, 2 H), 2.43 (s, 3 H), 2.8–3.1 (m, 2 H), 3.88 (bs, 1 H), 7.35 (d, J = 8.1 Hz, 2 H), 7.51 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ (* reveals the presence of a second diastereomer) 21.32, 23.39, 31.47*, 31.88, 53.51*, 53.62, 66.02*, 66.10, 124.05*, 124.11, 129.87, 139.60, 139.82*, 141.42.

3-Hydroxy-4,4-dimethylpentyl *p*-tolyl sulfide, 8: ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 1.55–1.85 (m, 3 H), 2.31 (s, 3 H), 2.9–3.2 (m, 2 H), 3.4 (m, 1 H), 7.09 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.97 (q, J = 124 Hz), 25.60 (q, J = 125 Hz), 32.25 (t, J = 126 Hz), 33.87 (t, J = 142 Hz), 34.93 (s), 78.64 (d, one of the peaks obscured by $CHCl_3$), 129.66 (d, J = 158 Hz), 130.01 (d, J = 162 Hz), 132.75 (s), 136.06 (s). Anal. Calcd for $C_{14}H_{22}SO$: C, 70.53; H, 9.32. Found: C, 70.35; H, 9.32.

3-Hydroxy-4,4-dimethylpentyl *p*-tolyl sulfoxide, 8SO: ^{1}H NMR ($CDCl_3$) δ (* in the minor diastereomer) 0.89 (s, 9 H), 0.90* (s, 9 H), 1.55–1.78 (m, 1 H), 1.9–2.12 (m, 1 H), 2.41 (s, 3 H), 2.8–3.15 (m, 3 H), 3.88* (d, J = 7.3 Hz, 1 H), 3.92 (d, J = 7.3 Hz, 1 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H).

3-Hydroxy-4,4-dimethylpentyl *p*-tolyl sulfone, 8SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9 H), 1.55–1.68 (m, 1 H), 1.93–2.07 (m, 1 H), 2.45 (s, 3 H), 3.1–3.44 (m, 4 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 8.1 Hz, 2 H).

4,4-Dimethyl-2-pentenyl *p*-tolyl sulfone, 8O2: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 2.44 (s, 3 H), 3.71 (d, J = 6.7 Hz, 2 H), 5.32 (dt, J = 6.7, 15.7 Hz, 1 H), 5.43 (d, J = 15.7 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.70 (d, J = 8.1 Hz, 2 H).

3-Hydroxy-3-methylpentyl *p*-tolyl sulfide, 9: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.5 Hz, 3 H), 1.16 (s, 3 H), 1.38 (s, 1 H), 1.50 (q, J = 7.5 Hz, 2 H), 1.73–1.79 (m, 2 H), 2.32 (s, 3 H), 2.93–2.99 (m, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{13}H_{20}SO$: C, 69.58; H, 9.00. Found: C, 69.53; H, 8.97.

3-Hydroxy-3-methylpentyl *p*-tolyl sulfoxide, 9SO: ^{1}H NMR ($CDCl_3$) δ (* peaks due to second diastereomer) 0.86 (t, J = 7.7 Hz, 3 H), 0.86* (t, J = 7.7 Hz, 3 H), 1.13 (s, 3 H), 1.15* (s, 3 H), 1.25 (s, 1 H), 1.42–1.55 (m, 2 H), 1.68–1.94 (m, 2 H), 2.42 (s, 3 H), 2.76–2.9 (m, 1 H), 2.9–3.1 (m, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.51 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.17, 21.36, 26.00, 26.28*, 33.24, 34.54, 34.98*, 51.75, 51.80*, 71.56, 124.16, 129.87, 140.26, 141.37.

3-Hydroxy-3-methylpentyl *p*-tolyl sulfone, 9SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.5 Hz, 3 H), 1.13 (s, 3 H), 1.22 (s, 1 H), 1.47 (q, J = 7.5 Hz, 2 H), 1.8–1.9 (m, 2 H), 2.46 (s, 3 H), 3.15–3.25 (m, 2 H), 7.36 (d, J = 8.2 Hz, 2 H), 7.79 (d, J = 8.2 Hz, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-Tolyl Sulfide, 10.[54] A 1.2-g (48-mol) sample of Mg turnings and a small iodine crystal were placed in 100 mL of dry ether, and 6.1 g (49 mmol) of isopropyl bromide was added at a rate that maintained a vigorous reflux. After the addition was complete, 0.58 g (3 mmol) of 3-oxobutyl *p*-tolyl sulfide in 2 mL of dry ether was added dropwise. After 20 min of stirring water was added and the product extracted with ether. The ether washes were combined and dried with $MgSO_4$. The product was obtained in 21% yield after purification by chromatotron using 4/1 hexane/ethyl acetate as eluent: ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 7.0 Hz, 3 H), 0.91 (d, J = 7.0 Hz, 3 H), 1.10 (s, 3 H), 1.39 (s, 1 H), 1.70 (hept, J = 7.0 Hz, 1 H), 1.73–1.8 (m, 2 H), 2.32 (s, 3 H), 2.94–3.02 (m, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.84 (q, J = 125 Hz), 17.52 (q, J = 125 Hz), 20.98 (q, J = 125 Hz), 22.80 (q, J = 124 Hz), 28.97 (t, J = 139 Hz), 37.18 (d, J = 128 Hz), 38.89 (t, J = 127 Hz), 74.72 (s), 129.65 (d, J = 159 Hz), 129.82 (d, J = 159 Hz), 132.73 (s), 136.04 (s).

3-Hydroxy-3-methylpentyl *p*-tolyl sulfoxide, 10SO: ^{1}H NMR ($CDCl_3$) δ (* peak revealing the presence of a second diastereomer) 0.83–0.93 (m, 6 H), 1.06 (s, 3 H), 1.07* (s, 3 H), 1.65–1.95 (m, 3 H), 2.02* (s, 1 H), 2.07 (s, 1 H), 2.42 (s, 3 H), 2.8–3.1 (m, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 7.51 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.9, 17.0, 17.5*, 17.6*, 21.4, 22.7, 31.6, 31.7*, 37.2, 37.8*, 51.5, 51.8*, 73.6, 124.1, 124.2*, 129.9, 140.0, 141.0. Anal. Calcd for $C_{14}H_{22}SO_2$: C, 66.08; H, 8.73. Found: C, 66.02; H, 8.72.

3-Hydroxy-3-methylpentyl *p*-tolyl sulfone, 10SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 3 H), 0.90 (d, 6.8 Hz, 3 H), 1.05 (s, 3 H), 1.37 (bs, 1 H), 1.64 (hept, J = 6.8 Hz, 1 H), 1.8–1.9 (m, 2 H), 2.1–3.3 (m, 2 H), 2.46 (s, 3 H), 7.36 (d, J = 7.8 Hz, 2 H), 7.78 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0 (q, J = 126 Hz), 17.6 (q, J = 126 Hz), 21.8 (q, J = 127 Hz), 22.7 (q, J = 126 Hz), 31.9 (t, J = 129 Hz), 37.7 (d, J = 127 Hz), 52.1 (t, J = 137 Hz), 73.7 (s), 128.2 (d, J = 165 Hz), 130.1 (d, J = 161 Hz), 136.3 (s), 144.5 (s). Anal. Calcd for $C_{14}H_{22}SO_3$: C, 62.80; H, 8.22. Found: C, 61.63; H, 8.21.

3-Isopropyl-3-butenyl *p*-tolyl sulfone, 10O1: ^{1}H NMR ($CDCl_3$) δ 0.98 (d, J = 7.0 Hz, 6 H), 2.18 (hept, J = 7.0 Hz, 1 H), 2.45 (m, 2 H), 2.46 (s, 3 H), 3.18 (m, 2 H), 4.65 (s, 1 H), 4.76 (s, 1 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.57, 21.64, 26.9, 34.0, 55.4, 108.2, 128.1, 129.9, 136.2, 144.7, 151.8.

(*E*)-3,4-Dimethyl-2-pentenyl *p*-tolyl sulfone, 10O2, was isolated as a mixture along with a small amount of **10O3**: ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 7.3 Hz, 6 H), 1.24 (s, 3 H), 2.24 (hept, J = 7.3 Hz, 1 H), 2.44 (s, 3 H), 3.78 (d, J = 7.9 Hz, 2 H), 5.2 (t, J = 7.9 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H) [peaks at 0.74 (d, J = 6.8 Hz, 6 H), 3.90 (d, J = 8.3 Hz, 2 H), 5.08 (t, J = 8.1 Hz, 1 H) revealed the presence of a small amount of **10O3**]; ^{13}C NMR ($CDCl_3$) δ 13.5 (q, J = 126 Hz), 20.9 (q, J = 126 Hz), 21.6 (q, J = 127 Hz), 37.0 (d, J = 128 Hz), 56.0 (t, J = 137 Hz), 108.6 (d, J = 161 Hz), 128.7 (d, J = 166 Hz), 129.5 (d, J = 160 Hz), 136.0 (s), 144.4 (s), 151.7 (s).

3-Hydroxy-3,4,4-trimethylpentyl *p*-tolyl sulfide, 11: ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9 H), 1.15 (s, 3 H), 1.36 (s, 1 H), 1.7–2.0 (m, 2 H), 2.31 (s, 3 H), 2.9–3.5 (m, 2 H), 7.10 (d, J = 8.2 Hz, 2 H), 7.26 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.89, 20.98, 25.16, 29.64, 35.55, 38.21, 76.37, 129.57, 129.65, 132.94, 135.93.

3-Hydroxy-3,4,4-trimethylpentyl *p*-tolyl sulfoxide, 11SO: ^{1}H NMR ($CDCl_3$) δ (* peak revealing the presence of a second diastereomer) 0.92* and 0.94 (s, 9 H), 1.08 (s, 3 H), 1.7–1.9 (m, 2 H), 2.04* (s, 1 H), 2.07 (s, 1 H), 2.42 (s, 3 H), 2.68–3.2 (m, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H).

(53) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons Inc.: New York, 1967; Vol. 1.

(54) Clennan, E. L.; Oolman, K. A.; Yang, K.; Wang, D.-X. *J. Org. Chem.* **1991**, *56*, 4286–4289.

3-Hydroxy-3,4,4-trimethylpentyl *p*-tolyl sulfone, 11SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H), 1.06 (s, 3 H), 1.25 (s, 1 H), 1.75–1.9 (m, 1 H), 2.0–2.1 (m, 1 H), 2.46 (s, 3 H), 3.05–3.18 (m, 1 H), 3.28–3.4 (m, 1 H), 7.36 (d, J = 8.2 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H).

3-*tert*-Butyl-3-butenyl *p*-tolyl sulfone, 11O1: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 2.46 (s, 3 H), 2.47 (m, 2 H), 4.56 (s, 1 H), 4.89 (s, 1 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.81 (d, J = 8.1 Hz, 2 H). The two hydrogens α to the sulfonyl group were obscured by other peaks in the reaction mixture.

(*E*)-3,4,4-Trimethyl-2-pentenyl *p*-tolyl sulfone, 11O2: ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 2.44 (s, 3 H), 3.86 (d, J = 7.7 Hz, 2 H), 5.25 (t, J = 7.7 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H). The vinyl methyl group was not observed because of overlap.

3-Hydroxy-3,4-dimethylpentyl *p*-methoxyphenyl sulfide, 12: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 7.3 Hz, 3 H), 0.90 (d, J = 6.6 Hz, 3 H), 1.08 (s, 3 H), 1.38 (s, 1 H), 1.65–1.8 (m, 3 H), 2.9–3.0 (m, 2 H), 3.80 (s, 3 H), 6.85 (d, J = 8.6 Hz, 2 H), 7.36 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.82 (q, J = 125 Hz), 17.49 (q, J = 130 Hz), 22.78 (q, J = 126 Hz), 30.40 (t, J = 140 Hz), 37.06 (d, J = 125 Hz), 38.90 (t, J = 124 Hz), 55.32 (q, J = 144 Hz), 75.74 (s), 114.54 (d, J = 159 Hz), 126.38 (s), 132.96 (d, J = 161 Hz), 158.82 (s).

3-Hydroxy-3,4-dimethylpentyl *p*-methoxyphenyl sulfoxide, 12SO: ^{1}H NMR ($CDCl_3$) δ (* reveals the presence of a second diastereomer) 0.85* (d, J = 7.8 Hz, 3 H), 0.87 (d, J = 6.8 Hz, 3 H), 0.92* (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.07 (s, 3 H), 1.08* (s, 3 H), 1.65–1.75 (m, 1 H), 1.75–1.9 (m, 2 H), 2.17 (s, 1 H), 2.8–3.1 (m, 2 H), 3.86 (s, 3 H), 7.04 (d, J = 8.8 Hz, 2 H), 7.56 (d, J = 8.8 Hz, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-methoxyphenyl sulfone, 12SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.26 (s, 1 H), 1.64 (hept, J = 6.8 Hz, 1 H), 1.84–1.94 (m, 2 H), 3.16–3.3 (m, 2 H), 3.89 (s, 3 H), 7.03 (d, J = 8.8 Hz, 2 H), 7.84 (d, J = 8.8 Hz, 2 H).

3-Isopropyl-3-butenyl *p*-methoxyphenyl sulfone, 12O1: ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 6.8 Hz, 6 H), 2.18 (hept, J = 6.8 Hz, 1 H), 2.42–2.45 (m, 2 H), 3.16–3.22 (m, 2 H), 3.90 (s, 3 H), 4.60 (s, 1 H), 4.80 (s, 1 H), 7.03 (d, J = 9.0 Hz, 2 H), 7.85 (d, J = 9.0 Hz, 2 H).

(*E*)-3,4-Dimethyl-2-pentenyl *p*-methoxyphenyl sulfone, 12O2: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.8 Hz, 6 H), 1.25 (s, 3 H), 3.78 (d, J = 8.0 Hz, 2 H), 3.88 (s, 3 H), 5.21 (t, J = 8.0 Hz, 1 H), 6.98 (d, J = 8.8 Hz, 2 H), 7.77 (d, J = 8.8 Hz, 2 H). The isopropyl methine hydrogen was lost in the noise.

3-Hydroxy-3,4-dimethylpentyl phenyl sulfide, 13: ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 7.3 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.11 (s, 3 H), 1.39 (s, 1 H), 1.71 (hept, J = 7.0 Hz, 1 H), 1.75–1.86 (m, 2 H), 2.96–3.09 (m, 2 H), 7.15–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 16.84 (q, J = 125 Hz), 17.50 (q, J = 125 Hz), 22.71 (q, J = 126 Hz), 28.10 (t, J = 140 Hz), 37.15 (d, J = 123 Hz), 38.70 (t, J = 127 Hz), 74.73 (s), 125.8 (d, J = 162 Hz), 128.81 (d, J = 161 Hz), 128.87 (d, J = 161 Hz), 136.54 (s). Anal. Calcd for $C_{13}H_{20}SO$: C, 69.58; H, 9.00. Found: C, 69.67; H, 9.01.

3-Hydroxy-3,4-dimethylpentyl phenyl sulfoxide, 13SO: ^{1}H NMR ($CDCl_3$) δ (* peaks revealing the presence of a second diastereomer) 0.81* (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.8 Hz, 3 H), 0.89* (d, J = 6.8 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 1.04 (s, 3 H), 1.06* (s, 3 H), 1.62–1.7 (m, 1 H), 1.77–1.95 (m, 2 H), 2.77–3.09 (m, 2 H), 7.24–7.62 (m, 5 H).

3-Hydroxy-3,4-dimethylpentyl phenyl sulfone, 13SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.84 (d, J = 6.8 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 1.03 (s, 3 H), 1.23 (s, 1 H), 1.62 (hept, J = 7.0 Hz, 1 H), 1.79–1.93 (m, 2 H), 3.13–3.3 (m, 2 H), 7.56 (m, 2 H), 7.64 (m, 2 H), 7.90 (m, 2 H).

3-Isopropyl-3-butenyl phenyl sulfone, 13O1: ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 6 H), 2.18 (hept, J = 6.8 Hz, 1 H), 2.42–2.46 (m, 2 H), 3.17–3.21 (m, 2 H), 4.58 (s, 1 H), 4.78 (s, 1 H), 7.57 (m, 2 H), 7.65 (m, 1 H), 7.91 (m, 2 H).

(*E*)-3,4-Dimethyl-2-pentenyl phenyl sulfone, 13O2: ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.8 Hz, 6 H), 1.23 (s, 3 H), 3.78 (d, J = 8.0 Hz, 2 H), 5.19 (t, J = 8.0 Hz, 1 H), 7.5–7.54 (m, 2 H), 7.59–7.64 (m, 1 H), 7.84 (m, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-fluorophenyl sulfide, 14: ^{1}H NMR ($CDCl_3$) δ 0.84 (d, J = 7.3 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 1.08 (s, 3 H), 1.33 (s, 1 H), 1.62–1.8 (m, 3 H), 2.9–3.01 (m, 2 H), 6.95–6.99 (m, 2 H), 7.31–7.34 (m, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-fluorophenyl sulfoxide, 14SO: ^{1}H NMR ($CDCl_3$) δ (* reveals the presence of a second diastereomer) 0.85* (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 6.8 Hz, 3 H), 0.92* (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.07 (s, 3 H), 1.09* (s, 3 H), 1.25 (s, 1 H), 1.65–1.95 (m, 3 H), 2.78–2.93 (m, 1 H), 2.98–3.12 (m, 1 H), 7.21–7.26 (m, 2 H), 7.61–7.65 (m, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-fluorophenyl sulfone, 14SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 6.8 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.25 (bs, 1 H), 1.6–1.7 (hept, J = 6.8 Hz, 1 H), 1.8–1.95 (m, 2 H), 3.15–3.31 (m, 2 H), 7.24–7.28 (m, 2 H), 7.93–7.96 (m, 2 H).

3-Isopropyl-3-butenyl *p*-fluorophenyl sulfone, 14O1: ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 6.8 Hz, 6 H), 2.18 (hept, J = 6.8 Hz, 1 H), 2.42–2.46 (m, 2 H), 3.19–3.23 (m, 2 H), 4.61 (s, 1 H), 4.81 (s, 1 H), 7.22–7.28 (m, 2 H), 7.93–7.97 (m, 2 H).

(*E*)-3,4-Dimethyl-2-pentenyl *p*-fluorophenyl sulfone, 14O2: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.8 Hz, 6 H), 1.25 (s, 1 H), 2.24 (hept, J = 6.8 Hz, 1 H), 3.80 (d, J = 8.0 Hz, 2 H), 5.21 (t, J = 8.0 Hz, 1 H), 7.18–7.26 (m, 2 H), 7.85–7.89 (m, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-chlorophenyl sulfide, 15: ^{1}H NMR ($CDCl_3$) δ 0.88 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.12 (s, 3 H), 1.31 (s, 1 H), 1.68–1.84 (m, 3 H), 2.94–3.07 (m, 2 H), 7.26 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.83 (q, J = 126 Hz), 17.51 (q, J = 126 Hz), 22.69 (q, J = 126 Hz), 28.31 (t, J = 140 Hz), 38.57 (t, J = 127 Hz), 74.69 (s), 128.98 (d, J = 166 Hz), 130.10 (d, J = 163 Hz), 131.69 (s), 135.12 (s).

3-Hydroxy-3,4-dimethylpentyl *p*-chlorophenyl sulfoxide, 15SO: ^{1}H NMR ($CDCl_3$) δ (* reveals the presence of a second diastereomer) 0.84* (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 6.8 Hz, 3 H), 0.92* (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.08* (s, 3 H), 1.25 (s, 1 H), 1.6–1.95 (m, 3 H), 2.77–3.13 (m, 2 H), 7.51 (d, J = 8.8 Hz, 2 H), 7.57 (d, J = 8.8 Hz, 2 H).

3-Hydroxy-3,4-dimethylpentyl *p*-chlorophenyl sulfone, 15SO$_2$: ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.24 (s, 1 H), 1.65 (hept, J = 6.8 Hz, 1 H), 1.81–1.94 (m, 2 H), 3.15–3.32 (m, 2 H), 7.56 (d, J = 8.5 Hz, 2 H), 7.86 (d, J = 8.5 Hz, 2 H).

3-Isopropyl-3-butenyl *p*-chlorophenyl sulfone, 15O1: ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.8 Hz, 6 H), 2.18 (hept, J = 6.8 Hz, 1 H), 2.41–2.45 (m, 2 H), 3.18–3.23 (m, 2 H), 4.61 (s, 1 H), 4.82 (s, 1 H), 7.57 (d, J = 8.3 Hz, 2 H), 7.87 (d, J = 8.3 Hz, 2 H).

(*E*)-3,4-Dimethyl-2-pentenyl *p*-chlorophenyl sulfone, 15O2: ^{1}H NMR ($CDCl_3$) δ 0.94 (d, J = 6.8 Hz, 6 H), 1.27 (s, 3 H), 2.23 (hept, J = 6.8 Hz, 1 H), 3.81 (d, J = 8.2 Hz, 2 H), 5.20 (t, J = 8.2 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 2 H).

3-Hydroxypropyl *m*-chlorophenyl sulfide, 16, was synthesized by nucleophilic substitution of bromide in 3-bromo-1-propanol using the modified method of Nambara and Matsuhisa[42b] as reported for the synthesis of 6: ^{1}H NMR ($CDCl_3$) δ 1.89 (p J = 6.8 Hz, 2 H), 3.04 (t, J = 6.9 Hz, 2 H), 3.76 (t, J = 5.9 Hz, 2 H), 7.1–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 29.7, 31.4, 61.08, 125.83, 126.58, 128.05, 129.83, 134.60, 138.58.

3-Hydroxypropyl *p*-fluorophenyl sulfide, 17, was synthesized by nucleophilic substitution of bromide in 3-bromo-1-propanol using the modified method of Nambara and Matsuhisa[42b] as reported for the synthesis of 6: ^{1}H NMR ($CDCl_3$) δ 1.83 (p, J = 6.4 Hz, 2 H), 2.09 (bs, 1 H), 2.97 (t, J = 7.3 Hz, 2 H), 3.73 (t, J = 5.9 Hz, 2 H), 6.96–7.03 (m, 2 H), 7.32–7.37 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.47, 31.59, 61.12, 115.96 (d, J_{CF} = 21.9 Hz), 130.92, 132.14 (d, J_{CF} = 8.6 Hz), 161.67 (d, J_{CF} = 246.6 Hz).

3-Hydroxypropyl phenyl sulfide, 19, was synthesized in 61% yield by nucleophilic substitution of bromide in 3-bromo-1-propanol using the modified method of Nambara and Matsuhisa[42b] as reported for the synthesis of 6: ^{1}H NMR ($CDCl_3$) δ 1.86 (p, J = 6.6 Hz, 2 H), 2.12 (bs, 1 H), 3.01 (t, J = 7.3 Hz, 2 H), 3.73 (t, J = 6.4 Hz, 2 H), 7.14–7.35 (m, 5 H).

Butyl *p*-fluorophenyl sulfide, 24: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.38–1.46 (m, 2 H), 1.53–1.61 (m, 2 H), 2.86 (t, J = 7.3 Hz, 2 H), 6.9–7.1 (m, 2 H), 7.2–7.35 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.61, 21.84, 31.24, 34.65, 115.88 (d, J_{CF} = 22 Hz), 131.70, 131.93 (d, J_{CF} = 132 Hz), 161.59 (d, J_{CF} = 246 Hz).

Butyl *m*-chlorophenyl sulfide, 26: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.41–1.49 (m, 2 H), 1.60–1.68 (m, 2 H), 2.92

(t, J = 7.3 Hz, 2 H), 7.09–7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.59, 21.92, 30.95, 32.87, 125.54, 126.36, 127.83, 129.77, 134.59, 139.41.

2-Hydroxyethyl *p*-tolyl sulfide, 27, was synthesized by a modified method of Nambara and Matsuhisa[42b] using sodium methoxide rather than KOH as the base. The product was obtained in 90% yield after purification on the chromatotron. ^{1}H NMR ($CDCl_3$) δ 2.1 (bt, 1 H), 2.33 (s, 3 H), 3.06 (t, J = 6.1 Hz, 2 H), 3.70 (dt, J = 4.9, 6.1 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.03, 38.10, 60.13, 129.85, 130.78, 131.12, 137.04.

2-Hydroxyethyl *p*-tolyl sulfoxide, 27SO,[48] was synthesized in 77% yield by treating **27** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.87–2.95 (m, 1 H), 3.07–3.15 (m, 1 H), 3.9–4.04 (m, 1 H), 4.13–4.24 (m, 2 H), 7.34 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.31, 56.49, 59.00, 123.93, 130.01, 139.65, 141.64.

5-Hydroxypentyl *p*-tolyl sulfoxide, 29SO, was synthesized in 78% yield by treating **29** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 1.4–1.85 (m, 6 H), 2.41 (s, 3 H), 2.54 (bs, 1 H), 2.75–2.86 (m, 2 H), 3.6 (t, J = 6.0 Hz, 2 H), 7.32 (d, J = 7.9 Hz, 2 H), 7.50 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.33 (q, J = 127 Hz), 21.93 (t, J = 129 Hz), 24.80 (t, J = 126 Hz), 32.02 (t, J = 126 Hz), 57.05 (t, J = 139 Hz), 61.97 (t, J = 141 Hz), 123.99 (d, J = 162 Hz), 129.86 (d, J = 161 Hz), 140.22 (s), 141.46 (s).

6-Hydroxyhexyl *p*-tolyl sulfoxide, 30SO, was synthesized in 94% yield by treating **30** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 1.33–1.8 (m, 8 H), 2.2 (bs, 1 H), 2.41 (s, 3 H), 2.75–2.86 (m, 2 H), 3.6 (t, J = 6.0 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.36, 22.12, 25.29, 28.37, 32.32, 57.14, 62.52, 124.01, 129.87, 140.53, 141.38.

6-Hydroxyhexyl *p*-tolyl sulfone, 30SO$_2$: ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (m, 9 H), 2.46 (s, 3 H), 3.04–3.1 (m, 2 H), 3.61 (t, J = 6.4 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.60, 22.66, 25.18, 27.99, 32.20, 56.23, 62.56, 128.02, 129.86, 136.11, 144.60.

Total Rate Constant (k_T) Determination. The kinetic apparatus consists of a Spectra-Physics DCR11 Nd:YAG pulsed laser with second and third harmonic capability and a germanium diode detector and has previously been described in detail.[11,20]

Sample preparation was conducted by adding varying amounts of a stock solution of the substrate to a stock solution of oxygen saturated Rose Bengal. This method insured the same Rose Bengal concentration in each experiment. At least five pseudo-first-order rate constants were collected for each substrate. This experiment was repeated at least twice with fresh stock solutions.

Chemical Rate Constant (k_r) Determination. The chemical rate constants were determined using the method of Higgins, Foote, and Cheng.[55]

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Supplementary Material Available: Plots for the competitive determination of k_r for **6**, **10**, **19**, **23**, and **27–30** and ^{1}H NMR spectra of new compounds (50 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(55) 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.
(56) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.
(57) Gordon, A. J.; Ford, R. A. *The Chemists Companion: A Handbook of Practical Data, Techniques, and References*; John Wiley & Sons: New York, 1972.

Cationic Carbon to Nitrogen Rearrangements in the Reactions of *N*-(Sulfonyloxy)amines with Aldehydes

Robert V. Hoffman* and James M. Salvador

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003-0001

Received March 6, 1992

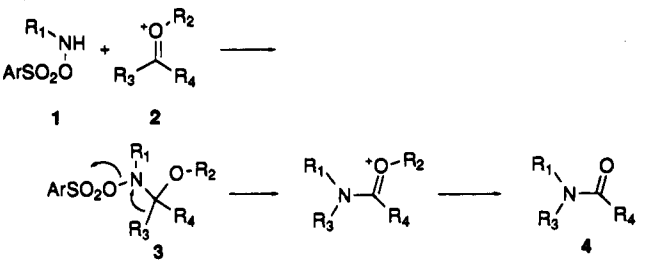
A series of aromatic and aliphatic aldehydes was reacted with *N*-((*p*-nitrobenzenesulfonyl)oxy)methylamine in chloroform. Products resulting from both carbon migration and hydride migration to nitrogen were isolated. The ratios of carbon to hydride migration products were used to clarify the reaction mechanism. The results support a two-step process in which cationic carbon to nitrogen rearrangement is rate determining.

Introduction

We have previously reported that *N*-(sulfonyloxy)amines **1** add rapidly to oxonium ions **2** generated from ketones or ketone derivatives. The resulting tetrahedral intermediates **3** undergo rapid skeletal rearrangement by cationic carbon to nitrogen migration and yield rearranged amides **4** as products. The general process is summarized in Scheme I.[1]

The needed oxonium ions **2** can be generated by protonation of either enol ethers[2] or ketones[3] or by acid-catalyzed elimination in acetals.[4] The *N*-(sulfonyloxy)amines **1** are produced from the reaction of amines with sulfonyl peroxides.[5] While initial studies often utilized *N*-((*p*-nitrobenzenesulfonyl)oxy)methylamine (**1a**, R_1 = Me, Ar = *p*-$NO_2C_6H_4$), a variety of other *N*-(nosyloxy)amines were used subsequently. These experiments revealed that the addition of *N*-(nosyloxy)amines to oxonium ions, which produces the tetrahedral rearrangement precursor **3**, is sensitive to steric size in the *N*-(nosyloxy)amine **1** as well as to ring strain effects in cyclic oxonium ions **2**. Thus, best results were obtained when R_1 is methyl or a primary

Scheme I



(1) Hoffman, R. V. *Tetrahedron* **1991**, *47*, 1109.
(2) Hoffman, R. V.; Salvador, J. M. *J. Chem. Soc., Perkins Trans. 1* **1989**, 1375.
(3) Hoffman, R. V.; Salvador, J. M. *Tetrahedron Lett.* **1989**, *30*, 4207.
(4) Hoffman, R. V.; Salvador, J. M. *Tetrahedron Lett.* **1991**, *32*, 2429.
(5) Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34.

0022-3263/92/1957-4487$03.00/0