additional 1 g of H_2O_2 solution (total 0.054 mol of H_2O_2) was added, and the reaction was stirred an additional 11 h. After removal of methylene chloride in vacuo, the mixture was poured onto ice–water and cooled in the freezer. The acetic acid–water layer was decanted from the oil which formed, and the oil was crystallized from 95% ethanol to yield 3.95 g (79%) of phenyl benzenethiosulfonate (**3l**), mp 42–45 °C (lit.[7b] mp 45 °C).

4-*tert*-Butylphenyl 4-*tert*-Butylbenzenethiosulfonate (3m). To a solution of 908 mg (2.75 mmol) of bis(*tert*-butylphenyl) disulfide[25] in 25 mL of chloroform stirring at 0 °C was dropwise added 1.22 g (6.0 mmol, 85% pure) of *m*-chloroperbenzoic acid in 25 mL of $CHCl_3$. After 1.5 h of stirring at room temperature, the solution was washed three times with saturated aqueous $NaHCO_3$ and twice with water and dried over anhydrous $MgSO_4$. The white solid obtained upon evaporation of solvent in vacuo was recrystallized from ethanol to yield 700 mg (70%) of **3m** as needles, mp 147.5–149.5 °C (lit.[26] mp 149–150 °C). Gas chromatographic analysis (programmed 200–300 °C at 20 °C/min) indicated that **3m** was decomposing in the gas chromatograph.

Exchange Experiments between Thiosulfonates 3g, 3i, 3l, and 3m. The following is a representative procedure.

A solution of 139 mg (0.5 mmol) of **3i** and 125 mg (0.5 mmol) of **3l** in 10 mL of absolute ethanol was refluxed by using a 100 °C oil bath.

The reactions of combinations **3i,3l**, **3l,3g**, and **3i,3g** were analyzed by GC (programmed 200–300 °C at 20 °C/min) and TLC (silica gel, chloroform eluant), using compounds **3j**, **3h**, and **3d** as reference standards to determine whether or not exchange was occurring. After 24 h of reflux, it was clear that only a few percent of unsymmetrically substituted thiosulfonates was formed. The reaction solutions were analyzed by GC/MS, and the residues obtained upon evaporation of solvent were analyzed by direct-probe mass spectrometry; the mass spectral data obtained confirmed that only minor amounts of exchange products had been formed.

The reactions of combinations **3m,3i**, **3m,3l**, and **3m,3g** were analyzed by TLC, NMR spectroscopy, and mass spectrometry. TLC (silica gel, chloroform eluant) indicated three to four components in each case. Solvent was removed in vacuo and each residue obtained was analyzed by NMR spectroscopy (benzene). The upfield singlet (of the two singlets centered at δ 1.0, $\Delta(\delta) \simeq$ 2.5 Hz) of **3m** showed a slight (<1 Hz) but discernible split. Addition of increasing amounts of $Eu(fod)_3$ to the NMR samples either did not significantly improve the separation of peaks or else decreased the resolution of the spectra. Direct-probe mass spectral analysis (over a probe temperature range of 25–75 °C) of the reaction residues indicated the presence of considerable amounts of unsymmetrically substituted thiosulfonates. The solid residues obtained by evaporation of solutions of **3m,3i**, **3m,3l**, and **3m,3g** in anhydrous diethyl ether or pentane gave mass spectral analyses which indicated the formation of very little or no crossover products, while TLC analyses were essentially identical with those of the reaction mixtures.

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Registry No. 1a, 26886-04-4; **1c**, 71032-17-2; **1d**, 71032-18-3; **1e**, 71032-19-4; **1f**, 71032-20-7; **3a**, 1200-28-8; **3b**, 71032-21-8; **3c**, 1213-40-7; **3d**, 28823-18-9; **3e**, 17046-99-0; **3f**, 4973-66-4; **3g**, 1146-44-7; **3h**, 1142-97-8; **3i**, 2943-42-2; **3j**, 3541-14-8; **3k**, 71032-22-9; **3l**, 1212-08-4; **3m**, 31197-50-9; potassium *p*-toluenethiosulfonate, 28519-50-8; potassium methanethiosulfonate, 6340-98-3; potassium benzylthiosulfonate, 71032-23-0; potassium phenylthiosulfonate, 16599-39-6; potassium *p*-chlorophenylthiosulfonate, 42546-07-6; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; benzenesulfenyl chloride, 931-59-9; *p*-chlorobenzenesulfenyl chloride, 933-01-7; *p*-bromobenzenesulfenyl chloride, 1762-76-1; methanesulfenyl chloride, 5813-48-9; toluene-α-*d*, 1861-00-3; *p*-toluenesulfonyl-α-*d* chloride, 71032-24-1; *o*-toluenesulfonyl-α-*d* chloride, 71032-25-2; *p*-toluenethiol-α-*d*, 71032-26-3; *p*-toluenesulfenyl-α-*d* chloride, 71032-27-4; potassium *p*-toluenethiosulfonate-α-*d*, 71032-28-5; triphenylarsine, 603-32-7; triphenylarsine sulfide, 3937-40-4; *p*-tolyl trisulfide, 51193-08-9; phenyl disulfide, 31819-07-5; bis(*tert*-butylphenyl) disulfide, 110-06-5.

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Reaction of Trialkyl Phosphites with Organic Trisulfides. Synthetic and Mechanistic Aspects[1]

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The reaction of trialkyl phosphites with organic trisulfides to give a mixture of unsymmetrical and symmetrical disulfides and the corresponding phosphorothioates is described. Mechanistic aspects are discussed with respect to four possible ionic pathways. The synthetic potential for the preparation of unsymmetrical disulfides is examined and is found to be particularly useful for alkyl methyl disulfides.

The reaction of a trialkyl phosphite with an alkyl halide to form the dialkyl ester of a phosphonic acid and a new alkyl halide (Arbuzov reaction) is well-known in organic chemistry.[2]

$$RX + (R'O)_3P \rightarrow [(R'O)_3\overset{+}{P}R\ X^-] \rightarrow (R'O)_2P(O)R + R'X$$

Analogous reactions have been shown to occur between trialkyl phosphites and organic disulfides to yield the corresponding O,O,S-trisubstituted phosphorothioates and sulfides.[3] An ionic process, involving the rate-determining

(1) Organic Sulfur Chemistry. Part 35. For part 34, see D. N. Harpp, D. F. Mullins, K. Steliou, and I. Triassi, *J. Org. Chem.*, companion paper in this issue.

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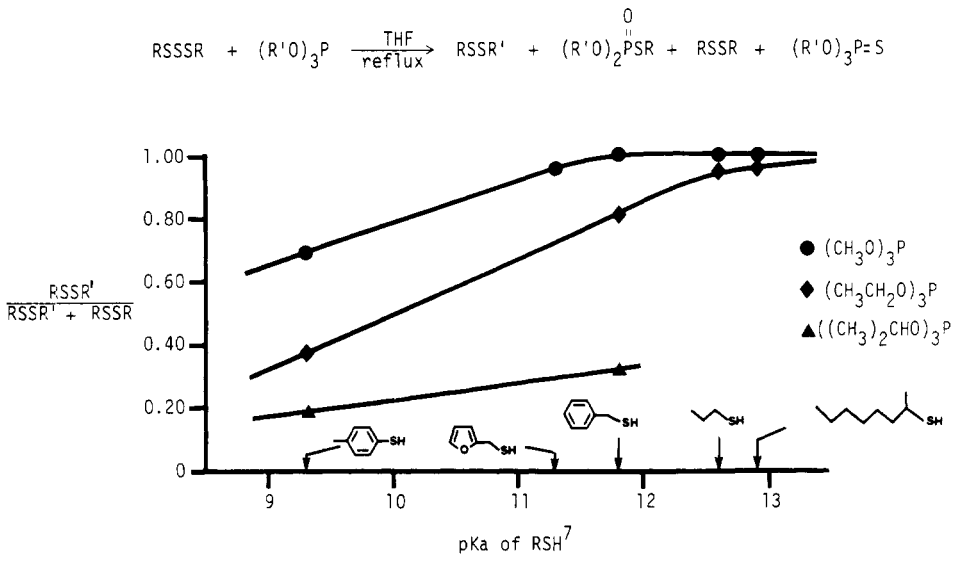

Figure 1. Reaction of trialkyl phosphites with trisulfides.

formation of the phosphonium intermediate, has been proposed as the mechanism of this reaction.[3a,g]

$$RSSR + (R'O)_3P \rightarrow [(R'O)_3\overset{+}{P}SR\ \overset{-}{S}R] \rightarrow (R'O)_2P(O)SR + RSR'$$

As part of a continuing interest in the reaction of organosulfur compounds with trivalent phosphorus compounds,[4] we have investigated the reaction of trisulfides with trialkyl phosphites. This reaction might be expected to proceed by any or all of the pathways shown in eq 1–4.

$$RSSSR + (R'O)_3P \rightarrow [(R'O)_3\overset{+}{P}SSR\ \overset{-}{S}R] \rightarrow RSSR' + (R'O)_2P(O)SR \quad (1)$$

$$[(R'O)_3\overset{+}{P}SR\ \overset{-}{S}SR] \xrightarrow{R \neq \text{aryl}} RSSR + (R'O)_3P{=}S \quad (2)$$

$$[(R'O)_3\overset{+}{P}SSR\ \overset{-}{S}R] \rightarrow RSSR + (R'O)_3P{=}S \quad (3)$$

$$[(R'O)_3\overset{+}{P}SSR\ \overset{-}{S}R] \rightarrow RSR' + (R'O)_2P(O)SSR \quad (4)$$

Preliminary experiments demonstrated the rate of reaction of dibenzyl trisulfide with trimethyl phosphite to be a function of solvent polarity, increasing in the order cyclohexane < benzene < tetrahydrofuran < acetone < acetonitrile. The very slow reactions in cyclohexane and benzene did not permit a practical analysis of the reaction products;[5] however, the reactions in the more polar media revealed a strong dependency of product composition with solvent. While reaction in either acetone or acetonitrile produced nearly equal amounts of dibenzyl and benzyl methyl disulfides,[6] use of THF as solvent cleanly gave benzyl methyl disulfide and the corresponding phosphorothioate (eq 1) as the sole products.

Table I. Reaction of Trialkyl Phosphites with Trisulfides[a]

$$RSSSR + (R'O)_3P \xrightarrow[\text{reflux}]{THF} RSSR' + (R'O)_2P{=}SR + RSSR + (R'O)_3P{=}S$$

R	R'	% products[b] RSSR'	RSSR
4-$CH_3C_6H_4$	CH_3	69	31
4-$CH_3C_6H_4$	CH_3CH_2	37	63
4-$CH_3C_6H_4$	$(CH_3)_2CH$	19	81
2-$(C_4H_3O)CH_2$	CH_3	95	5
$C_6H_5CH_2$	CH_3	100	0[c]
$C_6H_5CH_2$	CH_3CH_2	81	19
$C_6H_5CH_2$	$CH_3CH_2CH_2CH_2$	74	26
$C_6H_5CH_2$	$(CH_3)_2CH$	32	68
$CH_3CH_2CH_2$	CH_3	100	0[c]
$CH_3CH_2CH_2$	CH_3CH_2	94	6
$CH_3(CH_2)_5CHCH_3$	CH_3	100	0[c]
$CH_3(CH_2)_5CHCH_3$	CH_3CH_2	96	4

[a] All reactions were performed under dry nitrogen or argon by using a 75 °C oil bath and dried THF. [b] As determined by GC, these product ratios are corrected for GC detector response (see Experimental Section) and for the 5–6% disulfide impurity present in the dipropyl and di-2-octyl trisulfides. [c] Also, no $(R'O)_3P{=}S$ detected by GC.

It was of interest to study the reaction products for a variety of trialkyl phosphites and trisulfides; the results are summarized in Table I. As might be expected, increased steric hindrance in R' of the phosphite ($(R'O)_3P$) decreases the yield of the Arbuzov-type product (RSSR') relative to the desulfurized product (RSSR). Tris(2-chloroethyl)phosphite reacted at a very slow rate (rendering product analysis impractical), presumably due to a decrease in the nucleophilicty of phosphorus caused by the electron-withdrawing effect of the three chlorine atoms. The effect of varying the trisulfide appears to be related

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(5) The partial decomposition of dibenzyl trisulfide to dibenzyl disulfide in the gas chromatograph and the low GC detector response for *O,O,O*-trimethyl phosphorothioate necessitated a complete reaction for determination of the relative amounts of products.

(6) In both acetone and acetonitrile the ratio of $C_6H_5CH_2SSCH_3/(C_6H_5CH_2S)_2$ was 46/54.

to the pK_a of the corresponding thiol, as depicted in Figure 1. Thus the ratio of unsymmetrical and symmetrical disulfide products is apparently a function of the steric hindrance of the alkyl group of the trialkyl phosphite, as well as the leaving-group ability of the mercaptide anion from the trisulfide.

It should be noted that except when an excess of phosphite was used in the reactions with ditolyl trisulfide, there was no unsymmetrical sulfide (as in eq 4) observed in the product mixture. The only products detected were those given in eq 1–3, and some isomerization of *O,O,O*-trimethyl phosphorothioate[3d,h,8] was observed.

$$(CH_3O)_3P{=}S \xrightarrow{\Delta} (CH_3O)_2P(O)SCH_3$$

In the analogous disulfide–phosphite reaction, conditions promoting free radicals yield symmetrical sulfide and *O,O,O*-trialkyl phosphorothioate $(R'O)_3PS$.[3b,g,h,9] Under the mild reaction conditions employed in the trisulfide reactions it seemed unlikely that contributions from radical processes would be significant. This was confirmed, as the addition of hydroquinone (4 mol %) had a negligible effect on the product ratios for the reaction of ditolyl trisulfide and triethyl phosphite in THF and the reaction of dibenzyl trisulfide and trimethyl phosphite in acetonitrile.

The symmetrical disulfide formed in these reactions could arise either by eq 2 or 3 or by a combination of these two mechanisms. When R is aryl, the pathway given by eq 2 is most unlikely as a displacement at the carbon α to sulfur is required. However, the reactions with ditolyl trisulfide yielded *increased* amounts of symmetrical disulfide, relative to the reactions with the dialkyl trisulfides (see Table I and Figure 1). Thus it appears that eq 2 does not represent the major source of symmetrical disulfide. Further, the reaction of trialkyl phosphites with organic disulfides under ionic conditions does not produce symmetrical sulfides by the analogous route (eq 6), unless R is acyl or aroyl.[3g,10]

$$RSSR + (R'O)_3P \rightarrow [(R'O)_3\overset{+}{P}SR\ \overset{-}{S}R] \rightarrow RSR' + (R'O)_2P(O)SR \quad (5)$$

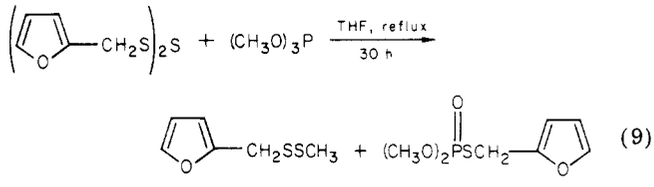
$$\not\rightarrow RSR + (R'O)_3P{=}S \quad (6)$$

It is proposed, then, that the major mechanistic pathways involved in these reactions of trisulfides with trialkyl phosphites are given by eq 1 and 3. If, as suggested for the corresponding disulfide reaction,[3a,g] the formation of the phosphonium salt is rate-determining, it seems reasonable that displacement of thiomercaptide ion would be favored over mercaptide ion, at least in medium- and low-polarity solvents. This would explain the predominance of the products of eq 1 over those of eq 3 observed in the reactions of the alkyl trisulfides with trimethyl phosphite in THF. In polar solvents, solvation might stabilize the mercaptide and thiomercaptide anions sufficiently so that both pathways (eq 1 and 3) are viable. The increased amount of symmetrical disulfide obtained in acetone and acetonitrile for the reaction of dibenzyl trisulfide and trimethyl phosphite is in qualitative agreement with this hypothesis. Increased steric size in R′ of the phosphite ($(R'O)_3P$) would be expected to slow the second step of the mechanism of eq 1 and thus increase, relatively, the amounts of the products due to eq 3, as was observed. The direct resonance stabilization of an aryl mercaptide anion is not operative for an aryl thiomercaptide anion, and thus increased amounts of eq 3 products over eq 1 products might be expected. This is reflected in the experimental results obtained for the *p*-tolyl trisulfide reactions. Similarly, other factors affecting the stability of the mercaptide anion would likely have a lesser effect on a thiomercaptide, thus explaining the pK_a relationship demonstrated in Figure 1.

Finally, the synthetic utility of this reaction was examined. While several efficient methods of preparing unsymmetrical disulfides are known,[11] their effectiveness is not always fully appreciated.[12] The trisulfide–phosphite reaction provides a useful alternative for the synthesis of unsymmetrical dialkyl disulfides, especially methyl alkyl disulfides in which the yield of symmetrical disulfide is minimal. The advantages to this procedure are the avoidance of the gaseous and highly toxic methanethiol[13] and the ready availability of the required trisulfide by reaction of the corresponding thiol with sulfur dichloride or an azole sulfur transfer reagent.[14] Additionally, the O,O,S-trisubstituted phosphorothioates may be obtained in high yield and purity. The general procedure consists of refluxing the phosphite and trisulfide in THF for an appropriate period as monitored by GC, evaporating the solvent, and separating the products by distillation (isolated yields average 80%; eq 7–9). Only in the preparation of ethyl

$$(C_6H_5CH_2S)_2S + (CH_3O)_3P \xrightarrow[30\ h]{THF,\ reflux} C_6H_5CH_2SSCH_3 + (CH_3O)_2P(O)SCH_2C_6H_5 \quad (7)$$

$$(CH_3CH_2CH_2S)_2S + (CH_3CH_2O)_3P \xrightarrow[7\ days]{THF,\ reflux} CH_3CH_2CH_2SSCH_2CH_3 + (CH_3CH_2O)_2P(O)SCH_2CH_2CH_3 \quad (8)$$



(9)

(7) The pK_a data are based on the values 4-$CH_3C_6H_4SH$ = 9.3, 2-$(C_4H_3O)CH_2SH$ = 11.3, $C_6H_5CH_2SH$ = 11.8, 1-C_4H_9SH = 12.6, and 2-C_4H_9SH = 12.9 from B. Dmuchovsky, F. B. Zienty, and W. A. Vredenburgh, *J. Org. Chem.*, **31**, 865 (1966).

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(12) The problem of producing unsymmetrical disulfides in a clean fashion is critical in any synthesis of this group. It should be pointed out that under *neutral* reaction conditions[11a,e-g] disulfide interchange is a problem only in the synthesis of unsymmetrical *diaryl* disulfides; nonneutral procedures induce exchange of all disulfide types. There appears to be confusion in the literature on this point:[11g] (a) K. C. Mattes, O. L. Chapman, and J. A. Klun, *J. Org. Chem.*, **42**, 1814 (1977); (b) D. Armitage, M. J. Clark, and C. C. Tso, *J. Chem. Soc., Perkin Trans. 1*, 680 (1972). A report on the exchange rates of unsymmetrical diaryl disulfides has appeared: A. B. Sullivan and K. Boustany, *Int. J. Sulfur Chem., Part A*, 1, 121 (1971).

(13) Flammable gas; odor of rotten cabbage. Lethal concentration for rats in air is 10 000 ppm: M. Windholz, Ed., "The Merck Index", 9th ed., Merck & Co., Inc., Rahway, NJ, 1976, p 776.

(14) (a) D. N. Harpp, K. Steliou, and T. H. Chan, *J. Am. Chem. Soc.*, **100**, 1222 (1978); (b) A. Schöberl and A. Wagner, *Methoden Org. Chem. (Houben-Weyl), 4th Ed.*, **9**, 87 (1955).

propyl disulfide, where the precursor trisulfide contained 6% dipropyl disulfide impurity and where the formation of 6% dipropyl disulfide side product has been noted (Table I), was the unsymmetrical disulfide isolated not of high purity (eq 8). This example represents a case of lesser synthetic value, as the desired product is not easily separated from the starting materials and side products.

Of partiuclar interest was the preparation of furfuryl methyl disulfide, which has been reported to be a prime odor constituent of freshly baked bread.[15] The phosphite–trisulfide reaction was successful in providing a good yield of this compound (eq 9), which was identical in all respects with material previously prepared in our laboratory.[11a] Once again however, our olfactory investigations of this substance could not lead us to describe the disagreeable odor as representative of baked bread. At best, the smell of a heavily taped vial was vaguely reminiscent of burnt toast. The structural difference between this compound and others having a fried bread (crust) odor/flavor has been pointed out.[16]

Experimental Section

Trimethyl, triethyl, and triisopropyl phosphite were homogeneous by GC and used directly. Tri-*n*-butyl phosphite was distilled before use. Cyclohexane was dried over 4 Å sieves, benzene was distilled from sodium, tetrahydrofuran was distilled from the blue sodium ketyl of benzophenone, acetone was dried over 4 Å sieves, and acetonitrile was distilled from phosphorus pentoxide.

Sulfur Dichloride Purification. Technical-grade sulfur dichloride was fractionally distilled at atmospheric pressure, and the fraction with bp 50–64 °C was collected. After addition of ca. 0.1% PCl_5, this red liquid was redistilled into a receiver containing ca. 0.01% PCl_5; bp 59–60 °C (lit.[18] bp 59 °C).

Symmetrical Trisulfides. These were prepared by the procedure described by Schöberl and Wagner.[14b] The preparation of furfuryl trisulfide is representative. To sulfur dichloride (3.09 g, 30 mmol) which had been freshly distilled twice, stirring in 300 mL of anhydrous diethyl ether, was added dropwise furfuryl mercaptan (6.84 g, 60 mmol). After 2 h, the solvent was removed under reduced pressure to yield a brown liquid which crystallized upon cooling on dry ice. The solid was treated with activated charcoal in hot ethanol and recrystallized from ethanol to yield 3.44 g of needles, mp 31–32 °C. The mother liquor was evaporated, crystallized by cooling on dry ice, and triturated with pentane to yield 2.88 g of tan solid, mp 26–28 °C, for a total yield of 6.32 g (82%): NMR ($CDCl_3$) δ 7.3 (m, 1 H), 6.2 (m, 2 H), 4.0 (s, 2 H); IR (KBr) 1500, 1395, 1240, 1205, 1150, 1005, 930, 740, 735 cm^{-1}; MS *m/e* (rel intensity) 258 (2.6, M^+), 82 (100), 53 (18.5), 45 (9.1). Anal. Calcd for $C_{10}H_{10}O_2S_3$: C, 46.48; H, 3.90;, S, 37.23. Found: C, 46.22; H, 3.94; S, 37.46.

Similarly prepared were dibenzyl trisulfide [82%, mp 47–47.5 °C (hexanes) (lit.[19] mp 49 °C)], di-4-tolyl trisulfide [86%, mp 82–84 °C (hexanes) (lit.[20] mp 80–81 °C), anal. C, H, S], and di-*n*-propyl trisulfide [82%, bp 69–72 °C (1.6 mm) [lit.[21] 68–69 °C (0.9 mm)], ca. 6% disulfide by GC].

From (±)-2-octyl mercaptan[22] and sulfur dichloride was similarly prepared di-2-octyl trisulfide. In this case the reaction solution was washed twice with water and twice with saturated $NaHCO_3$ solution, dried ($MgSO_4$), evaporated, filtered through 2 times its weight of silica gel with hexanes, and evaporated to yield a nearly colorless oil (93% yield; ca. 6% disulfide by GC): NMR (CCl_4) δ 3.0 (m, 1 H), 2.0–0.7 (m, 16 H); MS *m/e* (rel intensity) 322 (46.5, M^+), 210 (35.6), 178 (30.0), 145 (67.1), 113 (100), 69 (69.4). Anal. Calcd for $C_{16}H_{34}S_3$: C, 59.56; H, 10.62; S, 29.82. Found: C, 59.65; H, 10.67; S, 30.05.

In some of the above cases cooling of the reaction mixture in an ice–water bath was required, as the ether began to reflux. Only in the case of difurfuryl trisulfide was treatment with activated charcoal necessary.

GC Standards. The thiol–thiophthalimide method[11e,f] was used to prepare benzyl methyl disulfide [79% yield from benzyl mercaptan and methyl thiophthalimide, bp 78–82 °C (0.6 mm), n^{23} 1.5994 (lit.[12b] bp 64 °C (0.2 mm), n^{24}_D 1.5996)], benzyl ethyl disulfide [86% yield from benzyl mercaptan and ethyl thiophthalimide, bp 58–59 °C (0.025 mm), n^{22} 1.5862 (lit.[11a] bp 69–71 °C (0.2 mm), n^{23}_D 1.5841)], benzyl isopropyl disulfide [87% yield from benzyl mercaptan and isopropyl thiophthalimide, bp 58–60 °C (0.015 mm), anal. C, H, S, n^{21} 1.5728 (lit.[11d] n^{25}_D 1.5698)], and benzyl *n*-butyl disulfide [72% yield from 1-butyl mercaptan and benzylthiophthalimide, bp 74–76 °C (0.025 mm), n^{20} 1.5654 (lit[11e] bp 114 °C 1.1 mm)]. In all cases the isolated unsymmetrical disulfide was free from any symmetrical disulfides, by GC and NMR. The GC flame-ionization detector molar-response factors of these compounds, relative to dibenzyl disulfide = 1.00, ranged from 0.62 to 0.80. The GC response factors of the alkyl *p*-tolyl disulfides were assumed to be approximately equal to the analogous alkyl benzyl disulfides, as ditolyl and dibenzyl disulfide were found to give essentially equal responses.

The results (Table I) for the propyl and 2-octyl trisulfide experiments are corrected for the 5–6% disulfide impurity found in each of these trisulfides, by use of triphenylphosphine sulfide as internal standard. The product ratios were identical with those obtained in reactions having no Ph_3PS present. The disulfide products in each of these reactions were assumed to have nearly equal GC response factors; thus, the number in Table I for these experiments presumably represent the *minimum* amount of RSSR′ formed.

O,O,O-Tributyl phosphorothioate ($(C_4H_9O)_3PS$) was found to have a GC retention time nearly identical with that of benzyl *n*-butyl disulfide, by GC and GC/MS. Thus, a sample of tributyl phosphite was heated with an excess of sulfur in benzene for 15 min, at which time GC indicated complete conversion to the phosphorothioate. After addition of a known amount of dibenzyl disulfide, GC analysis indicated a molar response factor of 0.84 for *O,O,O*-tri-*n*-butyl phosphorothioate (relative to dibenzyl disulfide = 1.00). This allowed a correction for the amount of phosphorothioate contained in the GC peak for benzyl *n*-butyl disulfide, giving the result in Table I.

Reaction of Trisulfides with Trialkyl Phosphites. The following is representative. To a solution of 0.5 mmol of trisulfide in 5 mL of dry THF was added 0.55 mmol of trialkyl phosphite (except in the case of ditolyl trisulfide, where only 0.5 mmol of trialkyl phosphite was added). The solution was then heated to reflux under dry nitrogen or argon by using a 75 °C bath. The reaction was monitored by GC and found to require from 3 h for ditolyl trisulfide and trimethyl phosphite to ca. 10 days for di-2-octyl trisulfide and triethyl phosphite. The identity of each peak in the gas chromatograms was determined by comparison with an authentic sample and/or by GC/MS analysis. The ratios of products in Table I generally represent the average of the integrations of gas chromatograms from three injections of product

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(17) Unless stated otherwise, chemical reagents were obtained from commerical sources and were used directly. Melting points were obtained on a Gallenkamp block apparatus and are uncorrected. Boiling points are also uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer, calibrated with the 1601 cm^{-1} band of a polystyrene film. Nuclear magnetic resonance spectra were measured by using a Varian Associates T-60 spectrometer. Mass spectra were obtained on an AEI-MS-902 or LKB 9000 mass spectrometer using a direct insertion probe, while gas chromatographic–mass spectral analyses were performed by using a Hewlett Packard 5984A system. Gas chromatographic analyses were obtained by using a Hewlett Packard F & M Model 5751A research chromatograph, equipped with a 6 ft × 0.125 in. stainless-steel column of 5% OV-101 on Chromosorb 750 (100/120 mesh), and a Perkin-Elmer Model 194B printing integrator. Organic microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

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mixture; in many cases, duplicate experiments were performed and found to confirm the results.

Benzyl Methyl Disulfide. To a solution of benzyl trisulfide (4.17 g, 15 mmol) in 100 mL of dry THF was added trimethyl phosphite (2.11 g, 17 mmol). The mixture was refluxed (75 °C bath) under argon for 30 h, at which time GC analysis indicated complete reaction. The solution was then evaporated under reduced pressure and distilled to give four fractions of colorless liquid: (a) 2.12 g (83%), bp 56–57 °C (0.02 mm), homogeneous benzyl methyl disulfide by GC, n^{21} 1.6000 [lit.[12b] bp 64 °C (0.2 mm), n^{24}_D 1.5996]; (b) 0.37 g, 40–98 °C (0.015 mm), mixed fraction; (c) 0.97 g, bp 98–102 °C (0.015 mm), 92% *O,O*-dimethyl *S*-benzyl phosphorothioate and 8% benzyl methyl disulfide by GC; (d) 1.95 g, bp 102–107 °C (0.015 mm) [lit.[23a] bp 98 °C (0.01 mm)], homogeneous phosphorothioate by GC, n^{21} 1.5431. An overall yield of 84% (97% pure) of phosphorothioate was obtained.

Ethyl Propyl Disulfide. To a solution of di-*n*-propyl trisulfide (3.64 g, 20 mmol) in 125 mL of dry THF was added triethyl phosphite (3.65 g, 22 mmol). The mixture was refluxed (75 °C bath) under argon for 7 days, at which time GC analysis indicated essentially complete reaction. The solution was then evaporated under reduced pressure and distilled to give six fractions of colorless liquid: (a) 0.80 g, bp 47–48 °C (7 mm) [lit.[11g] bp 104–106 °C (80 mm)], ethyl propyl disulfide contaminated by a few percent of triethyl phosphite by GC; (b) 1.32 g, bp 19–20.5 °C (0.50 mm), 80% EtSSPr and 20% PrSSPr by GC; (c) 1.30 g, bp 20.5–72 °C (0.50 mm), three fractions of mixtures of EtSSPr, PrSSPr, $(EtO)_3PS$, PrSSSPr, and $(EtO)_2P(O)SPr$ by GC; (d) 3.02 g (71%), bp 72–74 °C (0.50 mm), homogeneous *O,O*-diethyl *S*-propyl phosphorothioate by GC, n^{20} 1.4589 [lit.[23b] bp 90 °C (1.2 mm), n^{20}_D 1.4581]. The overall yield of ethyl propyl disulfide was 78% (12% dipropyl disulfide) and that of the phosphorothioate was 86% (last two fractions, overall 95% pure).

Furfuryl Methyl Disulfide. To a solution of furfuryl trisulfide (3.87 g, 15 mmol) in 100 mL of dry THF was added trimethyl phosphite (2.11 g, 17 mmol). The mixture was refluxed (75 °C bath) under argon for 30 h, at which time GC analysis indicated complete reaction. The solution was then evaporated under reduced pressure and distilled to give four fractions: (a) 0.29 g of colorless liquid, bp 49–50.5 °C (0.50 mm), 75% furfuryl methyl disulfide and 25% *O,O,O*-trimethyl phosphorothioate by GC; (b) 1.66 g (69%) of colorless liquid, bp 50.5–51.5 °C (0.50 mm), homogeneous furfuryl methyl disulfide by GC, identical in all respects (odor, NMR, IR, GC/MS) with that previously prepared,[11a] n^{23} 1.5644 [lit.[11a] bp 60–61 °C (0.8 mm), n^{23}_D 1.5661]; (c) 0.33 g, bp 33–98 °C (0.015 mm), mixed fraction; (d) 2.92 g (88%) of slightly yellow liquid, bp 98–106 °C (0.015 mm), two mixed fractions, overall 94% *O,O*-dimethyl *S*-furfuryl phosphorothioate and 6% furfuryl disulfide by GC and GC/MS. The phosphorothioate was further purified by flash chromatography[24] (4:1 ethyl acetate/petroleum ether) to yield an analytical sample: n^{22} 1.5127; NMR ($CDCl_3$) δ 7.3 (m, 1 H), 6.3 (m, 2 H), 4.1 (d, 2 H, J_{HP} = 14 Hz), 3.7 (d, 6 H, J_{HP} = 13 Hz); IR(neat) 1260, 1020 cm^{-1}; MS *m/e* (rel intensity) 222 (14, M^+), 113 (14), 81 (100), 79 (8). Anal. Calcd for $C_7H_{11}O_4PS$: C, 37.84; H, 4.99; P, 13.94. Found: C, 37.63; H, 5.07; P, 13.72.

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Registry No. Di-4-tolyl trisulfide, 4991-51-9; difurfuryl trisulfide, 71243-23-7; dibenzyl trisulfide, 6493-73-8; di-*n*-propyl trisulfide, 6028-61-1; di-2-octyl trisulfide, 71243-24-8; trimethyl phosphite, 121-45-9; triethyl phosphite, 122-52-1; triisopropyl phosphite, 116-17-6; tri-*n*-butyl phosphite, 102-85-2; methyl 4-tolyl disulfide, 57266-34-9; ethyl 4-tolyl disulfide, 61565-48-8; isopropyl 4-tolyl disulfide, 29627-31-4; furfuryl methyl disulfide, 57500-00-2; benzyl methyl disulfide, 699-10-5; benzyl ethyl disulfide, 21230-16-0; benzyl butyl disulfide, 16601-16-4; benzyl isopropyl disulfide, 57413-29-3; methyl propyl disulfide, 2179-60-4; ethyl propyl disulfide, 30453-31-7; methyl 2-octyl disulfide, 71243-25-9; ethyl 2-octyl disulfide, 71243-26-0; 4-tolyl disulfide, 103-19-5; furfuryl disulfide, 4437-20-1; benzyl disulfide, 150-60-7; propyl disulfide, 629-19-6; 2-octyl disulfide, 1574-31-8; sulfur dichloride, 10545-99-0; furfuryl mercaptan, 98-02-2; (±)-2-octyl mercaptan, 10435-81-1; *O,O*-dimethyl *S*-benzyl phosphorothioate, 7205-16-5; *O,O*-diethyl *S*-propyl phosphorothioate, 20195-06-6; *O,O,O*-trimethyl phosphorothioate, 152-18-1; *O,O*-dimethyl *S*-furfuryl phosphorothioate, 71243-27-1.

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Cyclic Trisulfides by Alkoxide Decomposition of Bis(sulfenyl) Thiocarbonates[1]

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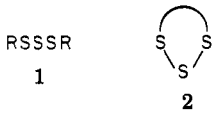
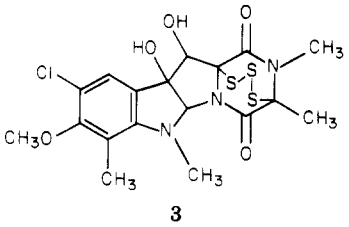
A series of bis(sulfenylated) thiocarbonates ($CH_3O_2SS(CH_2)_nSSCO_2CH_3$) was prepared and treated with potassium *tert*-butoxide in an effort to synthesize monocyclic trisulfides. In all cases (n = 2–10), polymeric material was obtained, and no target compounds were isolated. For n = 6, 7, 8, 10, cyclic bis(trisulfides) (dimers) were formed in moderate yield. Structural evidence for these macrocycles derives largely from MS, ^{13}C NMR, and osmometric molecular weight determinations.

While organic trisulfides **1** are a well-known class of



1 **2**

compounds, having such diversity as to have a role in marine[2] and insect life,[3] their cyclic versions **2** are much less common; only a few are naturally occurring. Representative among the several sulfur-containing metabolites from the fungus *Pitomyces chartarum* is the bicyclic trisulfide sporidesmin E (**3**).[4] Two others (**4** and **5**) have



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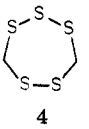

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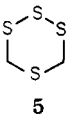

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