a literature procedure and used without purification, was added. The reaction mixture was stirred for 2 h with cooling. Removal of the solvent by flash evaporation yielded the desired product as a white solid: 0.8 g (100%); mp 62.5–73 °C dec; [Cl⁺] = 100%; ^{1}H NMR ($CDCl_3$) δ 2.6 (s, 2 H), 2.5–2.0 (m, 10 H), 1.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 70.00 (s, C-1), 65.03 (s, C-3), 46.18 (t, C-2), 45.68, 35.73, 33.59, 31.25 (C-4-10).

Pyrolysis of Sulfonamide Derivatives. General Procedure. Injection of 10 μL (20–35% w/w) of 1-(*N,N*-dichlorosulfonamido)-3-chloroadamantane in CH_2Cl_2 into the GLC (15% SE-30 on Chromosorb W, stainless-steel column, 7 ft × $^1/_4$ in.; metal injector port; temperature 350 °C; column temperature 170 °C; He flow rate 60 mL/min) gave five peaks: (1) *m/e* 205, (2) *m/e* 240, (3–5) *m/e* 276. Peaks 1 and 2 were identified by retention time, peak enhancement, and mass spectral comparison with authentic materials. Isotopic clusters of chlorine in the mass spectrum were used in the identification of peaks 3–5; however, the structures of the individual isomers were not ascertained.

Purification of Cumene. A literature[28b] procedure gave pure material by fractional distillation; bp 151–152 °C (754 torr).

***N,N*-Dichlorobenzamide.** Undistilled *tert*-butyl hypochlorite[33] (13 g, 0.12 mol) was cooled in CH_2Cl_2 (50 mL) to 0 °C with an ice bath in the absence of light and moisture. Benzamide (7 g, 0.06 mol) in cold CH_2Cl_2 (75 mL) was added in one portion. The resulting solution was stirred for 2 h at 0 °C and for 1 h at room temperature. Concentration on the rotary evaporator yielded a dark green oil: 9.1 g (0.048 mol, 80%); [Cl⁺] = 99%; ^{1}H ($CDCl_3$) δ 8.3–7.6 (m, 5 H).

1-Adamantanecarboxamide. Adamantane-1-carbonyl chloride (6.6 g, 0.037 mol) in dry dioxane (40 mL) was added dropwise to concentrated ammonium hydroxide solution (150 mL). Filtration yielded 3.5 g of off-white solid, mp 184–191 °C. Concentration of the mother liquor provided an additional 1.1 g of solid. Recrystallization (dry hexane) gave a white powder: 4.1 g (62%); mp 187.5–190 °C (lit.[34] mp 189 °C); ^{1}H NMR ($CDCl_3$) δ 2.3–1.7 (m, 15 H), 1.1 (s, 2 H); IR ($CDCl_3$) 3650, 1720, 1630 cm^{-1}.

***N,N*-Dichloro-1-adamantanecarboxamide.** A prior procedure[29] gave a viscous, odorless, yellow oil, which was dissolved in petroleum ether (bp 30–60 °C) and filtered to remove 0.35 g of solid ([Cl⁺] = 50%). Concentration of the filtrate yielded a yellow-green oil which immediately turned to a light yellow solid: 5 g (0.020 mol, 71%), [Cl⁺] = 97–98%; mp 36.5–40 °C. Recrystallization (Skelly B) yielded light green crystals: mp 38–38.5 °C (sinster at 37 °C); [Cl⁺] = 99%; ^{1}H NMR ($CDCl_3$) δ 2.2–2.0 (s, 8 H), 2.0–1.7 (s, 7 H); IR ($CDCl_3$) 1750, 1470, 1350, 1010 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}Cl_2NO$: C, 53.24; H, 6.09; N, 5.64. Found: C, 54.03; H, 6.51; N, 5.69.

1-Adamantyl Isocyanate. The method of Stetter and Wulff[35] was used to obtain material [mp 141–143 °C (lit.[34] mp 144–145 °C)] which was found to contain a small amount of 1-bromoadamantane: ^{1}H NMR ($CDCl_3$) δ 2.6–1.6, (m, 11 H), 1.0 (s, 4 H); mass spectrum, *m/e* (relative intensity) 215 (3), 177 (8), 135 (100), 134 (11), 121 (12), 120 (86), 119 (4); IR ($CDCl_3$) 2225 (w) cm^{-1}.

Pyrolysis of Carboxamide Derivatives. General Procedure. Injection of 10 μL of a solution (11.4% w/w) of *N,N*-dichlorobenzamide in CH_2Cl_2 into the gas–liquid chromatograph (30% SE-30 on Chromosorb W; copper column, 8 ft × $^1/_4$ in.; metal injector; temperature 250 °C; column temperature 110 °C; He flow rate 90 mL/min) gave one major peak in addition to peaks due to air and solvent. Phenyl isocyanate was identified by comparison of retention times, peak enhancement (GLC), mass spectrum, and IR spectrum with those of authentic material. Injection of 30 μL of neat *N,N*-dichlorobenzamide yielded predominantly phenyl isocyanate. However, three other smaller peaks were detected with the following molecular ions: (2) *m/e* 103, (3) *m/e* 140, (4) *m/e* 155. The isotopic cluster for chlorine showed no. 4 to be a chlorinated phenyl isocyanate.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. *N,N*-Dichlorobenzenesulfonamide, 473-29-0; *N,N*-dibromobenzenesulfonamide, 938-05-6; *N,N*-dichloro-4-toluenesulfonamide, 473-34-7; 3-chloro-1-sulfonamidoadamantane, 78610-03-4; 1-(*N,N*-dichlorosulfonamido)-3-chloroadamantane, 78610-04-5; *N,N*-dichlorobenzamide, 22180-78-5; 1-adamantanecarboxamide, 5511-18-2; adamantane-1-carbonyl chloride, 2094-72-6; *N,N*-dichloro-1-adamantanecarboxamide, 78624-42-7.

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Intermediates in the Peroxy Acid Oxidation of Phenyl Phenylmethanethiosulfinate[1,2]

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The *m*-chloroperoxybenzoic acid (MCPBA) oxidation of phenyl phenylmethanethiosulfinate (**9**) in $CDCl_3$ has been studied. Low-temperature ^{1}H NMR and ^{13}C NMR spectra show that phenyl phenylmethanethiosulfonate (**7**), phenylmethanesulfonic acid (**26**), and phenylmethanesulfinic acid (**27**) are formed during the early stages of oxidation. Although **7** may be formed via direct attack of MCPBA at the sulfinyl sulfur atom of **9**, the presence of **7**, **26**, and **27** is also explicable in terms of formation and rearrangement of metastable α-disulfoxide (**13**) and sulfenyl sulfinate (**14**) intermediates.

The formation of α-disulfoxides (**3**) and sulfenyl sulfinates (**4**) as intermediates in the oxidation of disulfides (**1**) or thiosulfinates (**2**) to thiosulfonates (**5**) has been suggested for in vivo[3,4] and in vitro[4-17] reactions (Scheme I). Attempts to prepare these long-sought elusive interme-

(1) Previous paper in the series: Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *Org. Magn. Reson.*, in press.
(2) Presented at The Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 28, 1980, and the 8th Annual Meeting of NOBCChE, Chicago, IL, Apr 24, 1981.
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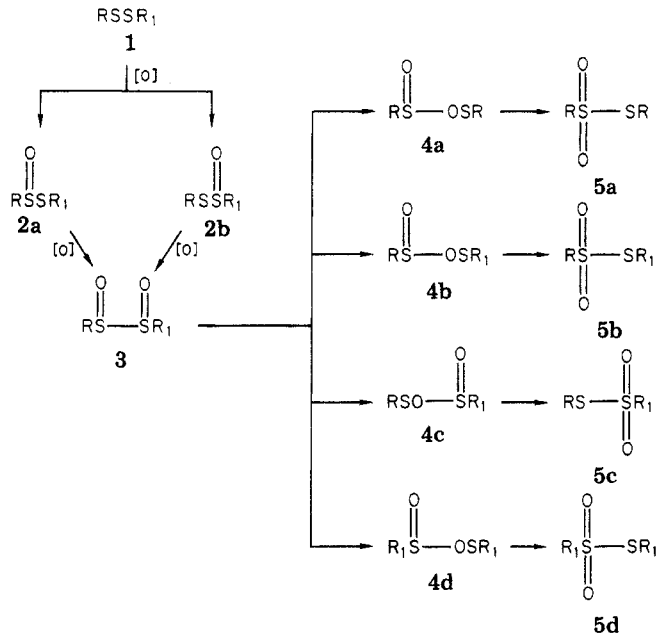
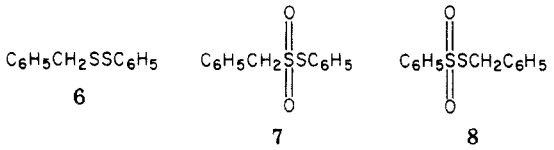
Scheme I

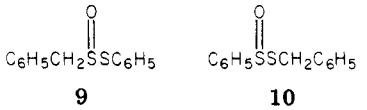


diates (3, 4) from cystine,[5,6] sulfinyl chlorides,[13] and alkyl or aryl arenethiosulfinates[7,10-12,15-17] have been unsuccessful. α-Disulfoxides 3 have been proposed as intermediates in the hydrolysis of methanesulfinyl chloride[18] and in the reaction of methyl chloromethyl sulfide with dimethyl sulfoxide.[19] It seems to be quite generally agreed that a head-to-tail combination of sulfinyl radicals gives sulfenyl sulfinates (4),[2,7,14,15,20-25] which can rearrange to thiosulfonates (5) via sulfonyl and thiyl radicals.[17]

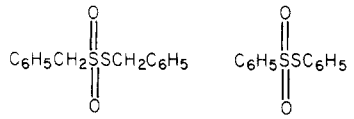
The oxidation of phenyl phenylmethyl disulfide (6) with 2 equiv of *m*-chloroperoxybenzoic acid (MCPBA) has been reported to give phenyl phenylmethanethiosulfonate (7;



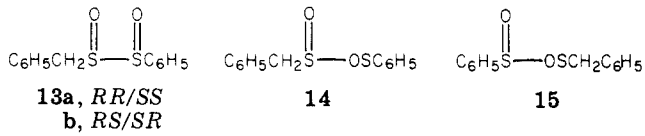
~65% yield via ^{1}H NMR spectral assay, 45% isolated yield) and no (<3%) phenylmethyl benzenethiosulfonate (8),[24] which suggests that phenyl phenylmethylthiosulfinate (9)[24-30] and not phenylmethyl benzenethiosulfinate (10) is



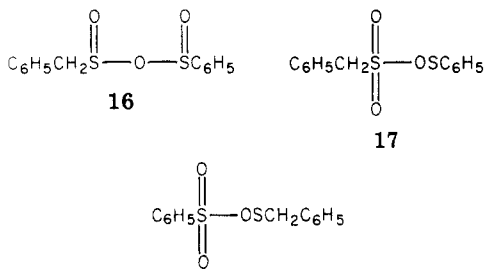
the initial oxidation product. Moreover, the absence of phenylmethyl phenylmethanethiosulfonate (11) and phenyl benzenethiosulfonate (12) implied that oxidation occurred *exclusively* at the sulfinyl sulfur atom of 9 to give 7 directly.[24]



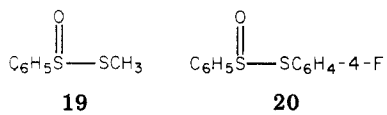
Initial attack of oxidant on thiosulfinate 9 or 10 could, in principle, occur either at the sulfenyl sulfur atom or at the sulfinyl sulfur atom.[7,10-17,31] In the terminology of hard and soft acids and bases (HSAB), sulfinyl sulfur is expected to be a noticeably softer electrophilic center than sulfonyl sulfur but a relatively harder electrophilic center than sulfenyl sulfur. Thus, oxidation of 9 or 10 at the sulfenyl sulfur atom would be expected to lead to diastereomeric α-disulfoxides 13 which could rearrange to sulfenyl sulfinates 14 and 15. Oxidation of 14 and 15 could give diastereomeric sulfinic anhydrides 16 and sulfenyl sulfonates 17 and 18.



13a, *RR/SS*
b, *RS/SR*



The *four* thiosulfonate products from the peracetic acid oxidation of methyl benzenethiosulfinate (19)[11,31] and 4-fluorophenyl benzenethiosulfinate (20)[10], respectively, are explicable in terms of α-disulfoxide (3) intermediates. Moreover, we have observed that the MCPBA oxidation of neopentyl neopentanethiosulfinate (21) in $CDCl_3$ led to



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(31) One cannot unequivocally expect that electrophilic oxidation of 9 by MCPBA would occur at sulfenyl sulfur rather than sulfinyl sulfur. It may be possible that the sulfenyl sulfur atom, oxing to conjugation with the phenyl ring, may actually be less "electron rich" than the sulfinyl sulfur atom which is attached to the benzyl carbon atom.[10]

Table I. ^{1}H NMR Chemical Shifts (δ) of the Products from the MCPBA Oxidation of 9 in $CDCl_3$ [a-c]

probable structures	shift (−30 °C, 0.17 h[c])	yield, %[d]	shift (0 °C, 2.5 h[c,e])	yield, %[d]	shift (25 °C, 6.0 h[c])	yield, %[d]	shift (25 °C, 48 h[c])	yield, %[d]
$C_6H_5CH_2SO_2SC_6H_5$ (7)	4.46	34	4.45	41	4.44	52	4.44	61
$C_6H_5CH_2S(O)SC_6H_5$[f] (9)	4.37	39	4.36	38	4.35	20	4.35	11
	4.41		4.40		4.40		4.40	
$C_6H_5CH_2SO_3H$ (26)	4.32	11	4.30	11	4.30	11	4.29	7
$C_6H_5CH_2SO_2H$ (27) or 14	4.06	15	4.04	7		0		
$C_6H_5CH_2SO_2SCH_2C_6H_5$ (11)		0	4.17	4	4.21	9	4.21	12
			4.02		4.03		4.03	
$C_6H_5CH_2SSC_6H_5$ (6)		0		trace		trace	3.94	3
$C_6H_5CH_2SSCH_2C_6H_5$ (30)		0		0		1.5	3.60	4

[a] Me_4Si was used as internal standard; the spectrometer frequency was 250.13 MHz. [b] Only the methylene hydrogens of the phenylmethyl group are tabulated. [c] Time after filtering product mixture at −45 °C. [d] Percent of relative integrals. [e] Product mixture was maintained at −30 °C for 1 h after filtration and then raised to 0 °C. [f] Only the inner satellites of the AB quartet are tabulated.

Table II. ^{13}C NMR Chemical Shifts (δ) of the Products from the MCPBA Oxidation of 9 in $CDCl_3$ [a,b]

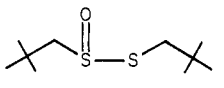
probable structures	shift (−30 °C, 0.33 h[c])	yield, %[d]	shift (25 °C, 3.0 h[c])	yield, %[d]
$C_6H_5CH_2SO_2SC_6H_5$ (7)	65.38	44	66.27	66
$C_6H_5CH_2SO_2H$ (27) or 14	63.52	10		0
$C_6H_5CH_2S(O)SC_6H_5$ (9)	61.69	34	62.44	21
$C_6H_5CH_2SO_3H$ (26)	57.70	10	57.97	12
$C_6H_5CH_2SO_2SCH_2C_6H_5$ (11)		0	40.94	2.0
			69.14	

[a] Me_4Si was used as an internal standard; the spectrometer frequency was 62.89 MHz. [b] Only the methylene carbon atom of the phenylmethyl group is tabulated. [c] Time after filtering product mixture at −45 °C. [d] Percent of relative integrals (broad-band decoupling only).

Table III. ^{1}H NMR and ^{13}C NMR Chemical Shifts of Reference Compounds[a,b]

organosulfur compound	^{1}H NMR, δ[c]		^{13}C NMR, δ[d]	
	CH_2	Ar H	$^{13}CH_2$	$^{13}C_6H_5$
$C_6H_5CH_2SSC_6H_5$ (6)[24]	3.91	7.1-7.6	43.3	126.1-129.3
$C_6H_5CH_2SO_2SC_6H_5$ (7)	4.43	7.3-7.6	66.08	127.6-136.2
$C_6H_5CH_2S(O)SC_6H_5$ (9)	4.33 (J = 12.9 Hz), 4.43	7.4-7.6	62.59	128.7-135.3
$C_6H_5S(O)SCH_2C_6H_5$ (10)	4.22 (J = 13.2 Hz), 4.42		36.99	
$C_6H_5CH_2SO_2SCH_2C_6H_5$ (11)	4.04, 4.21	7.35	40.85, 69.01	127.8-134.9
$C_6H_5SO_2SC_6H_5$ (12)		7.31-7.63		127.5-143.0
$C_6H_5CH_2SO_3H$ (26)	4.30		58.36	128.0-134.28
$C_6H_5CH_2SO_2H$ (27)	4.02	7.32 (s), 7.22-7.46	64.46	128.4-130.6
$C_6H_5CH_2SO_3CH_3$ (28)	4.22	7.38 (s)	56.66	127.9-130.7
$C_6H_5CH_2SO_2OSO_2CH_2C_6H_5$ (29)	4.76	7.44	60.46	125.7-131.1
$C_6H_5CH_2SSCH_2C_6H_5$ (30)	3.60		43.31	126.9-137.4
$C_6H_5SSC_6H_5$ (31)				127.2-137.1
$C_6H_5S(O)SC_6H_5$ (32)				

[a] In $CDCl_3$ with Me_4Si used as an internal reference. Compound 27 in 20% $CDCl_3$-CH_3OH. [b] Data from this work. [c] Compound 28 at 90.0 MHz, compounds 9, 10, and 12 at 250.13 MHz, and others at 60 MHz. [d] Compounds 9, 11, 12, 27, 28, and 30-32 at 22.63 MHz and compounds 10, 27, and 29 at 62.89 MHz.



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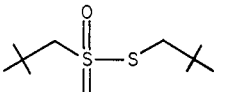
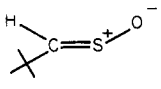


22

neopentyl neopentanethiosulfonate (22), (*E*)- and (*Z*)-2,2-dimethylpropanethial *S*-oxides (23 and 24), and neopentanesulfinic acid (25).[7]



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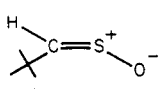

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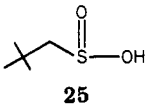

25

We have investigated the low-temperature MCPBA oxidation of 9 in $CDCl_3$ in order to determine whether 6 and 9 are unique systems, to ascertain whether α-disulfoxides (13), sulfenyl sulfinates (14 and 15), sulfinic anhydrides (16), and/or sulfenyl sulfonates (17 and 18) are reaction intermediates, and to observe whether sulfine formation is general for thiosulfinates with an α-hydrogen atom adjacent to sulfinyl sulfur.

Results

The MCPBA oxidation of 9 was performed at −30 °C in $CDCl_3$ under a nitrogen atmosphere. The product mixture was filtered under an inert atmosphere at −45 °C, and the ^{1}H NMR and ^{13}C NMR spectra of the filtrate were taken as soon as possible (Tables I and II). Approximately 13 mol of 7 precipitated during the filtration. In addition to 7, the initial product mixture contained 9, phenylmethanesulfonic acid (26),[32] and a compound to which either the sulfenyl sulfinate 14 or phenylmethanesulfinic acid (27) structure could be assigned.

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$C_6H_5CH_2SO_3R$ $C_6H_5CH_2SO_2H$ $(C_6H_5CH_2SO_2)_2O$

26, R = H **27** **29**
28, R = CH_3

ArSSAr

30, Ar = $C_6H_5CH_2$
31, Ar = C_6H_5

The ^1H NMR and ^{13}C NMR spectra of reference compounds phenylmethanesulfinic acid (**27**),[33,34] methyl phenylmethanesulfonate (**28**),[35] phenylmethanesulfonic anhydride (**29**),[36] phenyl methyl disulfide (**30**),[37] phenyl disulfide (**31**),[38] and phenyl benzenethiosulfinate (**32**) are given in Table III.[1]

It is seen in Tables I and II that as the temperature was raised from −30 to 0 °C, the concentrations of **7** increased, the formation of **11** commenced, and traces of **6** appeared. Six hours later, at 25 °C, the concentration of **7** and **11** had increased, the concentration of **9** had decreased, **14** or **27** had disappeared, the concentrations of **6** and **17** remained constant, and the formation of phenyl methyl disulfide (**30**) had started. After the mixture had been allowed to stand overnight at 25 °C, **26** began to precipitate. After 48 h at 25 °C, the concentration of **9** decreased and the concentration of **6**, **7**, **11**, and **30** increased, possibly via eq 1.[39]

$$\underset{\mathbf{9}}{C_6H_5CH_2S(O)SC_6H_5} \rightarrow 6 + 7 + 11 + 30 \qquad (1)$$

The ^1H NMR and ^{13}C NMR resonances for **27** (δ_H 4.02, δ_C 64.46) and the observed peaks at δ_H 4.06 and δ_C 63.52 at −30 °C in the product mixture are very close, considering the effect of temperature on chemical shifts. In order to determine whether the observed peaks are due to sulfenyl sulfinate **14** or phenylmethanesulfinic acid (**27**), we added a small amount of **27** to the cold reaction mixture. Although no new peaks appeared after addition of **27**, the resonances at δ_H 4.06 and δ_C 63.52 increased. When the cold reaction mixture containing added **27** was warmed to 25 °C, the resonances disappeared at a rate comparable to that without added **27**.[40,41] Thus, although the resonances at δ_H 4.06 and δ_C 63.52 may be due to **27**, the presence of **14** is not excluded.

In another experiment, the resonances ascribed to phenylmethanesulfinic acid (**27**) disappeared within a few minutes after the filtrate was allowed to warm to 25 °C. HPLC analysis of this filtrate showed the major components were **7** (67%), **9** (18%), **12** (15%), and traces of disulfides, possibly **6**, **30**, and **31**.[42-44] After this filtrate was extracted with water, **26**, and traces of *m*-chlorobenzoic acid (MCBA) were identified in the aqueous layer (NMR assay). Sulfonic acid **26** precipitated out of the filtrate solution over a 3-day period at 25 °C. Addition of phenylmethanesulfonic anhydride (**29**) to the filtrate led to the appearance of a signal at δ 4.76, while the resonance for **26** at δ 4.30 remained unchanged. Thus, the peak assignment for **26** is not due to **29**.

In order to intercept the easily hydrolyzable intermediates produced in the oxidation, we warmed the reaction mixture to 0 °C in the presence of 10% $NaHCO_3$ solution immediately after filtration at −45 °C (eq 2 and 3).

$$\underset{\mathbf{14}}{C_6H_5CH_2S(O)OSC_6H_5} \xrightarrow[NaHCO_3]{H_2O} \underset{\mathbf{27}}{C_6H_5CH_2S(O)ONa} + C_6H_5SOH \qquad (2)$$

$$2C_6H_5SOH \rightarrow \underset{\mathbf{32}}{C_6H_5S(O)SC_6H_5} + H_2O \qquad (3)$$

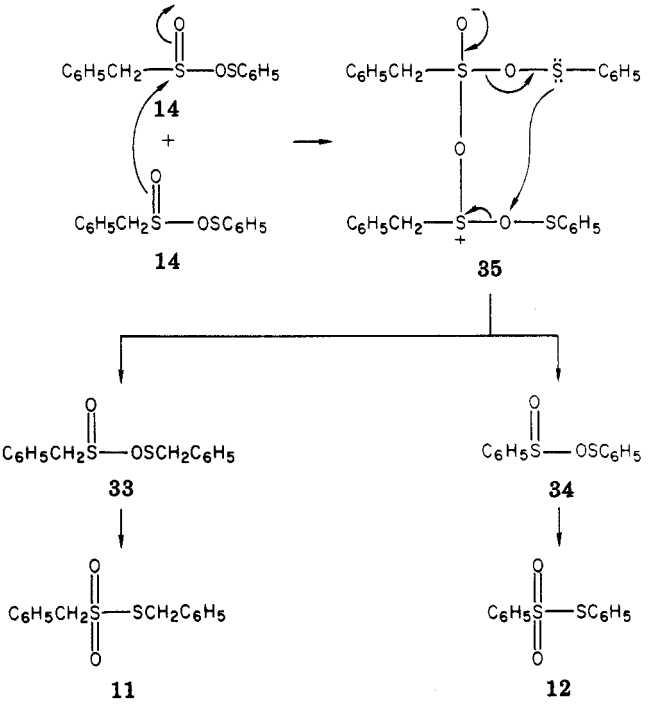
Analysis of the organic phase by HPLC for three experiments showed the following distributions of products: **7**, 50–59%; **9**, 28–30%; **12**, 15–18%; phenyl benzenethiosulfinate (**32**), traces to 5%.[26,45] In the experiments with

Table IV. Products from the Oxidation of Phenyl Phenylmethanethiosulfinate (9) with MCPBA and Treatment of Filtrate with $NaHCO_3$ Solution

compd	yield, % NMR[a]	yield, % HPLC[b]
$C_6H_5CH_2SO_2SC_6H_5$ (**7**)	52[b]	50-59
$C_6H_5CH_2S(O)SC_6H_5$ (**9**)	24	28-30
$C_6H_5CH_2SO_2SCH_2C_6H_5$ (**11**)	3	
$C_6H_5SO_2C_6H_5$ (**12**)	*d*	15-18
$C_6H_5CH_2SO_3H$ (**26**)	9	
$C_6H_5CH_2SO_2H$ (**27**)	11	
$C_6H_5S(O)SC_6H_5$ (**32**)	*d*	0-5

[a] NMR yields (±3%) are given. [b] Analyses from three experiments. [c] Includes amount precipitated during filtration at −45 °C. [d] NMR yields of **12** and **32** could not be determined owing to their overlapping aromatic resonances.

Scheme II



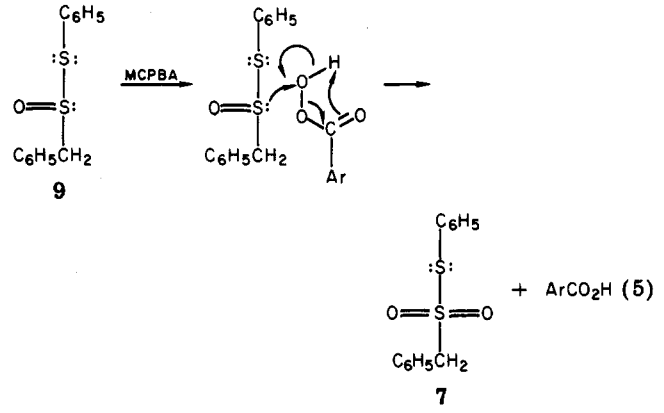
(33) Kice, J. L.; Engebrecht, R. H. *J. Org. Chem.* **1962**, *27*, 4654.
(34) Holmberg, B. *Ark. Kemi, Mineral. Geol.* **1940**, *14A*, no. 8.
(35) King, J. F.; Durst, T. *J. Am. Chem. Soc.* **1965**, *87*, 5684.
(36) King, J. F.; Aslam, M. *Can. J. Chem.* **1979**, *57*, 3278.
(37) Legler, L. E.; Jindal, S. L.; Murray, R. W. *Tetrahedron Lett.* **1972**, 3907.
(38) "Nuclear Magnetic Resonance Spectra"; Sadtler Research Laboratories Inc.: Philadelphia, PA, 1968; No. 286.
(39) It has been reported that during the oxidation of **6** with 1.6 equiv of MCPBA the singlet due to the methylene group of **6** disappeared and two new singlets appear at δ 4.33 and 4.43. The singlet at δ 4.43 is due to the benzylic protons of **7**, and the singlet at δ 4.33 was assigned to the methylene protons of **9**. However, we observed that the benzylic protons of **9** are diastereotopic (Tables I and III). The chemical shift difference (~0.01 ppm) of the inner satellites of the AB quartet is detectable at 60 MHz.
(40) Sulfinic acids react fairly readily with thiosulfinates, giving thiosulfonates.[26,41] Moreover, in the presence of strong acid in an aprotic solvent, sulfinic acids are also likely to decompose fairly readily.
(41) Kice, J. L.; Large, G. B. *J. Org. Chem.* **1968**, *33*, 1940.
(42) Compound **11**, although stable on a silica gel TLC slide, decomposed on analytical HPLC on silica gel. In a standard injection of **7**, **11**, and **12**, it was found that **11** or traces of MCPBA did not interfere. Thiosulfonates are known to scramble on silica gel.[43]
(43) Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1979**, *44*, 4135.
(44) Pure **26** does not appear to be appreciably soluble in $CDCl_3$.
(45) Backer, H. J.; Kloosterziel, C. N. *Recl. Trav. Chem. Pays-Bas* **1954**, *73*, 129.

less than 5% **32**, trace amounts of several unidentified products with shorter retention times than **7**, **9**, **12**, and **32** were detected. Phenylmethanesulfonic acid (**26**) and phenylmethanesulfinic acid (**27**) were identified via NMR analysis of the aqueous layer. The yield of **27** was determined by NMR and by sodium nitrite titration (eq 4).[46-48] The composition of the reaction mixture is given in Table IV.

$$2\underset{\mathbf{27}}{C_6H_5CH_2SO_2H} + HONO \rightarrow (C_6H_5CH_2SO_2)_2NOH + H_2O \quad (4)$$

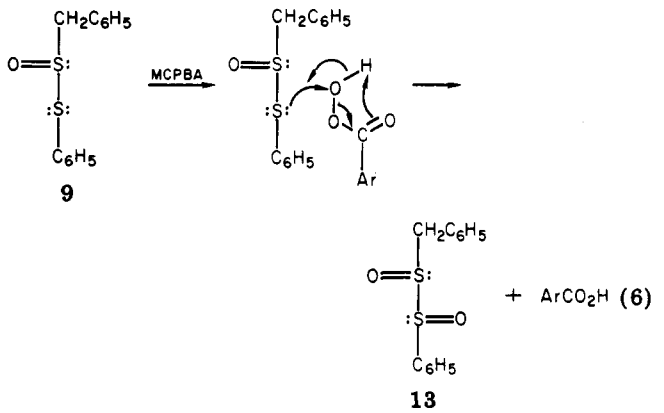
Discussion

Low-temperature ^1H NMR and ^{13}C NMR show that **7**, which may arise via direct oxidation at sulfinyl sulfur (eq 5), is not the exclusive product from the MCPBA oxidation

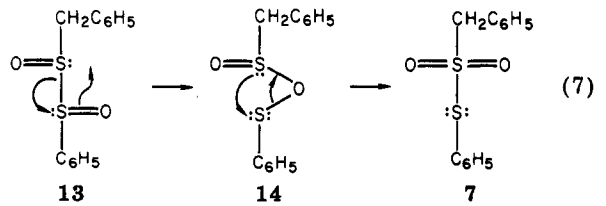


9 **7**

of **9** (Table I). In addition to **7**, the presence of **26** and **27** seems to require at least part of the oxidation to proceed via an α-disulfoxide (**13**) intermediate (eq 6). α-Disulfoxides **13** can result from electrophilic attack of MCPBA at the sulfenyl sulfur atom of **9**.[40,41] Molecular rearrangement of α-disulfoxides **13** can lead to **7** (eq 7).



9 **13**



(7)

13 **14** **7**

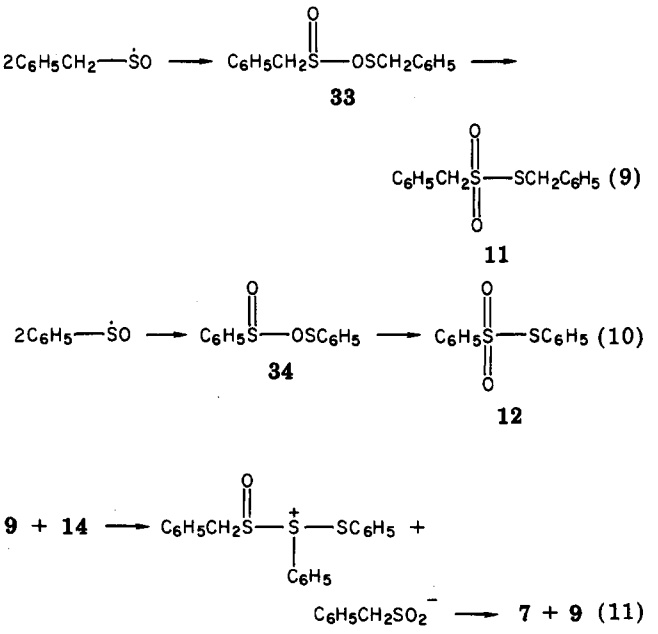
Whether most of **7** is formed by a reaction path going through an α-disulfoxide or, alternatively, by direct oxidation of the sulfinyl sulfur atom of **9** cannot be told from the experimental results.[10,49,50]

α-Disulfoxides **13** appear to rearrange preferentially to sulfenyl sulfinate **14**, owing to the electron-releasing effect of the benzyl group and/or to a more favorable electronic interaction of sulfenyl sulfur with the phenyl group.

The formation of **11** and **12** can occur partially by the following mechanisms (eq 8–10). Homolytic dissociation

$$\underset{\mathbf{14}}{C_6H_5CH_2S(O)OSC_6H_5} \rightarrow C_6H_5CH_2\text{-}\dot{S}O + C_6H_5\text{-}\dot{S}O \quad (8)$$

of **14** to sulfinyl radicals (eq 8), followed by preferential recombination to symmetrical sulfenyl sulfinates, can ultimately give thiosulfonates **11** and **12** as shown in eq 9 and 10, respectively. Alternatively, concerted (eq 7 or Scheme II) or ionic (eq 11) mechanisms can be imagined for the

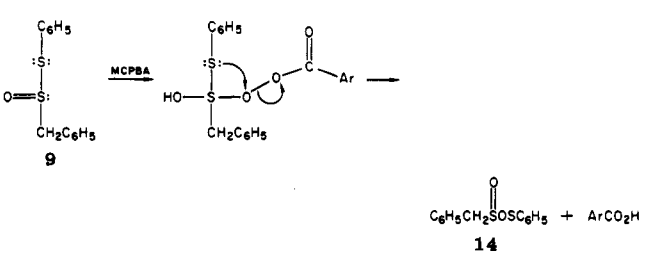


33 **11** **34** **12**

$$C_6H_5CH_2SO_2^- \longrightarrow 7 + 9 \quad (11)$$

isomerization of sulfenyl sulfinates like **14** to thiosulfonates. Mechanisms involving phenylmethanesulfonyl radicals ($C_6H_5CH_2\dot{S}O_2$) are considered less likely owing to the ease with which they lose sulfur dioxide.

The absence of sulfine formation during the oxidation of **9** is also of interest. It has been suggested that sulfines **23** and **24** could arise via a cycloelimination mechanism involving α-disulfoxide **36** or sulfinyl sulfenate **37**[7] (eq 12).

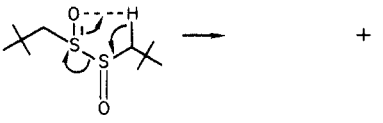


9 **14**

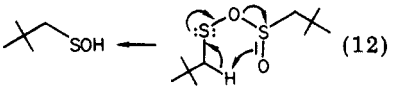
(46) Marvel, C. S.; Johnson, R. S. *J. Org. Chem.* **1948**, *13*, 822.
(47) Kice, J. L.; Bowers, K. W. *J. Am. Chem. Soc.* **1962**, *82*, 605.
(48) Lindberg, B. *Acta Chem. Scand.* **1963**, *17*, 383.

(49) Alternatively, formation of sulfenyl sulfinate **14** could be explained by a mechanism whereby MCPBA added to the sulfinyl group of **9** to give an intermediate which undergoes a Baeyer–Villiger type rearrangement. This mechanism is considered unlikely owing to the low degree of dissociation of MCPBA.[50]

(50) Curci, R.; Giovine, A.; Modena, G. *Tetrahedron* **1966**, *22*, 1235 and references cited therein.



36



(12)

37

Sulfenyl sulfinate **14**, which is formed in preference to sulfenyl sulfinate **15**, does not have the required hydrogen atom for cycloelimination adjacent to the sulfenyl sulfur atom (cf. **37**). Presumably, the α-disulfoxides **13** isomerize to **14** before they can undergo cycloelimination to sulfines.

The formation of phenylmethanesulfonic acid (**26**) is probably a result of the oxidation of **27**. The sulfinic acid **27** could easily result from the reaction of either MCBA or trace amounts of water with **14** (cf. eq 2).

$$\text{MCBA (or } H_2O) + \mathbf{14} \rightarrow \underset{\mathbf{27}}{C_6H_5CH_2S(O)OH} + ArC(O)OSC_6H_5\ (C_6H_5SOH) \quad (13)$$

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

NMR spectra were obtained on Bruker WH-90 and WM-250 Fourier transform NMR spectrometers which were controlled by Bruker Model B-NC-12 and Bruker Aspect 2000 computers, respectively, and on a Varian EM-360 NMR spectrometer.[1]

HPLC was accomplished on an EM "Hibar" silica gel analytical column with a UV detector and with 3% ethyl acetate–isooctane as eluant.

Commercial (Aldrich) deuteriochloroform was used. Other reagents and solvents were purified by standard procedures.

The following compounds were prepared as previously reported: phenylmethanesulfinic acid (**27**),[33,34] methyl phenylmethanesulfonate (**28**),[35] phenylmethanesulfonic anhydride (**29**),[36] phenylmethyl phenylmethanethiosulfonate (**11**),[51] phenyl benzenethiosulfinate (**32**).[45]

Phenyl phenylmethanethiosulfinate (9) was prepared by a modification of the method of Backer and Kloosterziel.[45] A solution of thiophenol (1.54 mL, 1.5 mmol) and pyridine (1.22 mL, 1.5 mmol) in 30 mL of ether was cooled to 0 °C. Phenylmethanesulfinyl chloride (2.62 g, 1.5 mmol) dissolved in 20 mL of ether was added dropwise with stirring. The mixture was stirred for another 30 min at 0 °C and another 15 min at room temperature. After filtration, the ether solution was washed successively with ice cold 1 M H_2SO_4 (10 mL), ice cold 5% $NaHCO_3$ (10 mL), and water (10 mL). Compound **9** was purified by flash chromatography on silica gel followed by low-temperature crystallization from ether: mp 50.5–51.5 °C; 46% yield; IR ($CDCl_3$) 1440 (m), 1078 (s), 1065 cm^{-1} (s, S=O).

Phenylmethyl Benzenethiosulfinate (10). The same procedure used for the preparation of **9** was employed.[45] Attempted purification by flash chromatography at 0 °C on silica gel with 15% ethyl acetate–petroleum ether gave **10** together with phenyl benzenethiosulfinate (**32**) and an unidentified product which contained only aryl groups. Attempts to recrystallize the unidentified material were unsuccessful: IR (thin film) 1440 (m), 1090 (s), 1060 cm^{-1} (s, S=O).

Phenyl benzenethiosulfonate (12) was prepared by oxidation of phenyl disulfide (**31**) with 2 equiv of $NaIO_4$ in an acetonitrile–water mixture. Compound **12** was recrystallized from petroleum ether; mp 42–43 °C (lit.[51] mp 45 °C).

Phenylmethanesulfonic acid (26) was prepared by passing sodium phenylmethanesulfonate[34] through a column of Rexyn (H^+) ion-exchange resin suspended in water, evaporating the water in vacuo, and drying the mixture by aceotroping off the remaining water with benzene.

Oxidation of Phenyl Phenylmethanethiosulfinate (9) with MCPBA. In a nitrogen atmosphere **9** (395 mg, 1.59 mmol) was dissolved in 1 mL of $CDCl_3$ and the mixture cooled to −30 °C in a dry ice/2-propanol bath. A solution of 81% MCPBA (340 mg, 1.59 mmol) in 4.5 mL of $CDCl_3$ was added dropwise to the solution of **9** with stirring. After addition (~5 min), the mixture was stirred for 55 min at −30 °C and then filtered at −45 °C. For the low-temperature NMR experiments, the filtrate was transferred to a 10-mm NMR tube via a Teflon tube with nitrogen pressure in order to avoid atmospheric contamination. ^1H NMR and ^{13}C NMR spectra were taken immediately after the transfer.

Oxidation of Phenyl Phenylmethanethiosulfinate 9 with MCPBA and Treatment with $NaHCO_3$ Solution. The oxidation was carried out as above on twice the scale. The filtrate was quickly warmed to 0 °C, an ice-cold 10% $NaHCO_3$ solution was added, and the mixture was vigorously stirred. The mixture was transferred to a separatory funnel, shaken, and separated. The organic phase was dried over Na_2SO_4. Anhydrous sodium acetate was used as the NMR reference. Sodium nitrite titration of the aqueous layer was carried out at 0 °C.[46-48]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **6**, 16601-17-5; **7**, 37945-60-1; **9**, 78609-87-7; **10**, 16599-27-2; **11**, 16601-40-4; **12**, 1212-08-4; **14**, 78609-88-8; **26**, 100-87-8; **27**, 4403-73-0; **28**, 5877-96-3; **29**, 72422-27-6; **30**, 150-60-7; **31**, 882-33-7; **32**, 1208-20-4; thiophenol, 108-98-5; phenylmethanesulfinyl chloride, 41719-05-5; sodium phenylmethanesulfonate, 57267-76-2.

(51) Bretschneider, H.; Klotzer, W. *Monatsh. Chem.* **1950**, *81*, 593.