evaporated (in vacuo) and the residue was chromatographed over alumina (30 g, eluant, Et_2O–hexanes, 3:7). Two fractions were obtained: F-1, 100 mL, 0.27 g; F-2, 100 mL, 0.22 g. Gas chromatographic analysis (5 ft × 0.25 in., 1.5% OV-101 on 100/120 mesh Chromosorb G, column temperature 150 °C) revealed that F-1 was a 1:5 mixture of **18** and **16** and F-2 was a 5:1 mixture of **16** and **17**. The components were identified by IR, ^1H NMR, and mass spectral analysis and confirmed by comparison with authentic mixtures. On the basis of fraction weights and VPC analysis, the yields were as follows: **16**, 22%; **17**, 2.5%; **18**, 2.25%, and 7% of **8** was recovered.

Oxidative Hydrolysis of Phenylacetic Acid (9). Phenylacetic acid (**9**, 0.68 g, 5 mmol) was oxidized with KO-*t*-Bu (2.80 g, 25 mmol), O_2, and 18-crown-6 (0.33 g, 1.25 mmol, 5.0 mol %) for 48 h at 25 °C as described in the general procedure. After the workup, the crude material was purified by column chromatography (silica, 5:95 (v/v) ether–hexane) to give **12** (0.13 g, 21%) which was identified by NMR and TLC, mp 114–116 °C.

Deuteration of Dihydrocinnamonitrile (4). A 50-mL, round-bottomed flask equipped with a magnetic stirring bar was charged with KO-*t*-Bu (0.45 g, 4 mmol), 18-crown-6 (0.05 g, 0.2 mmol, 5.0 mol %), and THF (15 mL). Dihydrocinnamonitrile (**4**, 0.131 g, 1 mmol) in THF (5 mL) was added dropwise and the solution stirred for 2 h, quenched with D_2O (2 mL), diluted with ether (20 mL), and washed with water (20 mL). The organic phase was dried ($MgSO_4$) and evaporated in vacuo to a pale yellow oil. ^{13}C NMR analysis indicated deuteration at the carbon α to the nitrile function: ^{13}C NMR ($CDCl_3$) 17.88 (m, 4, CHC(D)CN), 31.37 (s, 26, $C_6H_5CH_2$), 127.14 (s, 62, CH), 126.51 (s, 9, ipso carbon), 128.17 (s, 87), 128.7 (s, 100, ortho and meta carbons), 138.01 (s, 6, para carbon).

General Procedures for Entries in Table II. Potassium *tert*-butoxide (1.12 g, 10 mmol) and cyanohexadecane (**7**) in THF solution (25 mL) were stirred at the temperature and for the time period indicated. After addition of water, acidification, and extraction, hexadecanoic (palmitic) acid (**15**) was obtained in the specified yield as a white solid (lit.[18] mp 63–64 °C).

Entry 1. The reaction was conducted under an air atmosphere at 25 °C for 48 h. After workup, **15** was isolated (0.58 g, 90%) as an off-white solid, mp 61–63 °C.

Entry 2. The reaction was conducted under an air atmosphere at 25 °C for 72 h. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C, mmp 61–63 °C.

Entry 3. The reaction was conducted under an air atmosphere at 25 °C for 48 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as a white solid, mp 61–63 °C.

Entry 4. The reaction was conducted under an oxygen atmosphere at 25 °C for 48 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C.

Entry 5. The reaction was conducted under an air atmosphere at THF reflux for 1.5 h. After workup, **15** was isolated (0.05 g, 8%) as an off-white solid, mp 61–63 °C. Unreacted **7** (0.50 g, 79%) was recovered as a white solid, mp 32–34 °C.

Entry 6. The reaction was conducted under an air atmosphere at THF reflux for 1.5 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.26 g, 40%) as an off-white solid, mp 61–63 °C. Unreacted **7** (0.25 g, 39%) was recovered as a white solid, mp 31–32 °C.

Entry 7. The reaction was conducted under an oxygen atmosphere at THF reflux for 1.5 h. After workup, **15** was isolated (0.46 g, 73%) as a white solid, mp 61–63 °C. Unreacted **7** (0.16 g, 26%) was recovered as a white solid, mp 31–32 °C.

Entry 8. The reaction was conducted under an oxygen atmosphere at THF reflux for 1.5 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C.

Entry 9. KOH (0.66 g, 10 mmol, 85% pellets) and 18-crown-6 (0.132 g, 5 mmol), 5 mol %) were heated at reflux with **7** (0.63 g, 2.5 mmol) in THF (25 mL) under a dry O_2 atmosphere for 1.5 h. During this experiment, no ammonia could be detected. After workup, only a trace of **15** could be isolated. Unreacted **7** (0.53 g, 85%) was recovered as a white solid, mp 30–32 °C.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant which supported this work.

Registry No. **1**, 124-12-9; **2**, 4435-14-7; **3**, 140-29-4; **4**, 645-59-0; **5**, 74244-55-6; **6**, 21963-16-6; **7**, 5399-02-0; **8**, 2286-54-6; **9**, 103-82-2; **10**, 111-14-8; **11**, 98-89-5; **12**, 65-85-0; **13**, 13032-41-2; **14**, 884-36-6; **15**, 57-10-3; **16**, 119-61-9; **17**, 3531-24-6; **18**, 530-48-3; potassium *tert*-butoxide, 865-47-4.

Sulfur Heterocycles. 3. Heterogeneous, Phase-Transfer, and Acid-Catalyzed Potassium Permanganate Oxidation of Sulfides to Sulfones and a Survey of their Carbon-13 Nuclear Magnetic Resonance Spectra

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Although numerous oxidation methods are available for the transformation of sulfides into sulfones, low-molecular-weight, heterocyclic sulfides are often not amenable to these oxidation techniques. The method presented here is a general and economical oxidation using potassium permanganate and various catalysts. Nineteen low-molecular-weight and heterocyclic sulfides were successfully oxidized by variations of this technique, and the results are presented here. In addition, the carbon-13 NMR spectra of these compounds and about two dozen others are reported. General chemical shift trends are reported for selected compounds, and details can be found in the supplementary material.

During our recent studies of the thermal demasking of certain oxathiolane *S,S*-dioxides,[2,3] we required a general oxidation method for cyclic sulfides which was effective, rapid, and inexpensive. In addition, we required that the method be reasonably successful for the oxidation of acid-sensitive sulfides, some of which are hemithioacetals.

Although the oxidation of sulfides to sulfones has been accomplished by a variety of methods,[4] for most purposes, hydrogen peroxide (H_2O_2) or peracid (e.g., *m*-chloroper-

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(3) Gerdes, H. M.; Gokel, G. W. *Tetrahedron Lett.* **1979**, 3379.

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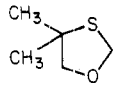
Table I. Solid-Liquid Permanganate Oxidation of 2-Isopropyl-1,3-oxathiolane (13)[a]

solvent	equiv of $KMnO_4$[b]	% yield[d]	solvent	equiv of $KMnO_4$[b]	% yield[d]
CCl_4[c]	2	5	$ClCH_2CH_2Cl$[c]	2	26
CCl_4[c]	5	6	CH_2Cl_2[c]	2	35
C_6H_6[c]	2	13	CH_2Cl_2	2	8
C_6H_6[c]	5	9	CH_2Cl_2[c]	5	41
C_6H_5Cl[c]	2	15	CH_2Cl_2	5	22

[a] At ambient temperature for 24 h according to eq 1. [b] Molar equivalents relative to sulfide; concentration in all runs was 0.04 M. [c] 18-Crown-6 polyether (0.1 molar equiv relative to the sulfide) used in these experiments. [d] Yields are for material having the expected IR and NMR spectral properties obtained at the end of the 24-h period.[8] The time was selected only for the purpose of comparison.

benzoic acid, mCPBA) has generally sufficed. These methods have not always proved satisfactory, however, and alternative methodology has been developed for more specialized applications.[5] Because of our primary interest in the oxidation of 4,4-dimethyl-1,3-oxathiolane (12),[2] we



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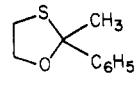

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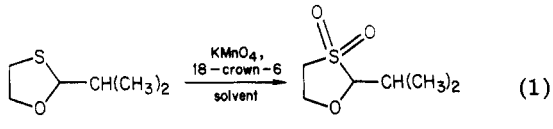
sought methods which had been applied to a directly related system. Few such examples may be found in the literature, although a low yield is reported for the oxidation of 2-methyl-2-phenyl-1,3-oxathiolane (17);[6] the hemithioacetal suffers ring opening.

On the basis of the apparent utility of phase-transferred permanganate ion in sundry organic oxidations,[7] we attempted to develop general conditions for the permanganate-mediated conversion of sulfides into sulfones. During the development of such a method, it became apparent that ^{13}C NMR data on such substituted, two-heteroatom systems were not readily available, and we report data for a number of such sulfur compounds here.

Results and Discussion

Our primary goal in this work was to develop a useful oxidation of cyclic sulfides, especially low-molecular-weight heterocycles, to sulfones. We assumed that a phase-transfer catalytic oxidation[7] using $KMnO_4$ would be useful and surveyed this method first.

Choice of Solvent. In order to determine what organic solvent would be most useful, we oxidized the acid-sensitive and modestly hindered sulfide 2-isopropyl-1,3-oxathiolane (13) in the presence of several common solvents (see eq 1 and Table I).



(1)

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Experiments were conducted both in the presence and absence of 18-crown-6 catalyst, with 2 or 5 equiv of $KMnO_4$/mol of starting sulfide. In all cases, the reactions were conducted at ambient temperature with vigorous stirring for 24 h.[8]

The principal findings of these studies are as follows: (1) the yields are somewhat better in the more polar of the solvents in this group; (2) when the solid–liquid system is employed, yields improve in the more polar solvent systems when a larger excess (5 vs. 2 equiv) of $KMnO_4$ is used. From the results presented in Table I, it seems clear that CH_2Cl_2 is generally the best of the solvents tested in terms of yield and economy. Safety is also a factor favoring this solvent. The increase in sulfone yield which occurs when a larger amount of solid $KMnO_4$ is employed suggests that there is at least some surface reaction.

Preparative Reactions. The successful oxidations recorded in Table II were conducted by using a CH_2Cl_2 solution of the sulfide in contact with twice its volume of equally concentrated aqueous $KMnO_4$ (100 mol % excess of $KMnO_4$) solution. The reaction mixtures were stirred vigorously at room temperature for 24–48 h unless either the substrate proved especially prone to undergo oxidation or the product appeared unstable to the reaction conditions. In such cases, shorter reaction times (specified in Table II) generally proved useful.

An important finding of this work is that the presence of a phase-transfer catalyst did not generally improve the reaction yield. In fact, we were unable to obtain useful yields of 2-phenyl-2-methyl-1,3-oxathiolane 3,3-dioxide under any of the conditions attempted. The indifference of the reaction to the presence of a phase-transfer catalyst suggests that the reaction is largely heterogeneous, not a surprising observation considering the polar nature of the substrates.

If the actual oxidation occurs largely at the phase boundary as presumed, the oxidation should slow as the number of carbons per sulfur or polar functional group increases. As anticipated, 2-*n*-hexyl-4,4-dimethyl-1,3-oxathiolane (18) was oxidized only slowly in the two-phase CH_2Cl_2/H_2O system. When a phase-transfer catalyst was added in these cases, enhanced yields were generally realized. The substituted heterocycles having six or seven carbons in the alkyl group could be oxidized by using the ptc method, but the workups were so difficult (emulsions, etc.) that yields were poor. In such cases, addition of glacial acetic acid proved efficacious.

Acetic acid has shown utility in many permanganate oxidations, and the oxidation of certain 1,2-dithiolanes in its presence has been reported.[18] More recently, several alkenes have been successfully converted to acyloins by using potassium permanganate in aqueous acetone in the presence of acetic acid.[19] The latter apparently served as both proton donor and organic/aqueous miscible cosolvent. Both of these roles are probably fulfilled in our

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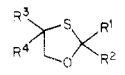
Table II. Preparation of Sulfones by Permanganate Oxidation[a]

compd	substrate	catal	mol % catal[b]	T, h	% yield[c] of sulfone: catal	% yield[c] of sulfone: no catal[d]	obsd mp, °C (or bp °C/torr)	lit. mp, °C (ref)
1	Et_2S	BTEAC[e]	10	12	98	95	71-73	72 (10)
2	$MeOCH_2SOMe$			0.25		68 (55)	(67/0.25)	
3	$MeOCH_2SCMe_3$			48		85	(78/0.08)	
4	$MeOCH_2SPh$			48		100 (95)[f]	67.5-68.5	69-70 (11)
5	tetramethylene sulfide	BTEAC	10	12	88	86	21-25	28-45 (12)
6	pentamethylene sulfide	BTEAC	10	12	94 (80)	93	97-98	97-98 (13)
7	hexamethylene sulfide	BTEAC	10	12	99 (78)	98	71.5-73	71-71.5 (14)
8	PhSMe	BTEAC	10	12	100	100	85.5-86.5	86-86.5 (15)
9	1,4-oxathiane	BTEAC	10	12	67 (43)	74	130-131	134 (16)
10	1,3-oxathiolane	BTEAC	10	11	32		87-88	87-88 (17)
				0.25		76 (66)		
								
	R^1 R^2 R^3 R^4							
11	Me Me H H			0.5		83 (73)	44-46	
12	H H Me Me			24		80 ± 5[g]	46-50	
13	*i*-Pr H H H			24		100 (91)	69-71	
14	Ph H H H	BTEAC	10	1.0	2.5		99-100	
				1.0		47		
				1.75		68		
				2.0		46		
15	CH_2Ph H H H			5.0		100 (72)	95-96.5	
16	4-tol H H H			2.0		46	131-133	
				3.5		38		
17	Ph Me H H	BTEAC	10	1.0	0			56-57 (6)
		BTEAC	10	24	0			
				12		0		
18	n-C_6H_{13} H Me Me	Bu_4NHSO_4	10	68	73[h] (49)		oil	
		HOAc[i]	200	14	87 (67)			
				96		64 (32)		
19	n-C_6H_{13} Me Me Me			48		0	oil	
				96		0		
		HOAc[i]	200	48	100 (64)			

[a] Sulfide (0.02 mol) dissolved in dichloromethane (50 mL) in contact with $KMnO_4$ (0.04 mol) in water (100 mL) for the time specified. [b] Mole percent; i.e., 100 mol % = 1 molar equiv. [c] Yield is of material which is pure by NMR and IR analysis. The numbers in parentheses refer to the yield of material whose spectral properties are as above but which are of analytical purity or have melting or boiling points identical with those in the literature. [d] All conditions identical with those of the catalyzed cases except for the absence of catalyst. [e] Benzyltriethylammonium chloride.[9] [f] 300 mol % $KMnO_4$ used in this experiment. [g] A range of 75-85% was observed in over a dozen oxidation reactions with these conditions. [h] Estimated by NMR to be 3:1 starting material-product. [i] Benzene used as solvent; see the Experimental Section.

cases involving acetic acid as well.

Carbon-13 Magnetic Resonance Spectra. Although this report is primarily concerned with the oxidation of sulfur-containing heterocycles, we felt it would be valuable to record the ^{13}C NMR spectra to augment the existing literature.[20-27] A brief summary of our data is presented in Table III; the complete table is available as supplementary material.

Chemical Shift Trends. In all of the five-, six-, and seven-membered rings examined (including 1,3-oxathiolane and 1,4-oxathiane), the effect of monoxidation at sulfur was to shift the α-carbon resonances downfield by about 20 ppm (20.2 ± 2.3 ppm). Dioxidation of these sulfur compounds produced generally smaller shifts.

The chemical shifts of the 1,3-oxathiolane ring carbons were identified with the following shift ranges: C-2, 91.7 ± 4.3 ppm; C-4, 33.4 ± 1.2 ppm; C-5, 71.0 ± 1.3 ppm. In the substituted 1,3-oxathiolane 3,3-dioxides, the chemical shift ranges were as follows: C-2, 92.2 ± 4.2 ppm; C-4, 52.6 ± 5.4 ppm. The C-5 chemical shift depended on ring substitution. When C-2 was substituted, C-5 was in the range 62.9 ± 2.1 ppm, and when substituted at C-4, the chemical shift of C-5 was 79.9 ± 2.7 ppm. A detailed table of chemical shift data for approximately 40 sulfur compounds in various oxidation states is available as supplementary material.

Summary

We describe here a useful and economical method for the preparation of several small-ring sulfur heterocycles. The reaction appears to be largely heterogeneous, being only marginally affected by most phase-transfer catalysts, although addition of acetic acid proved beneficial for the especially lipophilic compounds.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary device and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 as Nujol mulls unless otherwise

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Table III. Representative ^{13}C NMR Chemical Shifts of Compounds Containing both Oxygen and Sulfur in Various Oxidation States[a]

no.	compd	chemical shift[b] methyl	1[c]	2[c]	4[c]	5[c]
20	$MeOC^1H_2SO_2$-C^2Me_3	60.5 (Me), 23.1 (Bu)	83.0	59.3		
21	$MeOCH_2SO_2Ph$[d]	61.0	87.7			
10	1,3-oxathiolane			72.2	32.2	71.8
22	1,3-oxathiolane 3-oxide			93.3	53.7	68.8
23	1,3-oxathiolane 3,3-dioxide			82.7	49.1	67.8
11	2,2-dimethyl-1,3-oxathiolane	31.3		92.0	34.6	70.4
24	2,2-dimethyl-1,3-oxathiolane 3,3-dioxide	21.2		90.0	47.5	60.8
25	4,4-dimethyl-1,3-oxathiolane 3,3-dioxide	19.1		82.8	55.4	79.0
26	2,4,4-trimethyl-1,3-oxathiolane 3,3-dioxide[e]	13.9, 18.8, 21.3		88.8	55.5	77.0
27	2-(trimethylsilyl)-4,4-dimethyl-1,3-oxathiolane 3,3-dioxide[e]	-3.8, 19.3, 21.4		89.0	56.6	82.3
28	2-phenyl-4,4-dimethyl-1,3-oxathiolane 3,3-dioxide[e]	19.1, 21.5		94.5	55.6	77.3

[a] Additional data is given as supplementary material. [b] Spectra recorded in $CDCl_3$ and shifts are reported in parts per million relative to internal Me_4Si. Shifts are probably accurate to ±0.3 ppm. [c] IUPAC position number is used unless otherwise indicated. [d] Aromatic carbons observed at 128.6, 129.1, 133.9, and 137.1 ppm. [e] Assignment of the 4-methyl group shifts to *E* or *Z* carbons relative to the 2-substituent is uncertain.

specified and are calibrated against the 1601-cm^{-1} band of polystyrene. Proton NMR spectra were recorded on either a Varian A60A or EM-360 spectrometer as ca. 15 wt % solutions in $CDCl_3$ unless otherwise specified. Carbon-13 NMR spectra were recorded either on a JEOL JNM-PS-100 spectrometer (operating at 25.19 MHz) equipped with a Nicolet Instrument Corp. computer or on a Varian CFT-20 as $CDCl_3$ solutions. All chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. Mass spectra were determined on an AEI MS-902 instrument at an ionizing voltage of 79 eV. Gas chromatographic analyses were conducted by using either a Varian Associates Model 2720 or 920 analytical gas chromatograph equipped with a thermal conductivity detector and a 5 ft × 0.25 in., 10% SE-30 column on NAW Chromosorb P. Helium was used as a carrier gas, and the flow rate was ca. 60 mL/min.

Solvents and reagents, including the sulfides, were the best grade commercially available and were used without further purification unless otherwise specified.

Procedure for 18-Crown-6-Catalyzed Solid/Liquid Phase-Transfer $KMnO_4$ Oxidation of 2-Isopropyl-1,3-oxathiolane (13; See Table I). 2-Isopropyl-1,3-oxathiolane (13; 2.64 g, 0.02 mol) and 18-crown-6 (0.53 g, 0.002 mol, 10 mol %) were dissolved in 50 mL of solvent. The specified (Table I) amount of $KMnO_4$ was then added, and the mixture was stirred vigorously for 24 h at ambient temperature. The reaction mixture was filtered, and the reaction vessel was rinsed with 50 mL of solvent which was also filtered. Water (100 mL) was added to the filtrate, and the phases were separated after the mixture was shaken. If the organic phase contained suspended MnO_2, it was filtered, washed with 50 mL of water, and dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude material was recrystallized from hexane. Isolated yields are recorded in Table I. Crown ether was excluded where indicated.

General Procedure for Two-Phase Oxidation of Sulfides (Table II). Procedure A. The appropriate sulfide (0.02 mol), CH_2Cl_2 (50 mL), water (100 mL), and benzyltriethylammonium chloride (BTEAC; 0.46 g, 0.002 mol, 10 mol %) were mixed in a 250-mL Erlenmeyer flask. $KMnO_4$ (6.32 g, 0.04 mol) was added, and the mixture was stirred vigorously at room temperature for 12 h. The mixture was filtered, and the reaction flask was rinsed with 50 mL of solvent which was poured through the filter. The phases were separated, and the aqueous phase was extracted with 50 mL of CH_2Cl_2. The combined organic phase was washed with 50 mL of H_2O containing a little hydrazine dihydrochloride (to reduce any remaining MnO_4^- or MnO_2) and 50 mL of brine and dried (Na_2SO_4). The solvent was removed by rotary evaporation to yield the crude sulfone, which in most cases was quite pure. If necessary, the crude material was purified by distillation or recrystallization.

Procedure B. Procedure B was the same as procedure A except that no catalyst was used.

Oxidation of Diethyl Sulfide (1) in the Presence of BTEAC. Diethyl sulfide (1, 1.80 g) was oxidized as described in procedure A. After the workup, diethyl sulfone (2.40 g, 98%) was isolated as a white solid, mp 71–73 °C.

Oxidation of 1 Without Catalyst. Compound 1 (1.80 g) was oxidized according to procedure B. After the workup, diethyl sulfone (2.33 g, 95%) was isolated as a white solid, mp 71–73 °C.

Preparation of Methoxymethyl Methyl Sulfoxide (2). A 100-mL, three-necked flask was fitted with a dropping funnel, an N_2 inlet, and a magnetic stirring bar and flame dried. NaOMe (44.3 g, 25% solution in MeOH) was added. The solution was cooled in an ice bath, and chloromethyl methyl sulfide (17.5 mL, 20.3 g, of a 95% solution, 0.20 mol) was added dropwise over 20 min. NaCl precipitated during the addition. The mixture was stirred for 30 min at 0 °C and allowed to warm to room temperature during an additional 15 min. The suspension was filtered, and K_2CO_3 was added to the filtrate. The mixture was cooled to 0 °C, H_2O_2 (30%, 100 mL) was added and the mixture then stirred for 1 h. The ice bath was removed, and stirring was continued until the temperature reached 30 °C (ca. 40 min). The solution was then cooled to 0 °C, and 50 mL of 30% H_2O_2 was added. Stirring was continued for an additional 1 h, and then K_2CO_3 (35 g) was added. After the mixture was stirred 10 min, the solution was extracted with CH_2Cl_2 (6 × 150 mL). The organic extracts were dried (Na_2SO_4) and rotary evaporated to yield essentially pure **2** (21.3 g, 99%) as a slightly yellow oil: NMR 2.54 (s, 3 H), 3.60 (s, 3 H), 4.38 (s, 2 H).

Oxidation of 2. Compound **2** (10.0 g) was dissolved in CH_2Cl_2 (200 mL) in a 1-L Erlenmeyer flask. Water (200 mL) and $KMnO_4$ (19.0 g, 0.12 mol) were added, the mixture was stirred vigorously for 15 min and then filtered, and the precipitate was washed with CH_2Cl_2 (200 mL). The filtrate was saturated with NaCl and extracted three times with a total of 400 mL of CH_2Cl_2. The extracts were dried (Na_2SO_4) and evaporated in vacuo to give the crude product (7.82 g, 68%) as a slightly yellow oil. Vacuum distillation afforded a colorless sample of comparable purity: bp 67 °C (0.25 torr); NMR 2.92 (s, 3 H), 3.72 (s, 3 H), 4.46 (s, 2 H). Anal. Calcd for $C_3H_8O_3S$: C, 29.02; H, 6.49. Found: C, 28.88; H, 6.60.

Preparation of Methoxymethyl *tert*-Butyl Sulfide (3). A 500-mL, three-necked flask equipped with a dropping funnel, a magnetic stirbar, and an N_2 inlet was flame dried, and then NaH (7.2 g, 50% dispersion in oil, 0.15 mol) was suspended in dry THF (200 mL). The stirred suspension was cooled in an ice bath, and *tert*-butyl mercaptan (17.1 mL, 13.67 g, 0.15 mol) was added during 10 min. The ice bath was removed and the mixture stirred vigorously for 15 min. The mixture was cooled again, and dry MeOH (30 mL) was added, slowly at first. The resulting brown solution was stirred for about 10 min, and chloromethyl methyl ether (11.75 mL, 12.45 g, 0.15 mol) was added during 5 min. The mixture was stirred for 15 min at 0 °C and then 15 min at ambient temperature. Et_2O (150 mL) was added, and the mixture was cooled to coagulate the salts. The mixture was filtered and the precipitate washed with Et_2O (50 mL). The filtrate was dried (Na_2SO_4), and the solvent was removed in vacuo to yield **3** (17.59 g) as a slightly yellow oil. Distillation through a 10-cm Vigreux column (bp 40–44 °C, water pump) yielded 54% of pure **3**: NMR 1.36 (s, 9 H), 2.32 (s, 3 H), 4.73 (s, 2 H).

Oxidation of 3. Methoxymethyl *tert*-butyl sulfide (10.00 g, 0.746 mol) was dissolved in CH_2Cl_2 (200 mL) in a 1-L Erlenmeyer flask. $KMnO_4$ (23.6 g, 0.149 mol) and water (200 mL) were added, and the mixture was stirred vigorously for 48 h. The mixture was filtered and the precipitate washed with CH_2Cl_2 (200 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (200 mL). The combined organic phase was washed with brine (100 mL) and dried (Na_2SO_4). After rotary evaporation, a light yellow oil (13.68 g) remained which was purified by fractionation through a 10-cm Vigreux column [bp 77–79 °C (0.08 torr)] to yield pure **21**: 10.55 g (85%); NMR 1.43 (s, 9 H), 3.67 (s, 3 H), 4.57 (s, 2 H). Anal. Calcd for $C_6H_{14}O_3S$: C, 43.34; H, 8.49. Found: C, 43.02; H, 8.58.

Preparation of Methoxymethyl Phenyl Sulfide (4). A flask equipped as described for **3** above was charged with sublimed KO-*t*-C_4H_9 (16.82 g, 0.15 mol) and dry THF (300 mL). The solution was cooled to 0 °C, and thiophenol (15.71 mL, 16.86 g, 98% pure, 0.15 mol) was added by syringe. The resulting thick slurry was diluted with MeOH (50 mL) and allowed to cool briefly before dropwise addition of chloromethyl methyl ether (0.15 mol). The mixture was stirred at 0 °C for 30 min and at room temperature for 15 min and was then diluted with Et_2O (150 mL). The mixture was filtered and the solid rinsed with more Et_2O (2 × 50 mL) which was added to the filtrate. The solution was dried (Na_2SO_4), and the crude sulfide was obtained as a yellow oil (22.91 g, 99%). The material appeared pure by NMR analysis [3.32 (s, 3 H), 4.87 (s, 2 H), 7.00–7.55 (m, 5 H)] and was used without further purification.

Oxidation of 4. Methoxymethyl phenyl sulfide (**4**; 6.16 g, 0.04 mol) was dissolved in CH_2Cl_2 (500 mL) in an Erlenmeyer flask. Water (200 mL) and $KMnO_4$ (19.0 g, 0.12 mol) were added, and the mixture was stirred vigorously for 48 h. The mixture was filtered, and the precipitate was washed with CH_2Cl_2. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (100 mL). The combined organic phase was washed with H_2O (50 mL) containing a small amount of $H_2NNH_2 \cdot 2HCl$ and with brine (50 mL) and then dried (Na_2SO_4). After rotary evaporation, **21** was obtained as a clear, colorless liquid which crystallized on cooling. Pure **21** (7.07 g, 95%; mp 67.5–68.5 °C) was obtained after recrystallization from THF–hexane (1:4): NMR 3.70 (s, 3 H), 4.57 (s, 2 H), 7.51–8.20 (m, 5 H).

Oxidation of 5 in the Presence of BTEAC. Tetramethylene sulfide (**5**; 1.76 g) was oxidized as described in procedure A. After the workup, sulfolane (2.10 g, 88%) was isolated as a colorless oil which solidified on cooling; mp 21–25 °C.

Oxidation of 5 without Catalyst. The reaction was conducted according to procedure B to give sulfolane: yield 2.06 g (86%); mp 19–25 °C.

Oxidation of 6 in the Presence of BTEAC. Pentamethylene sulfide (**6**, 2.04 g) was oxidized according to procedure A. After the workup, pentamethylene sulfone (2.53 g, 94%) was isolated as a white solid, mp 93–97 °C. The crude material was pure by NMR and IR analysis, but a sample was recrystallized from THF–hexane (1:2) to afford 2.15 g of product with a melting point of 97.5–98.5 °C.

Oxidation of 6 without Catalyst. Pentamethylene sulfide (**6**, 2.04 g) was oxidized as described in procedure B. After the workup, pentamethylene sulfone (2.50 g, 93%) was isolated as a white solid, mp 97–98.5 °C.

Oxidation of 7 in the Presence of BTEAC. Hexamethylene sulfide (**7**, 2.32 g) was oxidized according to procedure A. After the workup, hexamethylene sulfone (2.93 g, 99%) was isolated as a white solid, mp 64–70 °C. The crude material was pure by IR and NMR analysis, but a sample was recrystallized from THF–hexane (1:4) to yield hexamethylene sulfone: 2.30 g (78%); mp 71.5–73 °C.

Oxidation of 7 without Catalyst. Hexamethylene sulfide (**7**, 2.32 g) was oxidized as described in procedure B. After the workup, hexamethylene sulfone (2.90 g, 98%) was isolated as a white solid, mp 63–70 °C.

Oxidation of 8 in the Presence of BTEAC. Thioanisole (**8**, 2.48 g) was oxidized according to procedure A. After the workup, methyl phenyl sulfone (2.12 g, 100%) was isolated as a white solid, mp 85.5–86.5 °C.

Oxidation of 8 without Catalyst. Thioanisole (**8**, 2.48 g) was oxidized as described in procedure B. After the workup, methyl phenyl sulfone (3.11 g, 100%) was isolated as a white solid, mp 85–86.5 °C.

Oxidation of 9 in the Presence of BTEAC. 1,4-Oxathiane (**9**, 2.08 g) was oxidized according to procedure A. After the workup, 1,4-oxathiane 4,4-dioxide (1.83 g, 67%) was isolated as a white solid, mp 128–130 °C. After recrystallization from MeOH, 1,4-oxathiane 4,4-dioxide was isolated: 1.16 g (43%); mp 130–131 °C.

Oxidation of 9 without Catalyst. 1,4-Oxathiane (**9**, 2.08 g) was oxidized as described in procedure B. After the workup, 1,4-oxathiane 4,4-dioxide (2.00 g, 74%) was isolated as a white solid, mp 129–130 °C.

Preparation of 1,3-Oxathiolane (10). Paraformaldehyde (30.0 g, 1.0 mol), 2-mercaptoethanol (39.0 g, 0.50 mol), *p*-toluenesulfonic acid monohydrate (1 g), and benzene (250 mL) were placed in a 1-L flask equipped with a Dean–Stark trap. The solution was heated at reflux for 90 min, allowed to cool, washed with 5% aqueous Na_2CO_3 (2 × 100 mL) and brine (100 mL), and dried (Na_2SO_4). The solvent was removed by rotary evaporation, and crude **10** was distilled through a 30-cm Vigreux column to yield pure **10**: 26 g (58%); bp 112–124 °C (738 torr) [lit.[17] bp 125–127 (760 torr)]; NMR 2.88 (t, 2 H, J = 6 Hz), 2.86 (t, 2 H, J = 6 Hz), 4.70 (s, 2 H).

Oxidation of 10 in the Presence of BTEAC. 1,3-Oxathiolane (**10**, 1.80 g) was oxidized as described in procedure A. After the workup, 1,3-oxathiolane 3,3-dioxide (**23**; 0.77 g, 32%) was isolated as a white solid, mp 87–88 °C.

Oxidation of 10 without Catalyst. 1,3-Oxathiolane (**10**, 1.80 g) was oxidized as described in procedure B. After the workup, **23** was isolated (1.86 g, 76%) as a white solid which was pure by NMR. Recrystallization from MeOH afforded pure **23**: 1.62 g (66%); mp 87–88 °C; NMR 3.20 (t, 2 H, J = 7 Hz), 4.38 (s, 2 H), 4.46 (t, 2 H, J = 7 Hz).

Preparation of 2,2-Dimethyl-1,3-oxathiolane (11). 2,2-Dimethyl-1,3-oxathiolane was prepared from acetone (29.0 g, 0.5 mol) and 2-mercaptoethanol (39.0 g, 0.50 mol) as described above for the preparation of **10**. Pure **11** was isolated (47.0 g, 80%) as a colorless oil, bp 71–73 °C (70 torr).

Oxidation of 2,2-Dimethyl-1,3-oxathiolane (11). 2,2-Dimethyl-1,3-oxathiolane (**11**, 2.36 g) was oxidized as described in procedure B. The crude product (2.65 g, 88%) was pure by NMR analysis. Recrystallization from THF–hexane (1:4) afforded pure white **24**: 2.20 g (73%); mp 44–46 °C; NMR 1.51 (s, 6 H), 3.20 (t, 2 H), 4.28 (t, 2 H). Anal. Calcd for $C_5H_{10}O_3S$: C, 39.98; H, 6.71. Found: C, 39.85; H, 6.96.

Preparation of 4,4-Dimethyl-1,3-oxathiolane (12). 2-Methyl-2-mercaptopropan-1-ol (64.0 g, 0.60 mol) in benzene (300 mL) was placed in a 1-L, round-bottomed flask equipped with a reflux condenser and a Dean–Stark trap. Paraformaldehyde (36.0 g, 1.2 mol) and *p*-TsOH (1.15 g, 1 mol %) were added, and the mixture was stirred at reflux for 4 h. (At shorter reflux times, a seven-membered ring is isolated.) The mixture was worked up as described for **10** above. Pure **12** (43.0 g, 60%) was isolated after distillation through a 10-cm Vigreux column: bp 55–58 °C (40 torr); NMR 1.42 (s, 6 H), 3.57 (s, 2 H), 4.94 (s, 2 H). In addition, a compound which appeared to be 6,6-dimethyl-1,3-dioxa-5-thiacycloheptane (10 g, 11%) was isolated: bp 92–95 °C (40 torr); NMR 1.32 (s, 6 H), 3.67 (s, 2 H), 4.85 (s, 2 H), 4.90 (s, 2 H).

Oxidation of 12. 4,4-Dimethyl-1,3-oxathiolane (**12**, 14.2 g, 0.12 mol) was dissolved in CH_2Cl_2 (250 mL) and H_2O (250 mL) and $KMnO_4$ (38.0 g, 0.24 mol) were added. The mixture was stirred vigorously for 24 h and filtered, and the precipitate was rinsed with CH_2Cl_2 (250 mL) which was added to the filtrate. The organic phase was washed with H_2O (100 mL, containing 1% $H_2NNH_2 \cdot 2HCl$) and brine (100 mL) and then dried (Na_2SO_4). Pure 4,4-dimethyl-1,3-oxathiolane 3,3-dioxide (**25**; 13.6–15.3 g, 75–85%, ten runs; mp 46–50 °C) was obtained after rotary evaporation. A sample melting at 56–58 °C could be obtained after vacuum drying: IR (neat) 2970, 2925, 2865, 1460, 1436, 1300, 1157, 1120, 1065, 947, 920, 827, 765, 730, 695 cm^{-1}; NMR 1.37 (s, 6 H), 4.03 (s, 2 H), 4.47 (s, 2 H). Anal. Calcd for $C_5H_{10}O_3S$: C, 39.98; H, 6.71. Found: C, 39.63; H, 6.68.

Preparation of 2-Isopropyl-1,3-oxathiolane (13). Isobutyraldehyde (36.0 g, 0.50 mol), 2-mercaptoethanol (39.0 g, 0.50 mol), and TsOH (1 g, 1 mol %) were dissolved in benzene (250 mL), and the solution was heated at reflux until the theoretical

amount of water had separated (Dean–Stark trap). Evaporation of the solvent, followed by distillation through a 30-cm Vigreux column, afforded **13** (48.6 g, 72%) as a colorless oil, bp 55 °C (21 torr) [lit.[14a] bp 29 °C (2.5 torr)].

Oxidation of 2-Isopropyl-1,3-oxathiolane (13). 2-Isopropyl-1,3-oxathiolane (**13**, 2.64 g) was oxidized as described in procedure B. The crude product (3.29 g, 100%) was found to be pure by NMR analysis. Recrystallization from hexane afforded pure 2-isopropyl-1,3-oxathiolane 3,3-dioxide (2.99 g, 91%) as a white solid: mp 69.5–71 °C; NMR 1.10 (d, 6 H, J = 7 Hz), 2.10 (m, 1 H), 3.20 (m, 2 H), 3.73 (d, 1 H), 3.80–4.70 (m, 2 H). Anal. Calcd for $C_6H_{12}O_3S$: C, 43.90; H, 7.32. Found: C, 43.96; H, 7.59.

Oxidation of 2-Phenyl-1,3-oxathiolane (14). 2-Phenyl-1,3-oxathiolane (**14**) was oxidized according to procedure A. The crude product was contaminated with benzaldehyde and benzoic acid. Recrystallization from THF–hexane (1:1) afforded pure 2-phenyl-1,3-oxathiolane 3,3-dioxide: 0.99 g (25%); mp 99–100 °C; NMR 3.23 (m, 2 H), 4.86 (m, 2 H), 5.12 (s, 1 H), 7.45 (s, 5 H). Anal. Calcd for $C_9H_{10}O_3S$: C, 54.55; H, 5.05. Found: C, 54.55; H, 5.10.

Oxidation of 14 without Catalyst. Three separate samples of 2-phenyl-1,3-oxathiolane (**14**, 3.32 g each) were oxidized according to procedure B. The reaction times were 1.0, 1.75, and 2.0 h. After workup and recrystallization from THF–hexane (1:1), a product of melting point 99–100 °C was isolated in 47, 68, and 46% yields, respectively.

Oxidation of 2-Benzyl-1,3-oxathiolane (15). 2-Benzyl-1,3-oxathiolane (**15**, 3.32 g) was oxidized as described in procedure B. The crude product (4.26 g, 100%) was pure by NMR analysis. Recrystallization from THF–hexane (1:3) afforded pure 2-benzyl-1,3-oxathiolane 3,3-dioxide (**43**; 3.07 g, 72%) as a white solid: mp 95–96.5 °C; NMR 3.10 (m, 4 H), 4.16 (m, 3 H), 7.12 (s, 5 H). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.60; H, 5.66. Found: C, 56.71; H, 5.77.

Oxidation of 2-*p*-Tolyl-1,3-oxathiolane (16). Two samples of 2-*p*-tolyl-1,3-oxathiolane (**16**, 3.60 g each) were oxidized according to procedure B. The reactions were conducted for 2.0 and 3.5 h. After the workup, the sulfone, which was contaminated by *p*-tolualdehyde and *p*-toluic acid, was recrystallized from THF–hexane (1:4). 2-*p*-Tolyl-1,3-oxathiolane 3,3-dioxide (mp 131–133 °C) was isolated in 46 and 38% yields, respectively: NMR 2.38 (s, 3 H), 3.28 (pseudo t, 2 H), 4.45 (m, 2 H), 5.13 (s, 1 H), 7.32 (br s, 4 H). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.60; H, 5.66. Found: C, 56.41; H, 5.69.

Preparation of 2-Methyl-2-phenyl-1,3-oxathiolane (17). Acetophenone (60.0 g, 0.50 mol), 2-mercaptoethanol (39.0 g, 0.50 mol), and TsOH (1 g, 1 mol %) were dissolved in benzene (250 mL), and the mixture was heated at reflux as described for the preparation of **10** above. Vacuum distillation of the crude product through a 20-cm Vigreux column afforded 63.0 g (70%) of pure **17** as a colorless oil: bp 65–70 °C (0.05 torr); NMR 1.83 (s, 3 H), 2.98 (m, 2 H), 3.98 (m, 2 H), 7.33 (m, 5 H).

Attempted Oxidation of 17 in the Presence of BTEAC. Two samples of 2-methyl-2-phenyl-1,3-oxathiolane (**17**, 3.60 g each) were oxidized as described in procedure A for 1.0 and 24 h. After the workup, the only compound which could be identified in either case (by IR and NMR) was acetophenone.

Attempted Oxidation of 17 without Catalyst. 2-Methyl-2-phenyl-1,3-oxathiolane (**17**, 3.60 g) was oxidized as described in procedure B. After the workup, the only product which could be detected by IR and NMR was acetophenone.

Preparation of 4,4-Dimethyl-2-*n*-hexyl-1,3-oxathiolane (18). *n*-Heptanal (57.0 g, 0.50 mol), 2,2-dimethyl-2-mercaptoethanol (39.0 g, 0.50 mol), and TsOH (1 g, 1 mol %) were dissolved in benzene (250 mL), and the mixture was heated at reflux as described for the preparation of **10** above. Vacuum distillation of the crude product through a 20-cm Vigreux column afforded 70.7 g (70%) of pure **18** as a colorless oil, bp 77–78 °C (0.25 torr).

Oxidation of 18 in the Presence of Bu_4NHSO_4. 4,4-Dimethyl-2-*n*-hexyl-1,3-oxathiolane (**18**, 4.24 g, 0.20 mol), $KMnO_4$ (6.35 g, 0.04 mol), Bu_4NHSO_4 (0.65 g, 10 mol %), water (100 mL), and CH_2Cl_2 (50 mL) were placed in a 250-mL Erlenmeyer flask, and the mixture was stirred vigorously for 68 h. The reaction mixture was filtered and worked up as described above. After the extract was dried (Na_2SO_4) and the solvent evaporated, the crude product was obtained (3.51 g, 72%) as a yellow oil. After chromatography over alumina (ether–hexane, 1:9) a colorless oil was obtained (2.73 g) which appeared by NMR analysis to be a 1:3 mixture of starting material and product. The calculated amount of sulfone present was 2.38 g or 49%.

Acetic Acid Mediated Oxidation of 18. 4,4-Dimethyl-2-*n*-hexyl-1,3-oxathiolane (**18**; 40.4 g, 0.20 mol), $KMnO_4$ (63.2 g, 0.40 mol), HOAc (24.0 g, 0.40 mol), water (400 mL), and benzene (400 mL) were placed in a 2-L Erlenmeyer flask, and the mixture was stirred vigorously for 14 h at ambient temperature. The reaction mixture was then worked up as described above, except that the organic phase was extracted with 5% aqueous Na_2CO_3 solution. After the extract was dried (Na_2SO_4) and rotary evaporated, the product was obtained (40.9 g, 87%) as a yellow oil. After distillation through a 10-cm Vigreux column [bp 132–134 °C (0.1 torr)] the pure sulfone was obtained (31.1 g, 65%) as a colorless oil. Anal. Calcd for $C_{11}H_{22}O_3S$: C, 56.38; H, 9.46. Found: C, 56.06; H, 9.59.

Oxidation of 18 in the Absence of Catalyst. Compound **18** (11.6 g, 0.057 mol), $KMnO_4$ (22.7 g, 0.14 mol), water (100 mL), and benzene (100 mL) were combined in a 500-mL Erlenmeyer flask, and the mixture was stirred vigorously for 96 h at ambient temperature. The reaction was worked up as described above, and the crude sulfone was obtained (8.65 g, 64%) as a yellow oil which was distilled as above to afford pure 4,4-dimethyl-2-*n*-hexyl-1,3-oxathiolane 3,3-dioxide (4.26 g, 32%) as a colorless oil.

Acetic Acid Mediated Oxidation of 19.[29] 2,4,4-Trimethyl-2-*n*-hexyl-1,3-oxathiolane (**19**; 10.0 g, 0.046 mol), $KMnO_4$ (14.63 g, 0.093 mol), HOAc (5.56 g, 0.093 mol), water (100 mL), and benzene (100 mL) were mixed in a 500-mL Erlenmeyer flask, and the mixture was stirred vigorously for 48 h at ambient temperature. After workup as described above and distillation of the crude product (11.55 g, 100%) through a 10-cm Vigreux column, the pure sulfone (7.33 g, 64%) was isolated as a colorless oil, bp 127 °C (0.1 torr). Anal. Calcd for $C_{12}H_{24}O_3S$: C, 58.03; H, 9.74. Found: C, 57.87; H, 9.90.

Attempted Oxidation of 19 in the Absence of Catalyst. Compound **19** (15.00 g, 0.069 mol), $KMnO_4$ (21.93 g, 0.139 mol), water (100 mL), and benzene (100 mL) were mixed in a 500-mL Erlenmeyer flask, and the mixture was stirred vigorously for 96 h at ambient temperature. After the workup as described above, a slightly yellow oil (14.0 g) was isolated. NMR analysis indicated that this material was unchanged **19**.

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Registry No. **1**, 352-93-2; **2**, 31297-21-9; **3**, 74195-15-6; **4**, 13865-50-4; **5**, 110-01-0; **6**, 1613-51-0; **7**, 4753-80-4; **8**, 100-68-5; **9**, 15980-15-1; **10**, 2094-97-5; **11**, 5684-31-1; **12**, 73675-89-5; **13**, 17643-70-8; **14**, 5721-88-0; **15**, 24699-49-8; **16**, 22391-04-4; **17**, 5684-32-2; **18**, 74195-16-7; **19**, 74195-17-8; **20**, 74195-18-9; **21**, 15251-78-2; **22**, 54016-09-0; **23**, 10429-18-2; **24**, 74195-19-0; **25**, 73675-74-8; **26**, 73675-76-0; **27**, 73675-85-1; **28**, 73675-87-3; **30**, 620-32-6; **33**, 54016-09-0; **34**, 10429-18-2; *cis*-**37**, 74195-20-3; *trans*-**37**, 74195-21-4; **38**, 74195-22-5; **39**, 73675-86-2; **40**, 1900-74-9; **41**, 74195-23-6; **42**, 74195-24-7; **43**, 74195-25-8; **46**, 74195-26-9; **48**, 4988-34-5; **49**, 4988-33-4; **50**, 109-03-5; **51**, 107-61-9; **52**, 6251-34-9; **53**, 6251-33-8; chloromethyl methyl sulfide, 2373-51-5; *tert*-butyl mercaptan, 75-66-1; chloromethyl methyl ether, 107-30-2; thiophenol, 108-98-5; paraformaldehyde, 30525-89-4; 2-mercaptoethanol, 60-24-2; acetone, 67-64-1; 6,6-dimethyl-1,3-dioxa-5-thiacycloheptane, 74195-27-0; isobutyraldehyde, 78-84-2; acetophenone, 98-86-2; *n*-heptanal, 111-71-7; 2-hexyl-4,4-dimethyl-1,3-oxathiolane 3,3-dioxide, 73675-79-3; 2-hexyl-2,4,4-trimethyl-1,3-oxathiolane 3,3-dioxide, 74195-28-1; NaOMe, 124-41-4; KO-*t*-C_4H_9, 865-47-4; $KMnO_4$, 7722-64-7.

Supplementary Material Available: ^{13}C NMR data for selected sulfides, sulfoxides, and sulfones (8 pages). Ordering information given on any current masthead page.

(29) Prepared from **18** as described in ref 2.