similar to that of vpc peak 2 (compound XII) and the nmr spectrum was identical. On this basis, peak 3 was believed to be 2-methylmercapto-1-naphthol (XIII). Not enough of this compound could be isolated for a carbon–hydrogen analysis. Vpc peaks 4 and 5 exhibited ir spectra which were identical with those of 1- and 2-naphthols, respectively.

Decomposition of *tert*-Butyl 1-Naphthyl Ether.—Mixtures of potassium *tert*-butoxide, *tert*-butyl alcohol, and DMSO of the appropriate ratio (same as in Table I) were heated to the desired temperature in a dry three-necked round-bottom flask equipped with a thermometer, addition tube, and condenser. *tert*-Butyl 1-naphthyl ether was added at once through the addition tube. After the desired reaction time, the reaction mixture was added to cold water and worked up as described above for the 1-bromonaphthalene reaction. The neutral and acidic fractions were analyzed as described above. In every case the ether decomposed to the naphthol. At high temperature only 5–10% of the ether was recovered; the other 90–95% was the naphthol. At lower temperatures (80–100°) most (60%) of the ether was recovered.

Reaction of Naphthalene with the Base–DMSO Solution.—Naphthalene (0.13 g, 0.001 mol) was added to a solution of 25 ml (27.5 g, 0.35 mol) of DMSO, 6.0 g (0.08 mol) of *tert*-butyl alcohol, and 11.8 g (0.10 mol) of potassium *tert*-butoxide at 140°. After 40 min, the reaction was added to ice water and worked up as reported above for the 1-bromonaphthalene reaction. No acidic fraction was observed. The neutral fraction was analyzed as reported above to yield 47.3% recovered naphthalene, 7.6% 1-methylnaphthalene, and 0.6% 2-methylnaphthalene. No 1,2-dimethylnaphthalene was observed.

Reaction of Methylsulfinyl Carbanion with 1-Bromonaphthalene.—Methylsulfinyl carbanion was prepared according to the procedure of Corey and Chaykovsky[19] from 124.83 g (1.6 mol) of DMSO and 4.5 g (0.19 mol) of sodium hydride. This mixture was placed in a dry 500-ml three-necked round-bottom flask equipped with a thermometer, condenser, addition funnel, and magnetic stirring. The temperature was raised to 80° and 19.5 g (0.09 mol) of 1-bromonaphthalene was added at once. The reaction mixture immediately turned black and the temperature rapidly increased to 150°. After 15 min (the temperature had lowered to 104°), the mixture was added to ice water and worked up as reported above. The acidic fraction was analyzed as reported above to yield 3.8% XII, 1.3% XIII, 0.3% XIV, and 0.5% XV. The neutral fraction yielded (analyzed as reported above) 1.3% I, 2.7% III, and 0.3% II. Another compound (11.4%) was observed and isolated. The nmr spectra of this compound was the same as that reported by Zweig and coworkers[27] for 1-methylthionaphthalene. The ir spectrum was consistent with this structure.

Anal. Calcd for $C_{11}H_{10}S$: C, 75.81; H, 5.79. Found: C, 75.94; H, 5.63.

Registry No.—1-Bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; potassium *tert*-butoxide, 865-47-4.

(27) A. Zweig, J. E. Lancaster, and M. T. Negia, *Tetrahedron*, **23**, 2577 (1967).

The Chemistry of Thiolsulfonates and Related Derivatives. Nucleophilic Reactions on Sulfenyl Sulfur[1a]

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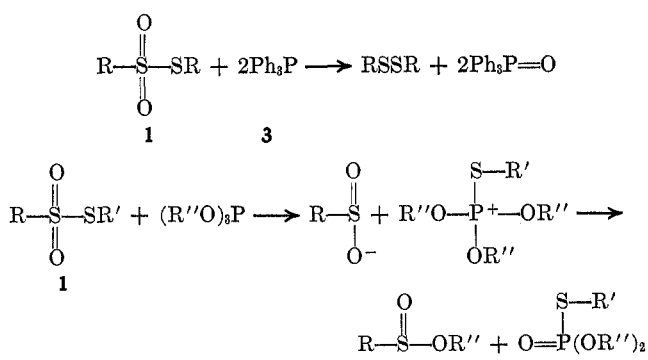
The reaction of thiolsulfonates with aminophosphines proceeds by nucleophilic attack on sulfenyl sulfur giving rise to sulfones and sulfinate esters as reaction products. This is in marked contrast to the reaction of triphenylphosphine (**3**) with thiolsulfonates where deoxygenation is observed. This dichotomy does not extend to the corresponding reaction of phosphines with sulfenylthiolsulfonates. Here, nucleophilic attack on sulfenyl sulfur is observed for both triphenylphosphine (**3**) and tris(diethylamino)phosphine (**4**). In addition, the desulfurization of cyclic thiosulfonates provides a new, general route to cyclic sulfinate esters.

As part of our continuing investigation of nucleophilic displacements on sulfenyl sulfur we have examined the reaction of a number of thiolsulfonates **1** and sulfenyl thiolsulfonates **2** with various trivalent phosphorus derivatives.

RSO_2SR (**1**) RSO_2SSR (**2**)

The behavior of trivalent phosphorus compounds toward disulfides and trisulfides has been shown to be a function of the type of substitution on the phosphorus atom (aminophosphines,[2,3] alkylphosphines,[3] arylphosphines,[3,4] and phosphites).[5]

Thiolsulfonates have been reported to undergo deoxygenation with triphenylphosphine[6] (**3**) or desulfurization with trialkyl phosphites.[7] In the latter reaction, the



sulfinate anion, presumably formed by nucleophilic displacement on sulfenyl sulfur, may react through oxygen to afford sulfinate esters or through sulfur to give sulfones. However, only products resulting from O-alkylation in an Arbusov-like rearrangement[8] are ob-

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(1) (a) Organic Sulfur Chemistry. IX. Part VIII: D. N. Harpp, D. K. Ash, T. G. Black, J. G. Gleason, B. A. Orwig, W. F VanHorn, and J. P. Snyder, *Tetrahedron Lett.*, 3551 (1970). (b) Holder of an NRCC Scholarship, 1968–1970. (c) Holder of an NRCC Bursary, 1969–1970.

(2) D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968).

(3) D. N. Harpp, and D. K. Ash, *Chem. Commun.*, 811 (1970).

(4) (a) S. Safe and A. Taylor, *ibid.*, 1466 (1969); (b) F. Feher and D. Kurz., *Z. Naturforsch. B*, **23**, 1030 (1968); (c) S. Hayashi, M. Furukawa, J. Yamomoto, and K. Hamamura, *Chem. Pharm. Bull.*, **15**, 1310 (1967); (d) C. Moore and B. Trego, *Tetrahedron*, **19**, 1251 (1963); (e) A. Schonberg and M. Z. Barakat, *J. Chem. Soc.*, 892 (1949).

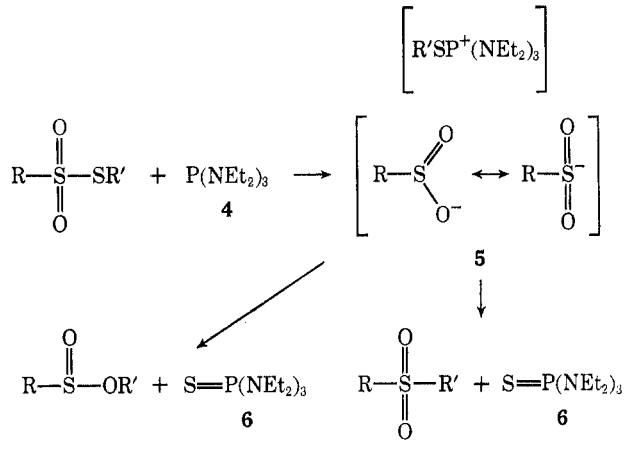
(5) H. I. Jacobson, R. G. Harvey, and E. V. Jensen, *J. Amer. Chem. Soc.*, **77**, 6064 (1955); C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959).

(6) L. Horner and H. Nickel, *Justus Liebigs Ann. Chem.*, **597**, 20 (1955).

(7) J. Michalski, T. Modro, and J. Wieczorkowski, *J. Chem. Soc.*, 1665 (1960).

(8) E. A. Arbusov, *Zh. Russ. Fiz.-Khim. Obshchest.*, **38**, 687 (1906).

SCHEME I



served. A highly nucleophilic aminophosphine such as tris(diethylamino)phosphine[9] (**4**) could be expected to react on sulfenyl sulfur displacing the ambident sulfinate anion **5** (Scheme I), an anion which may then undergo S- or O-alkylation giving rise to sulfone and/or sulfinate ester as products.

Results and Discussion

A variety of thiolsulfonates were prepared and treated with aminophosphine **4**. In most of the reactions investigated, sulfone was the only product observed. For example, methyl methanethiolsulfonate (**7**) and benzyl benzylthiolsulfonate (**9**) afforded dimethyl sulfone (**8**) and dibenzyl sulfone (**10**) in 80 and 70% yield, respectively. In both reactions, the absence of sulfinate ester was demonstrated by vpc. In a few cases, sulfinate esters were observed as minor by-products (10–30%) of the desulfurization reaction. For example, ethyl ethanethiolsulfonate (**11**) afforded both diethyl sulfone (**12**) (50%) and ethyl ethanesulfinate (**13**) (15%) on reaction with **4**. The results of these desulfurization reactions are summarized in Table I. In all cases, isolated yields were in excess of 65%; where only one product was formed, the absence of sulfinate ester was demonstrated by vpc analysis of the reaction mixture.

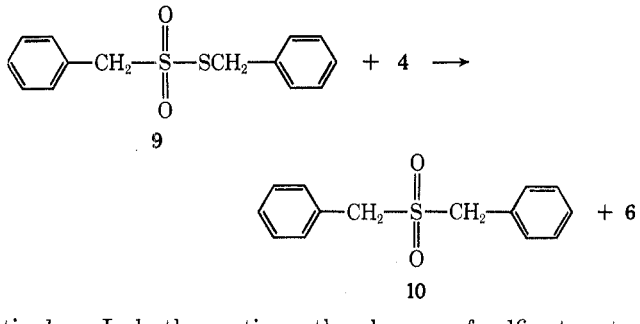
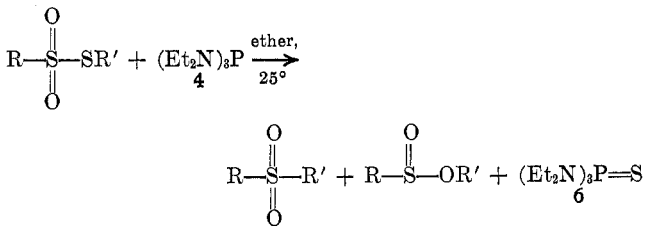


TABLE I



	R	R′	Product composition[a] R–S(=O)–R′	Product composition[a] R–S(=O)–OR′
14	CH_3–	$-CH_3$	66[b]	33[b]
15	CH_3–	$-C_2H_5$	61[c]	39[c]
16	CH_3–	$-CH_2$–	100	0
17	CH_3–	$-CH_2$–Br	100	0
18	CH_3–	$-CH_2$–CH_3	100	0
7	CH_3–	$-CH_3$	100	0
11	C_2H_5–	$-C_2H_5$	66	33
9	$C_6H_5CH_2$–	$-CH_2$–	100	0

[a] Product composition was determined by vpc analyses. Unless otherwise noted isolated yields of desulfurized products were better than 60%. [b] Low yields are due to separation difficulties. [c] No products were isolated.

The formation of both sulfone and sulfinate ester during desulfurization is indicative of the formation of an ambident sulfinate anion (Scheme I). Meek and Fowler[10] have demonstrated that O- and S-alkylation of the ambident *p*-toluenesulfinate anion is very sensitive to the structure of the alkylating agent. The sulfinate–sulfone distribution is consistent with the expected[11] behavior of such an ambident anion in that nucleophilic displacement by the sulfinate ion on a benzylic center (**16**, **17**, **18**) would proceed preferentially through the less electronegative atom (sulfur), while enhanced O-alkylation would be anticipated on an alkyl center (**14**, **15**). As is shown in Table I, this is, in fact, observed.[12]

The reactions of diaryl thiolsulfonates with phosphines are of special interest since neither sulfone nor sulfinate ester would be expected. When phosphine **4** was added to an ethereal solution of *p*-tolyl *p*-toluene-

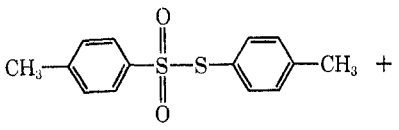
(9) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(10) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 3422 (1968).

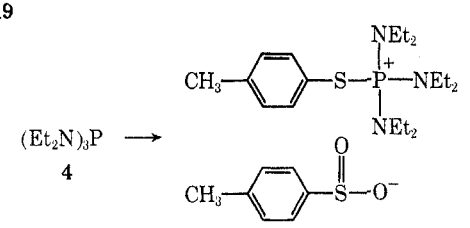
(11) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 296.

(12) This rationalization is not valid for compounds **7**, **9**, and **11** since in these cases both the sulfenyl (RS–) and sulfonyl (RSO_2–) radicals are varied.

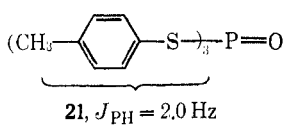
thiolsulfonate (**19**), a 1:1 thiolsulfonate–phosphine adduct **20** was isolated as a viscous, hygroscopic oil. The 60-MHz nmr spectrum of **20** exhibited a singlet and a



19



20, ^{31}P, δ −61.6



21, J_{PH} = 2.0 Hz

doublet (J_{PH} = 2.5 Hz) for the *p*-tolyl methyl resonances. The doublet results from seven-bond long-range coupling with the phosphorus nucleus. Analogous couplings have been observed in the spectrum of tri-*p*-tolyl phosphotrithioate (**21**) and for several other phosphines, phosphine oxides, and phosphonium salts.[13] The phosphonium salt structure of this adduct was confirmed by ^{31}P nmr spectroscopy in that adduct **20** exhibited a resonance at −61.6 ppm relative to H_3PO_4, consistent with that observed for other phosphonium salts (Table II).

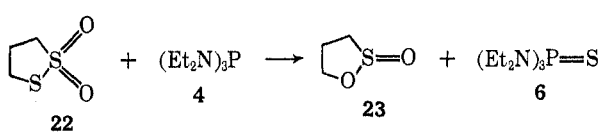
TABLE II

^{31}P NMR CHEMICAL SHIFTS

Compd	δ ^{31}P (relative to H_3PO_4)[a]
$(Et_2N)_3P$ (**4**)	−117.7
$(Et_2N)_3P{=}O$[b]	−23.5
$(Et_2N)_3P{=}S$ (**6**)	−78.5
$(Et_2N)_3\overset{+}{P}SCH_2Ph\ BF_4^-$[c]	−61.9
$(Et_2N)_3\overset{+}{P}SC_6H_4CH_3\ ^-SO_2C_6H_4CH_3$[c]	−61.6

[a] Recorded in benzene solution. [b] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967. [c] J. G. Gleason, Ph.D. Thesis, McGill University, June 1970.

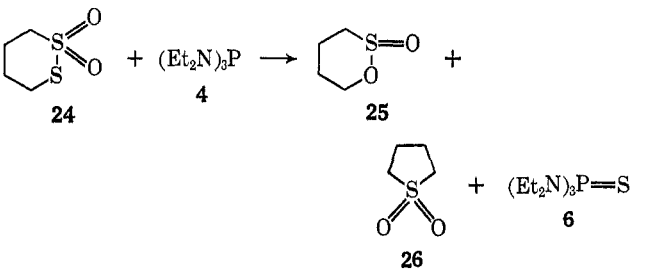
Cyclic thiolsulfonates, on treatment with aminophosphine **4**, yield sulfinate esters and not sulfones.[14] The addition of **4** to a benzene solution of 1,2-ditholane 1,1-dioxide (**22**) effected an exothermic reaction which on distillation provided 1,2-oxathiolane 2-oxide (**23**) in 92% yield.



22 **4** **23** **6**

(13) G. Singh and H. Zimmer, *J. Org. Chem.*, **30**, 417 (1965).
(14) D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969).

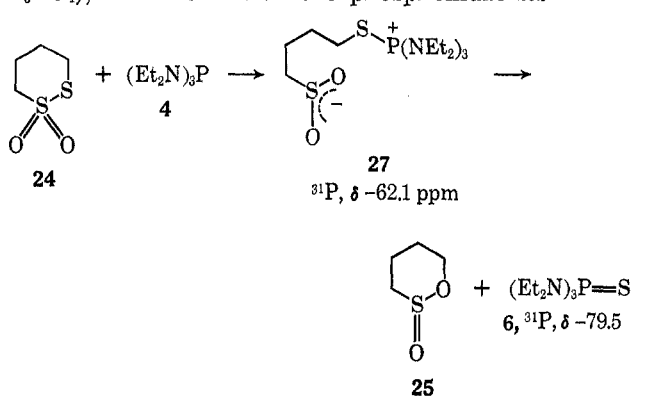
Similarly the reaction of 1,2-dithiane 1,1-dioxide (**24**) with **4** afforded a mixture consisting of 10% thiolane 1,1-dioxide (**26**) and 90% 1,2-oxathiane 2-oxide (**25**).



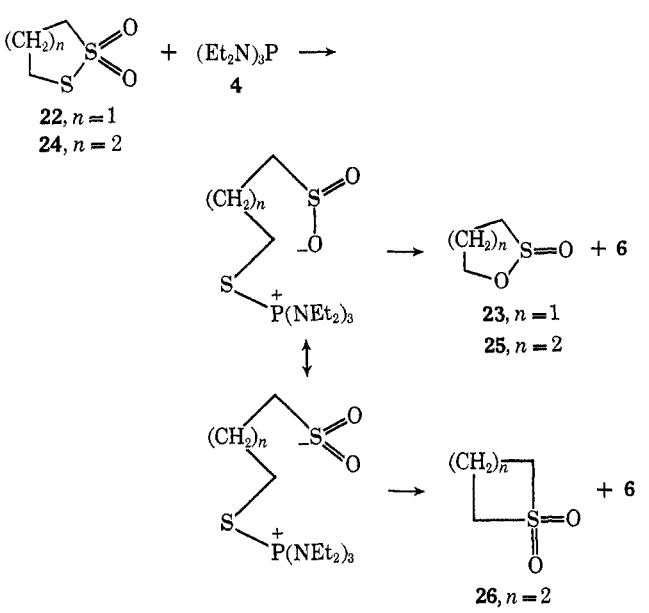
24 **4** **25** **26** **6**

This alicyclic sulfinate ester was subsequently isolated in 64% yield.

The formation of both sulfone **26** and sulfinate ester **25** during desulfurization of **24** would indicate that the reaction proceeds *via* the phosphonium salt **27**. This ionic intermediate was detected by ^{31}P nmr. Thus, when equimolar amounts of thiolsulfonate **24** and **4** were mixed in an nmr tube, an oil appeared immediately which exhibited a resonance at −62.1 ppm (relative to H_3PO_4), consistent with the phosphonium salt structure **27** (Table II). This signal slowly (5 min) disappeared and was replaced by a new resonance at −79.5 ppm, which is in good agreement with that observed for the aminophosphine sulfide **6** (Table II). Thus, it may be concluded that a phosphonium salt is formed as an intermediate in this reaction. The preferred formation of sulfinate ester appears to reflect the effect of ring size on the course of reaction.

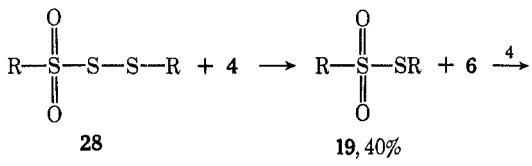


24 **4** **27** ^{31}P, δ −62.1 ppm **25** **6**, ^{31}P, δ −79.5

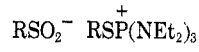


22, n = 1
24, n = 2
23, n = 1
25, n = 2
26, n = 2

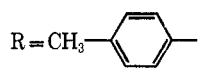
The behavior of sulfenyl thiolsulfonates toward triphenylphosphine (**3**) and tris(diethylamino)phosphine (**4**) was also examined. The reaction of *p*-tolylsulfenyl *p*-toluenethiolsulfonate (**28**) with aminophosphine **4** afforded three products: *p*-tolyl toluenethiolsulfonate (**19**), phosphonium salt **20**, and phosphine sulfide **6**.



28 **19**, 40%

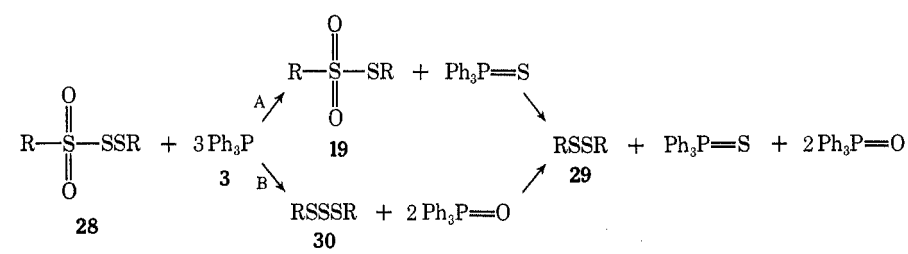


20, 60%



These observations are consistent with those obtained for the corresponding thiolsulfonate reaction.

In contrast, the reaction of sulfenyl thiolsulfonate **28** with 3 mol of triphenylphosphine (**3**) afforded only disulfide **29** (in addition to triphenylphosphine oxide and sulfide). The formation of disulfide in this reaction



may be rationalized in terms of two alternate pathways. Deoxygenation (path B) of **28** would afford the trisulfide **30** which is known[4b] to undergo rapid desulfurization to the disulfide **29**. Alternately, desulfurization of the sulfenyl thiolsulfinate prior to deoxygenation (path A) would also yield **29**.

When the reaction was performed with 1 molar equiv of triphenylphosphine (**3**), an 81% yield of thiolsulfonate **19** was realized. No trisulfide was observed. Thus, the reaction of **28** with triphenylphosphine proceeds *via* thiolsulfonate **19** as outlined in path A.

Experimental Section[15]

Preparation of Thiolsulfonates.—Benzyl phenylmethanethiolsulfonate[4c] (**9**), methyl methanethiosulfonate[16] (**7**), ethyl ethanethiolsulfonate[17a] (**11**), methyl,[17b] ethyl,[17a] benzyl,[4c] and *p*-tolyl[17c] *p*-toluenethiolsulfonates **14**, **15**, **16**, and **19** were prepared by reported procedures.

p-Bromobenzyl *p*-toluenethiolsulfonate (**17**) was prepared in 79% yield by the procedure of Boldyrev[18] from *p*-bromobenzyl bromide and potassium *p*-toluenethiolsulfonate, mp 84–85.5°.

Anal. Calcd for $C_{14}H_{13}BrO_2S_2$: C, 47.06; H, 3.67; S, 17.95. Found: C, 47.04; H, 3.76; S, 17.79.

p-Methylbenzyl *p*-toluenethiolsulfonate (**18**) was prepared in 60% yield by the procedure of Boldyrev[18] from *p*-methylbenzyl bromide and potassium *p*-toluenethiolsulfonate, mp 53–54°.

Anal. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.63; H, 5.51; S, 21.94. Found: C, 61.35; H, 5.45; S, 21.77.

1,2-Dithiolane 1,1-Dioxide (**22**).—A solution of 20.1 g (200 mmol) of 1,3-propanedithiol in 450 ml of acetic acid was cooled to 5° and 60 ml (600 mmol) of a 35% aqueous hydrogen peroxide solution was added dropwise. The mixture was stirred overnight, the acetic acid removed under vacuum (below 40°), and the residue diluted with water and extracted with ethyl acetate. After neutralization with sodium carbonate, the extract was dried and concentrated under vacuum. The residue was crystallized from ethyl acetate–ether to afford 7.3 g (26%) of colorless crystals: mp 24.5–26°; ir (KBr) 1325 and 1110 cm^{-1}; nmr ($CDCl_3$) τ 6.25 (t, 2 H, J = 6.5 Hz), 6.53 (t, 2 H, J = 7 Hz), 7.46 (m, 2 H); mass spectrum parent ion at m/e 138, fragments at 46, 45, 74, and 64.

Anal. Calcd for $C_3H_6S_2O_2$: C, 26.07; H, 4.38; S, 46.40. Found: C, 26.09; H, 4.58; S, 45.96.

1,2-Dithiane 1,1-Dioxide (**24**).—A solution of 30.5 g (250 mmol) of 1,4-butanedithiol in 250 ml of acetic acid was cooled in an ice bath and 75 ml (770 mmol) of 35% aqueous peroxide solution was added slowly such that the reaction temperature did not rise above 35°. After stirring for 18 hr, the solvent was removed under vacuum, and the residue diluted with water, neutralized with sodium bicarbonate and extracted with benzene; the benzene extract was dried and the solvent removed under vacuum to yield a viscous oil which was crystallized from ether to provide 10.5 g (28%) of white crystals, mp 52–55°, which after two crystallizations from ether provided a pure sample: mp 54–56° (lit.[19] mp 54.5–55°); nmr (CCl_4) τ 7.0 (m, 4 H), 7.9 (broad multiplet, 4 H).

Desulfurization of Methyl Methanethiolsulfonate (**7**).—To a solution of 2.50 g (20 mmol) of **7** in dry ether was added 5.50 g (22 mmol) of tris(diethylamino)phosphine (**4**) in 20 ml of dry ether. An oil, which deposited immediately on mixing **7** with **4**, slowly crystallized. Filtration and recrystallization from ethanol afforded 1.5 g (80%) of dimethyl sulfone, mp 108–109° (lit.[20] mp 109°).

Similar desulfurization reactions were performed on thiolsulfonates **9**, **11**, **14**, **16**, **17**, and **18**. These results are summarized below (thiolsulfonate, product, yield, melting point or boiling point): thiolsulfonate **9**, dibenzyl sulfone **10**, 65%, mp 154–155° (lit.[21] mp 151°); thiolsulfonate **11**,[22] diethyl sulfone **12**, 50%, mp 70–73° (lit.[23] mp 74°), and ethyl ethanethiolsulfinate **13**, 15%, bp 61–63° (10 mm) [lit.[24] bp 62° (16 mm); thiolsulfonate **14**,[22] methyl *p*-tolyl sulfone, 6%, mp 85–87° (lit.[25] mp 86–87°), and methyl *p*-toluenesulfinate, 13%, bp 100–104° (0.1 mm), $n^{25}D$ 1.548 (lit.[26] $n^{25}D$ 1.543); thiolsulfonate **16**, benzyl *p*-tolyl sulfone, 70%, mp 140–141° (lit.[27] mp 145°); thiolsulfonate **17**, *p*-bromobenzyl *p*-tolyl sulfone, 72%, mp

(15) All melting points were recorded on a Gallenkamp melting point apparatus and are corrected. ^{31}P nmr spectra were measured on a Varian Associates DP-60 instrument at an oscillator frequency of 19.3 MHz. Analyses were performed by Organic Micro-analyses, Montreal, and Scandanavian Microanalytical Laboratories, Denmark.

(16) H. J. Backer and G. J. deJony, *Recl. Trav. Chim. Pays-Bas*, **67**, 884 (1948).

(17) (a) R. Otto, *Chem. Ber.*, **15**, 123 (1882); (b) D. T. Gibson, *J. Chem. Soc.*, 2637 (1931); (c) F. Fries and W. Volk, *Chem. Ber.*, **42**, 1170 (1909).

(18) B. G. Boldyrev, L. M. Grivnak, S. A. Loleznikova, L. E. Kolmalova, and G. A. Voloshin, *Zh. Org. Khim.*, **3**, 37 (1967); *Chem. Abstr.*, **66**, 94769 (1967).

(19) L. Field and R. B. Barbee, *J. Org. Chem.*, **34**, 36 (1969).

(20) A. Saytzeff, *Justus Liebigs Ann. Chem.*, **144**, 148 (1867).

(21) A. E. Wood and E. G. Travis, *J. Amer. Chem. Soc.*, **50**, 1227 (1928).

(22) Products were separated by fractional distillation of the crude reaction mixture.

(23) S. F. Birch and W. S. G. Norris, *J. Chem. Soc.*, **127**, 1937 (1925).

(24) P. Carre and D. Liebermann, *C. R. Acad. Sci., Ser. C*, **200**, 2086 (1935).

(25) R. Otto, *Chem. Ber.*, **18**, 154 (1885).

(26) A. J. H. Houssa, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 1700 (1929).

(27) R. Otto, *Chem. Ber.*, **13**, 1278 (1880).

177–180° (lit.[28] mp 172°); thiolsulfonate **18**, *p*-methylbenzyl *p*-tolyl sulfone, 60%, mp 156–157° (lit.[29] mp 157°).

Desulfurization of Ethyl *p*-Toluenethiolsulfonate (15).—A solution of 2.16 g (10 mmol) of ethyl *p*-tolylthiolsulfonate (**15**) and 2.75 g (11 mmol) of the aminophosphine **4** in 10 ml of dry ether was stirred for 3 hr. The solvent was removed under vacuum and the residue was analyzed by vpc. By comparison of peak areas, the sulfone–sulfinate ester ratio was calculated to be 3:1. No pure products, however, were isolated from this reaction.

Attempted Desulfurization of *p*-Tolyl *p*-Toluenethiolsulfonate (19). Isolation of Adduct 20.—To a solution of 2.78 g (10 mmol) of *p*-tolyl *p*-toluenethiolsulfonate (**19**) in 10 ml of ether was added dropwise 2.50 g (10 mmol) of tris(diethylamino)phosphine (**4**). No heat was evolved; however, an oil precipitated immediately. The supernatant liquid was removed and the oil was washed eight times with fresh ether. The resulting oil was dried under vacuum for 24 hr to yield 5.0 g (92%) of adduct **20** as a tan, viscous, hygroscopic oil: nmr (benzene) τ 2.5 (m, 8 H, aromatic), 6.87 (m, 12 H, J_{HH} = 7 Hz, J_{PH} = 13 Hz), 7.60 (d, 3 H, J_{PH} = 2.5 Hz), 7.69 (s, 3 H), 8.85 (t, 18 H, J_{HH} = 7 Hz). The ^{31}P nmr of this adduct exhibited a strong resonance at −61.6 ppm relative to phosphoric acid.

Anal. Calcd for $C_{26}H_{44}N_3O_2PS_2 \cdot xH_2O$: C, 58.08; H, 8.63; N, 7.81; P. 5.76; S, 11.92. Found: C, 56.63; H, 8.93; N, 8.08; P, 5.45; S, 13.07. (Sample was reported to be highly hygroscopic.)

Desulfurization of 1,2-Dithiolane 1,1-Dioxide (22).—To a solution of 1.38 g (10 mmol) of 1,2-dithiolane 1,1-dioxide (**22**) in 25 ml of benzene was added dropwise 2.60 g (11 mmol) of tris(diethylamino)phosphine (**4**). An exothermic reaction occurred immediately upon addition of **4**. The mixture was stirred for 15 min, the solvent removed under vacuum, and the residue distilled under vacuum to yield 0.80 g (80%) of **23**: bp 48–49° (0.2 mm); $n^{25}D$ 1.4862; ir (film) 1105 cm^{-1} (S=O); nmr ($CDCl_3$) τ 6.55 (m, 2 H), 8.65 (m, 4 H); mass spectrum parent ion at *m/e* 106, fragments at 43, 58, 42, and 78.

Anal. Calcd for $C_3H_6SO_2$: C, 33.93; H, 5.70; S, 30.19. Found: C, 33.08; H, 5.92; S, 29.36.

Desulfurization of 1,2-Dithiane 1,1-Dioxide (24).—A solution of 4.50 g (29.6 mmol) of 1,2-dithiane 1,2-dioxide (**24**) in 50 ml of dry benzene was cooled in an ice bath and 7.80 g (31.6 mmol) of tris(diethylamino)phosphine (**4**) was added slowly. After stirring the mixture for 10 min, the solvent was removed under vacuum and the residue fractionally distilled under vacuum to yield 2.25 g (64%) of **25** as colorless oil, bp 58–64° (0.2 mm), which on redistillation afforded an analytical sample: bp 60–61° (0.5 mm); $n^{25}D$ 1.4862; ir (film) 1125 cm^{-1} (S=O).

Anal. Calcd for $C_4H_8O_2S$: C, 39.93; H, 6.70; S, 26.68. Found: C, 39.68; H, 6.73; S, 26.33.

***p*-Tolylsulfenyl *p*-Toluenethiolsulfonate (28).**—The method used was similar to that of Brooker, Child, and Smiles.[30] To a solution of 9.0 g (57 mmol) of *p*-toluenesulfenyl chloride[31] in 200 ml of anhydrous diethyl ether was added 13.3 g (59 mmol) of potassium *p*-toluenethiolsulfinate as a fine powder. The orange color of the sulfenyl chloride was discharged and a white precipitate of KCl formed. The reaction was stirred for 1.5 hr at room temperature and filtered, and the filtrate was evaporated to dryness. Crystallization of the crude solid from *n*-hexane gave 16.7 g (95%) of pale yellow crystals, mp 68.5–72.5°. Two recrystallizations from *n*-hexane afforded an analytical sample: mp 77.5–78.5°; ir (KBr) 1340 and 1140 cm^{-1} (–SO_2–); nmr (CCl_4) τ 2.15–3.0 (m, 8 H), 7.55 (singlet, 3 H), 7.65 (singlet, 3 H); mass spectrum parent ion *m/e* 310 fragments at 91, 123, 139, and 155.

Anal. Calcd for $C_{14}H_{14}O_2S_3$: C, 54.16; H, 4.54; S, 30.99. Found: C, 54.26; H, 4.49; S, 30.39.

Reaction of *p*-Tolylsulfenyl *p*-Toluenethiolsulfonate (28) with Tris(diethylamino)phosphine (4).—A solution of 0.25 g (1 mmol) of **4** in 25 ml of benzene was added slowly to 0.31 g (1 mmol) of **28** dissolved in 10 ml of benzene. The reaction was stirred for 6.5 hr at room temperature and the benzene was removed under vacuum. The residue was heated with *n*-hexane and an insoluble oil **20** (0.35 g) separated. The ^1H nmr of this oil was identical with that of **20** prepared by the reaction of **19** and **4**. The hexane soluble portion was chromatographed over silica gel. Elution with 1:1 hexane–chloroform afforded 0.10 g (40%) of *p*-tolyl *p*-toluenethiolsulfonate (**19**), which after crystallization from ethanol gave white crystals, mp and mmp 74–78° (lit.[32] mp 78.5–79.5°). Further elution gave 0.15 g of tris(diethylamino)phosphine sulfide (**6**).

Reaction of *p*-Tolylsulfenyl *p*-Toluenethiolsulfonate (28) with 3 Mol of Triphenylphosphine (3).—A solution of 2.36 g (9 mmol) of **3** in 50 ml of benzene was added over 1 hr to 0.93 g (3 mmol) of **28** dissolved in 50 ml of benzene. A precipitate formed and then redissolved after 2 hr. The reaction was stirred for 6 hr at room temperature, the benzene removed under vacuum, and the residue chromatographed over silica gel. Elution with 3:1 hexane–chloroform gave 0.50 g (68%) of di-*p*-tolyl disulfide (**29**) as a yellow oil which on crystallization from ethanol afforded white needles, mp 45.5–47.5° (lit.[4c] mp 47°). Elution with 1:1 hexane–chloroform provided, after crystallization from ethanol, 0.75 g (85%) of triphenylphosphine sulfide, mp 159–161.5° (lit.[4b] mp 161°). The use of 1:3 hexane–chloroform as eluent gave, after crystallization from diethyl ether, 0.95 g (57%) of triphenylphosphine oxide, mp 157–159° (lit.[33] mp 156°).

Reaction of *p*-Tolylsulfenyl *p*-Toluenethiolsulfonate (28) with Equimolar Triphenylphosphine (3).—A solution of 0.26 g (1 mmol) of **3** in 50 ml of benzene was added over 40 min to 0.31 g (1 mmol) of **28** dissolved in 50 ml of benzene. The reaction was stirred for 4 hr at room temperature, the benzene removed under vacuum, and the residue chromatographed over silica gel. Elution with 1:1 petroleum ether (30–60°)–chloroform gave a pale yellow solid, which, on crystallization from ethanol afforded 0.20 g (68%) of triphenylphosphine sulfide, mp 164–165° (lit.[4b] mp 161°). The filtrate was evaporated to dryness and crystallized from ethanol to produce 0.23 g (81%) of *p*-tolyl *p*-toluenethiolsulfonate (**19**), mp and mmp 71–75° (lit.[32] mp 78.5–79.5°).

Registry No.—**4**, 2283-11-6; $(Et_2N)_3P{=}O$, 2622-07-3; **6**, 4154-77-2; $(Et_2N)_3P^+SCH_2Ph\ BF_4^-$, 26893-33-4; **17**, 26885-97-2; **18**, 21668-99-5; **20**, 26885-99-4; **22**, 18321-16-9; **23**, 24308-28-9; **24**, 18321-15-8; **25**, 24308-29-0; **28**, 26886-04-4.

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