Attempted Reduction of 2-Methyl-2-vinylthiolane 1,1-Dioxide. To a suspension of $LiAlH_4$ in Et_2O (1.52 g, 40 mmol, in 100 mL) under nitrogen was added an ether solution of the sulfone (0.8 g, 5 mmol, in 50 mL) and the mixture warmed at reflux. GLC monitoring showed the slow disappearance of the sulfone peak was accompanied by the appearance of the **1a** peak, together with several other unidentified peaks of comparable magnitude. After 5 h, while unreacted sulfone was still present, the fraction of **1a** in the product was ~15%. No better results were obtained by changing the hydride/sulfone molar ratio. Similarly unsatisfactory results were obtained when the sulfone was allowed to react with 10 equiv of Red-Al in benzene at 80 °C for 2 h.

Methylation of 2-Vinylthiolane. To 10 mmol of the butyllithium–TMEDA complex[32] (1.6 M in hexane) at −10 °C was added 2-vinylthiolane (1.14 g, 10 mmol) dropwise. A yellow precipitate formed almost immediately while the temperature rose to −5 °C. (Attempted metalation at lower temperatures, −50 to −20 °C, for various lengths of time, followed by CH_3I quenching, led only to the recovery of unreacted 2-vinylthiolane, indicating metalation had not occurred at these low temperatures.) After 15 min at −5 °C, the temperature was brought down to −50 °C, and 10 mL of THF was added which dissolved the precipitate. Methyl iodide (1.2 equiv) was then added slowly, and stirring was continued until discoloration was complete. Conventional H_2O/CH_2Cl_2 workup gave, after drying and evaporation of the solvent, 1.00 g of an oil which on TLC appears to consist of at least three products. The ^1H NMR of the crude product shows clearly the δ 1.52 CH_3 singlet of **1a**, from the intensity of which the fraction of **1a** could be estimated at ca. 10%. Besides some unreacted starting material (~20%), two additional major species were present, accounting for the remaining 70% of the product. The presence in the ^1H NMR of two high-field triplets at δ 0.96 and 1.00 (J = 7.0 Hz) and their corresponding quartets at δ 2.05 and 2.02, respectively, suggests these species may be products of γ-alkylation, i.e., isomeric (*E*)- and (*Z*)-2-(1-propylidene)thiolane.

(32) Eberhardt, G. G.; Butte, W. A. *J. Org. Chem.* **1964**, *29*, 2928.

Registry No. **1a**, 71411-24-0; **1b**, 71411-26-2; **1c**, 71411-28-4; **2a**, 71411-29-5; **2b**, 71411-31-9; **2c**, 71411-33-1; **3**, 71411-34-2; **4**, 71411-35-3; **5**, 71411-36-4; **6**, 71411-37-5; **7**, 71411-38-6; *cis*-2-vinylthiolane 1-oxide, 71434-87-2; *trans*-2-vinylthiolane 1-oxide, 71434-88-3; *cis*-2-vinylthiane 1-oxide, 71434-89-4; *trans*-2-vinylthiane 1-oxide, 71434-90-7; *cis*-2-methyl-2-vinylthiolane 1-oxide, 71434-91-8; *trans*-2-methyl-2-vinylthiolane 1-oxide, 71434-92-9; methyl iodide, 74-88-4; *cis*-2-methyl-2-vinylthiane 1-oxide, 71434-93-0; *trans*-2-methyl-2-vinylthiane 1-oxide, 71434-94-1; ammonium hexafluorophosphate, 16941-11-0; 2-vinylthiolane 1,1-dioxide, 71411-39-7; 2-vinylthiolane, 57565-42-1; 2-methyl-2-vinylthiolane 1,1-dioxide, 71411-40-0; (*E*)-2-(1-propylidene)thiolane, 71411-41-1; (*Z*)-2-(1-propylidene)thiolane, 71411-42-2.

Chemistry of Sulfenic Sulfonic Thioanhydrides. Solvent-Dependent Sulfur Extrusion[1]

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Certain sulfenic sulfonic thioanhydrides (**1**) have been found to undergo spontaneous desulfurization to thiosulfonates (**3**) in polar solvents. Further, a novel feature of the chemistry of **3** was discovered in that these thiosulfonates have a tendency to undergo exchange in solution. Mechanisms involving solvent-stabilized sulfenium ions are proposed for both phenomena.

Although sulfenic sulfonic thioanhydrides (**1**)[2] have been known for over 50 years,[3] the chemistry of this class of compound has received little study. Displacement reactions with a variety of nucleophiles have been briefly investigated, and nucleophilic attack at sulfenyl sulfur to displace the thiosulfonate anion appears to be the major reaction pathway (eq 1).[3a-c] More recently, interactions

$$\underset{\mathbf{1}}{RSO_2SSR'} \xrightarrow{Nu^-} R'SNu + RSO_2S^- \qquad (1)$$

with trivalent phosphorus compunds have been examined.[3e,f] On the basis that thiosulfinates RS(O)SR′ (**2**),[4a] thiosulfonates RSO_2SR' (**3**),[4b,c] and disulfonic thioanhydrides RSO_2SSO_2R' (**4**)[4c] are deoxygenated by triphenylphosphine to the corresponding disulfide or trisulfide, it might be expected that **1** would be a viable precursor of trisulfides. However, earlier work demonstrated that desulfurization by triphenylphosphine precedes deoxygenation in **1**.[3e,f] Reaction with tris(diethylamino)phosphine is interesting in that desulfurization is followed by formation of a phosphonium salt, demonstrated for **1a** (R, R′ = 4-$CH_3C_6H_4$).[3f] The tendency for **1** to be desulfurized is further revealed in the conversion of **1b** to the corresponding thiosulfonate, after more than ten recrystallizations from ethanol (eq 2). Sulfur-35 labeling experiments have demonstrated that in this "spontaneous" extrusion of sulfur, and in the desulfuriza-

$$\underset{\mathbf{1b}}{4\text{-}CH_3C_6H_4SO_2S^{35}S(4\text{-}NO_2C_6H_4)} \xrightarrow{CH_3CH_2OH} 4\text{-}CH_3C_6H_4SO_2{}^{35}S(4\text{-}NO_2C_6H_4) + S^0 \qquad (2)$$

(1) Organic Sulfur Chemistry. 33. Part 32: D. N. Harpp, T. Aida, and T. H. Chan, *Tetrahedron Lett.*, 2853 (1979).

(2) IUPAC name; also known as sulfenyl thiosulfonates and sulfonyl disulfides and may be considered as partially oxidized trisulfides.

(3) (a) L. G. S. Brooker, R. Child, and S. Smiles, *J. Chem. Soc.*, 1384 (1927). (b) J. D. Loudon and A. Livingston, *ibid.*, 896 (1935). (c) O. Foss, *Acta Chem. Scand.*, **1**, 307 (1947). (d) The strong fungitoxic and phytotoxic properties of trichloromethanesulfenic arenesulfonic thioanhydrides have been demonstrated: J. H. Uhlenbroek and M. J. Koopmans, *Recl. Trav. Chim. Pays-Bas*, **76**, 657 (1957). (e) Y. Abe, T. Nakabayashi, and J. Tsurugi, *Bull. Chem. Soc. Jpn.*, **44**, 2744 (1971). (f) D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971). (g) The formation (9% yield) of 2-methylpropane-2-sulfenic benzenesulfonic thioanhydride ($PhSO_2SSBu$-*t*) in the sulfide-catalyzed decomposition of *tert*-butyl benzenethiosulfinate has been recently reported: T.-L. Ju, J. L. Kice, and C. G. Venier, *J. Org. Chem.*, **44**, 610 (1979).

(4) (a) J. F. Carson and F. F. Wong, *J. Org. Chem.*, **26**, 1467 (1961). (b) L. Horner and H. Nickel, *Justus Liebigs Ann. Chem.*, **597**, 20 (1955). (c) S. Hayashi, M. Furukawa, J. Yamamoto, and K. Hamamura, *Chem. Pharm. Bull.*, **15**, 1310 (1967).

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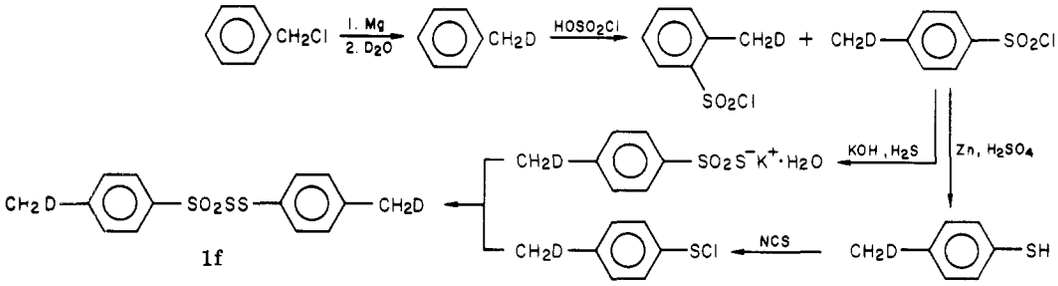
Scheme I. Synthetic Route to 4-(Methyl-*d*)benzenesulfenic 4-(Methyl-*d*)benzenesulfonic Thioanhydride (1f)



tion by triphenylphosphine as well, it is the central sulfur atom which is lost.[3e] A number of other types of compounds have also exhibited a spontaneous loss of sulfur.[5] While some of these are likely due to thermal decomposition, others appear to be solvent-related sulfur extrusions.[5c,d]

Apparently due to the susceptibility of sulfenic sulfonic thioanhydrides toward desulfurization, the reported members of this class of compound show little variety; other than 2,5-dichlorobenzenesulfenic 4-toluenesulfonic thioanhydride ($2,5\text{-}Cl_2C_6H_3SSSO_2C_6H_4CH_3$),[3a] **1b**,[3e] and our previously reported **1a**,[3f] all examples of **1** have R′ = 2-nitrophenyl, 2-nitro-4-chlorophenyl, 2-nitro-5-methylphenyl, or trichloromethyl groups.[3g]

We now report our efforts to synthesize new members of this class of compound and attempts to elucidate the mechanism by which some of these compounds extrude sulfur to yield the corresponding thiosulfonate.

Results and Discussion

The preparation of a number of new sulfenic sulfonic thioanhydrides (**1**) was attempted by the classical method.[3a] This proved to be successful in three cases (Table I), while in all other instances a fair to good yield of thiosulfonate resulted instead (Table II).[6] The range of stabilities of these thioanhydrides is quite remarkable. While compound **1c** is stable to recrystallization from acetic acid, the preparation of **1e** could not be reproduced. It was of particular interest that **1d** and **1a**[3f] lose one sulfur atom at room temperature in ethanol (eq 3). This facile sulfur

$$\underset{\substack{\mathbf{1a},\ R = 4\text{-}CH_3C_6H_4\\ \mathbf{1d},\ R = C_6H_5}}{4\text{-}CH_3C_6H_4SO_2SSR} \xrightarrow[\text{room temp}]{CH_3CH_2OH} \underset{\substack{\mathbf{3i},\ R = 4\text{-}CH_3C_6H_4\\ \mathbf{3j},\ R = C_6H_5}}{4\text{-}CH_3C_6H_4SO_2SR} + S^0 \quad (3)$$

extrusion reaction was examined under a variety of conditions. It was found that thioanhydride **1a** gave the thiosulfonate **3i** after 24 h at room temperature in the following solvents (solvent *Z* values[8a] and E_T values,[8a-c] respectively, are given parenthetically): 1:1 acetone–water (85.5, ...), methanol (83.6, 55.5), absolute ethanol (79.6, 51.9), glacial acetic acid (79.2, 51.2), 2-propanol (76.3, 48.6), acetonitrile (71.3, 46.0), dimethylformamide (68.5, 43.8), and dimethylformamide distilled from BaO (68.5, 43.8). Elution of thioanhydride **1a** through a silica gel column (*Z* value 88[8a]) with hexane–chloroform as eluant also gave the thiosulfonate **3i**. After 24 h at room temperature (unless otherwise indicated) in the following solvents (*Z* value, E_T value), **1a** was largely recovered: acetonitrile distilled from P_2O_5 (71.3, 46.0), acetone (65.7, 42.2), chloroform (63.2, 39.1), ethyl acetate (..., 38.1), tetrahydrofuran (..., 37.4), water-saturated diethyl ether, diethyl ether in 0.12 or 0.012 M HCl, refluxing diethyl ether (..., 34.6), anhydrous diethyl ether (..., 34.6), refluxing benzene (54, 34.5), and benzene (54, 34.5). It is clear from these results that the decomposition is dependent on the solvent polarity.

Table I. Preparation of Sulfenic Sulfonic Thioanhydrides (1)

$$RSO_2S^-K^+ + R'SCl \xrightarrow{Et_2O} \underset{\mathbf{1}}{RSO_2SSR'} + KCl$$

	R	R′	% yield	mp, °C (solvent)
1c	$4\text{-}CH_3C_6H_4$	$2,4\text{-}(NO_2)_2C_6H_3$	75	149.5-151 (acetic acid)[a]
1d	$4\text{-}CH_3C_6H_4$	C_6H_5	58	98-100 (ether)[b]
1e	CH_3	$4\text{-}Cl\text{-}C_6H_4$	71	37.5-39.5 (ether)[c]

[a] Anal. Calcd for $C_{13}H_{10}N_2O_6S_3$: C, 40.40; H, 2.61; N, 7.25; S, 24.87. Found: C, 40.39; H, 2.73; N, 7.22; S, 24.97. [b] Anal. Calcd for $C_{13}H_{12}O_2S_3$: C, 52.69; H, 4.08; S, 32.45. Found: C, 52.92; H, 3.82; S, 32.32. [c] Suitable IR, NMR, and mass spectral (parent ion at *m/e* 254) data were obtained; attempted further purification for analysis led to decomposition; attempts at reproducing this experiment led to thiosulfonate (see Table II).

Table II. Reaction of Potassium Thiosulfonates with Sulfenyl Chlorides to Form Thiosulfonates (3)

$$RSO_2S^-K^+ + R'SCl \xrightarrow{Et_2O} \underset{\mathbf{3}}{RSO_2SR'} + KCl + S^0$$

	R	R′	% yield	mp,[a] °C
3a	CH_3	$4\text{-}ClC_6H_5$	77	99.5-102[b]
3b	$C_6H_5CH_2$	$4\text{-}ClC_6H_5$	87	109-110[c]
3c	C_6H_5	$4\text{-}ClC_6H_5$	28	68.5-71.5[d]
3d	$4\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_5$	57	88.5-90[e]
3e	$4\text{-}CH_3C_6H_4$	$4\text{-}BrC_6H_5$	23	97.5-99.5[f]
3f	$4\text{-}CH_3C_6H_4$	CH_3	48	56.5-58.5[g]
3g	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	70	133-137[h]
3h	$4\text{-}ClC_6H_4$	C_6H_5	36	82.5-86[i]

[a] All products were recrystallized from anhydrous diethyl ether. [b] Lit.[7a] mp 102-103 °C. [c] Anal. Calcd. for $C_{13}H_{11}ClO_2S_2$: C, 52.26; H, 3.71. Found: C, 52.22; H, 3.84. [d] Lit.[7b] mp 72-73 °C. [e] Lit.[7b] mp 90 °C. [f] Lit.[3b] mp 107 °C. Anal. Calcd for $C_{13}H_{11}BrO_2S_2$: C, 45.6; H, 3.2; S, 18.7. Found: C, 46.07; H, 3.51; S, 19.66. [g] Lit.[3d] mp 57-58 °C. [h] Lit.[7c] mp 137-138 °C. [i] Lit.[7b] mp 81 °C.

(5) (a) B. P. Stark and A. J. Duke, "Extrusion Reactions", Pergammon Press, London, 1967, pp 91-107. (b) Diphenyl trisulfide: H. Lecher, *Ber. Dtsch. Chem. Ges.*, **58**, 417 (1925). (c) $(C_6H_5N{=}C(NHC_6H_5)S)_2$: P. K. Srivastava and M. Saleen, *Tetrahedron Lett.*, 2725 (1968). (d) R_2NSSO_2R': L. D. Markley and J. E. Dunbar, *J. Org. Chem.*, **37**, 2512 (1972). (e) R_2NSSCO_2R': J. J. D'Amico, F. G. Bollinger, and A. B. Sullivan, *Int. J. Sulfur Chem.*, **8**, 229 (1973). (f) D. N. Harpp, D. K. Ash, A. Granata, D. F. Montecalvo, and R. A. Smith, unpublished results.

(6) The formation of thiosulfonate in the attempted preparation of some sulfenic sulfonic thioanhydrides has been reported;[3e] however, the specific examples (other than $C_6H_5CH_2SO_2SSCH_2C_6H_5$ and $C_6H_5SO_2SSC_6H_5$) and yield of thiosulfonates have not been given.

(7) (a) B. G. Boldyrev and L. V. Vid, *Biol. Akt. Soedin.*, 165 (1965); *Chem. Abstr.*, **63**, 17950*g* (1965). (b) G. Kresze and W. Kort, *Chem. Ber.*, **94**, 2624 (1961). (c) G. Bulner and F. G. Mann, *J. Chem. Soc.*, 680 (1945).

(8) (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968, pp 301, 305. (b) M. H. Abraham, *Prog. Phys. Org. Chem.*, 11, 3 (1974). (c) C. Reichhardt, *Angew. Chem., Int. Ed. Engl.*, 18, 98 (1979).

In an attempt to determine the mechanism of this decomposition to thiosulfonate, we devised a crossover experiment to distinguish between intra- and intermolecular pathways. The deuterium-labeled thioanhydride **1f** was thus prepared via the sequence outlined in Scheme I. To test for crossover, we stirred equimolar amounts of **1a** and **1f** for 24 h in ethanol to effect desulfurization (eq 4); the

$$\underset{\mathbf{1f}}{CH_2DC_6H_4SO_2SSC_6H_4CH_2D} + \underset{\mathbf{1a}}{CH_3C_6H_4SO_2SSC_6H_4CH_3} \xrightarrow[-2S^0]{CH_3CH_2OH} {}^1/_2\underset{\mathbf{3i}}{CH_3C_6H_4SO_2SC_6H_4CH_3} + {}^1/_2(CH_2DC_6H_4SO_2SC_6H_4CH_3 + CH_3C_6H_4SO_2SC_6H_4CH_2D) + {}^1/_2\underset{\mathbf{3k}}{CH_2DC_6H_4SO_2SC_6H_4CH_2D} \quad (4)$$

thiosulfonate product was submitted for mass spectral analysis. A statistical distribution of d_0-, d_1-, and d_2-parent peaks was obtained in the mass spectrum, indicative of complete crossover, and therefore an intermolecular mechanism.

The nature of the sulfur extruded in this decomposition is of interest; if sulfur *atoms* are eliminated, they might be expected to be more reactive than elemental sulfur (S_8). It was found that triphenylarsine sulfide could not be prepared from triphenylarsine and elemental sulfur in either methanol or refluxing carbon disulfide,[9] nor could it be prepared from triphenylarsine and *p*-tolyl trisulfide in ether. However, a mixture of triphenylarsine and **1a** in methanol, benzene, or diethyl ether formed triphenylarsine sulfide and thiosulfonate **3i** in good yield (eq 5). As

$$\mathbf{1a} + Ph_3As \rightarrow \mathbf{3i} + Ph_3As{=}S \quad (5)$$

benzene and diethyl ether do not promote spontaneous sulfur extrusion of **1a**, this result is likely due to a nucleophilic displacement of sulfinate ion in the same manner that triphenylphosphine desulfurizes **1a**.[3f] Thus it is not yet clear whether or not an active form of sulfur is eliminated in this reaction. Similarly, the formation of $Ph_3As{=}S$ in the decomposition of 5-ethoxy-1,2,3,4-thiatriazole (**4**)[10] might also result by nucleophilic attack of Ph_3As on the sulfur atom of **4** rather than by a trapping of eliminated active sulfur.

It appears that the principal factor defining the stability of sulfenic sulfonic thioanhydrides is the nature of the sulfenyl group. The (trichloromethyl)sulfenyl moiety or a (2-nitrophenyl)sulfenyl group seems to provide a stability to the thioanhydride molecule toward decomposition in polar solvents.[3a,c-e] This may be considered to be due to a destabilization of the potential sulfenium ion RS^+ [3c,11] by the strong electron-withdrawing effect of these groups. Solutions of methanesulfenic 2,4,6-trinitrobenzenesulfonic anhydride [$2,4,6\text{-}(NO_2)_3C_6H_2SO_3SCH_3$] have been suggested to behave as sulfenium ion transfer agents[11a] with specific bonding interactions between sulfenium ion and solvent, rather than as solutions of "free" sulfenium ions. This may well explain the dramatic solvent dependency of the sulfur extrusions of thioanhydrides **1a** and **1d**. The stability of 2-nitrobenzenesulfenic 4-toluenesulfonic thioanhydride as compared to the stability of the corresponding 4-nitrobenzenesulfonic compound **1b** has been rationalized by consideration of an interaction between sulfur and an oxygen of the *o*-nitro group,[3e] proposed as the stabilizing factor in methyl 2-nitrobenzenesulfenate[12a] and 2-nitrobenzenesulfenyl chloride.[12b]

Scheme II

$$4\text{-}CH_3C_6H_4SO_2SSR \rightleftharpoons 4\text{-}CH_3C_6H_4SO_2S^- + {}^+SR \rightleftharpoons$$

1a, R = 4-$CH_3C_6H_4$
1d, R = C_6H_5

$$4\text{-}CH_3C_6H_4SO_2^- + S^\bullet + {}^+SR \overset{?}{\rightleftharpoons} 4\text{-}CH_3C_6H_4SO_2SR + S^\bullet$$

The solvent-dependent loss of sulfur from **1a** and **1b** is clean and quantitative. At no time was any disulfide detected; this side product would be expected if a radical mechanism were operative. Thus for all the above reasons, and since thiosulfonate ion has been suggested to be in equilibrium with sulfinate ion and sulfur,[13] the mechanism for spontaneous desulfurization is proposed as in Scheme II.

The possible reversibility of the last step of this mechanism is of some interest. If such an equilibrium exists in polar media, the results of the crossover experiment described earlier could be entirely due to an exchange between the thiosulfonate products, with no crossover having taken place during desulfurization. If this is so, an intramolecular pathway, possibly involving the dipolar intermediate **5**, might be operable (eq 6). Consistent with this,

$$\mathbf{1a} \longrightarrow \left[R{-}\overset{\overset{O}{\|}}{S}{-}\overset{+}{S}R' \;\; {}^-O \;\; S \right] \longrightarrow \mathbf{3i} + S^\bullet \quad (6)$$

5

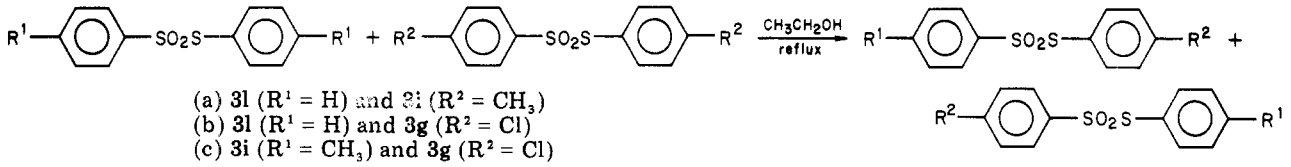
electron-withdrawing R′ could stabilize thioanhydrides by reducing the nucleophilicity of the sulfenyl sulfur, thus inhibiting formation of **5**.

Indeed, it was found that an equimolar mixture of the d_0- and d_2-thiosulfonates (**3i** and **3k**), recrystallized from chloroform or anhydrous ether, gave a mass spectrum essentially as calculated by addition of the spectra for the individual thiosulfonates. However, a mixture of these thiosulfonates recrystallized from ethanol or acetonitrile, or after 24 h in ethanol at room temperature, gave a mass spectrum which indicated *extensive or complete crossover*. This is quite remarkable, as such an exchange between thiosulfonates in polar solvents is, to our knowledge, not known.[14] In order to further investigate this phenomenon, we refluxed three pairs of aryl thiosulfonates in ethanol, the reaction being monitored by gas chromatography and TLC. To our surprise, the exchange process was extremely slow, as not more than a few percent of unsymmetrically substituted thiosulfonates was noted within 24 h of reflux (Scheme III).

GC/MS analysis of the reaction mixture, and direct-probe MS analysis of the reaction residue upon evaporation of solvent, also indicated only very minor amounts of crossover products. It seems unlikely that the methyl and methyl-d_1-substituted compounds should present a special case, and so 4-*tert*-butylphenyl 4-*tert*-butylbenzenethiosulfonate (**3m**) was prepared to confirm this. Reaction of **3m** with **3i** in refluxing ethanol for 24 h gave a product mixture which was analyzed by NMR spectroscopy, TLC, and mass spectrometry.[15] ^1H NMR spectroscopy, in the

(9) See also: K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 1875 (1963).
(10) (a) K. A. Jensen, A. Holm, and E. Huge-Jensen, *Acta Chem. Scand.*, **23**, 2919 (1969). (b) A. Holm, L. Carlsen, and E. Larsen, *J. Org. Chem.*, **43**, 4816 (1978).
(11) (a) G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Am. Chem. Soc.*, **90**, 1635 (1968), and references cited therein. (b) J. P. Marino, *Top. Sulfur Chem.*, 1 (1976).
(12) (a) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964). (b) E. N. Grivens and H. Kwart, *ibid.*, **90**, 378 (1968).
(13) (a) E. Muller, Ed., *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed*, **9**, 316 (1955). (b) J. L. Kice, private communication.
(14) Exchange of sulfonyl groups in thiosulfonates promoted by the action of sulfinate ion has been reported.[3b]
(15) Compound **3m** decomposed in the gas chromatograph.

Scheme III



(a) 3l (R^1 = H) and 3i (R^2 = CH_3)
(b) 3l (R^1 = H) and 3g (R^2 = Cl)
(c) 3i (R^1 = CH_3) and 3g (R^2 = Cl)

both very slowly formed

presence of $Eu(fod)_3$ shift reagent, revealed a slight split in the upfield *tert*-butyl signal. TLC on silica gel indicated three to four components, and direct-probe mass spectral analysis of the reaction product residue also indicated crossover products. Mass spectral analysis of the solid residue obtained by evaporation of a solution of **3m** and **3i** in anhydrous ether or pentane indicated essentially no crossover products. Thus, although this system did not allow a quantitative or entirely conclusive analysis,[15] it appears that **3m** exchanges with **3i** in ethanol or on silica gel (TLC) but not readily in anhydrous ether or pentane. Similar exchange behavior was indicated for **3m** with **3l** and **3g**.

Finally, the very slow exchange reaction between phenyl benzenethiosulfonate (**3l**) and 4-tolyl 4-toluenethiosulfonate (**3i**) in refluxing ethanol was carried out in the presence of 10 mol % of dibenzoyl peroxide, benzoquinone, and potassium iodide, monitoring by gas chromatography for 5 days. In none of these cases did the rate of formation of phenyl 4-toluenethiosulfonate (**3j**) significantly differ from that of the normal reaction.

The rate of exchange between aryl arenethiosulfonates was demonstrated to have a dramatic dependency on the para substituent. The results do, however, exhibit the same trend as for the stability of thioanhydrides **1**. The electron-donating *tert*-butyl substituent in **3m** would be expected to help stabilize a sulfenium ion; thus this thiosulfonate exchanges readily with compounds **3i**, **3l**, and **3g**. The *p*-methyl derivative **3i** also exchanges with its d_2-labeled analogue (**3k**) but not readily with compounds **3g** and **3l**, which would have little stabilizing effect to a sulfenium ion. The rate of exchange was also shown to be unaffected by the presence of a free-radical initiator, inhibitor, or strong nucleophile such as iodide ion. Thus the exchange process is likely caused by a dissociation of one of the thiosulfonates into sulfinate and solvent-stabilized sulfenium ions. This would appear to confirm the reversibility of the last step of the mechanism in Scheme II. Unfortunately, it appears that this exchange process rules out a clear distinction between the inter- and intramolecular mechanisms proposed earlier.

Experimental Section[16]

Preparation of Sulfenic Sulfonic Thioanhydrides (1a,c–e). The method used for **1a**, **1c**, and **1d** was similar to that of Brooker, Child, and Smiles[3a] and has been described previously for the preparation of **1a**.[3f] Thus, from 2,4-dinitrobenzenesulfenyl chloride and potassium *p*-toluenethiosulfonate[3d] was prepared **1c** (Table I): mp 149.5–151 °C (acetic acid); IR (KBr) 1340, 1140 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 9.1 (m, 1 H), 8.4 (m, 2 H), 7.9–7.3 (m, 4 H), 2.45 (s, 3 H); mass spectrum, parent ion at *m/e* 386, fragments at *m/e* 64, 62, 91, 198, 138, and 63. From benzenesulfenyl chloride[17] and potassium *p*-toluenethiosulfonate was prepared **1d** (Table I): mp 98–100 °C (ether); IR (KBr) 1340, 1140 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 7.85–7.15 (m, 9 H), 2.35 (s, 3 H); mass spectrum, parent ion at *m/e* 296, fragments at *m/e* 91, 155, 139, 65, 109, and 264. For the preparation of **1e**, the procedure was as follows. To a stirred solution of 4.5 g (25 mmol) of *p*-chlorobenzenesulfenyl chloride[17] in 100 mL of anhydrous diethyl ether was added 4.2 g (28 mmol) of potassium methanethiosulfonate[18] as a fine powder. After 5 min, 0.4 g (2.7 mmol) of the thiosulfonate salt was added, and this was repeated at 50 and 80 min. The reaction mixture was stirred 17 h at room temperature and then filtered to remove the KCl which had formed. The ether was evaporated from the filtrate under vacuum to yield a yellow solid which was recrystallized from diethyl ether to provide 4.5 g (71%) of **1e**, mp 36–39 °C. Three recrystallizations from ether afforded a sample: mp 37.5–39.5 °C; IR (KBr) 1320, 1140 (SO_2) cm^{-1}; NMR (CCl_4) δ 7.5 (m, 4 H), 3.22 (s, 3 H); mass spectrum, parent ion at *m/e* 254, fragments at *m/e* 143, 108, 175, and 159. An attempt at further purification by recrystallization led to decomposition, and further attempts to prepare **1e** yielded only thiosulfonate **3a**.

Thiosulfonates (3a–h). The following is a representative procedure for the isolation of thiosulfonates during the attempted preparation of sulfenic sulfonic thioanhydrides (see Table II). To a solution of 2.25 g (12.6 mmol) of *p*-chlorobenzenesulfenyl chloride in 50 mL of anhydrous diethyl ether was added 2.7 g (18 mmol) of potassium methanethiosulfonate as a fine powder. After 15 min the orange color of the sulfenyl chloride had discharged and a white precipitate had formed. Filtration, after stirring at room temperature for 3 h, gave 1.7 g of KCl plus unreacted thiosulfonate salt. Evaporation of the ether from the filtrate afforded a yellow solid which was recrystallized from ether to provide 2.25 g (77%) of **3a**, mp 99.5–102 °C (lit.[7a] mp 102–103 °C).

Sulfur Extrusion from Sulfenic Sulfonic Thioanhydrides 1a or 1d. The procedure outlined here is typical of the sulfur extrusion reactions described in the text. A solution of 200 mg of **1a**[3f] in 20 mL of solvent was stirred at room temperature. After 24 h, the solvent was removed in vacuo to quantitatively afford crude *p*-toluenethiosulfonate (**3i**) whose infrared spectrum was superimposable on that of an authentic sample. (It was found that as little as 5% of **1a** added to **3i** could be detected in the IR spectrum; thus the crude samples of **3i** obtained in these extrusion reactions must contain less than 5% unreacted **1a**.) The crude **3i** was then dissolved in *n*-hexane, and after decantation from the insoluble sulfur, the solution was cooled to yield 110 mg (61%) of **3i**, mp 72.5–75 °C (lit.[19] mp 78.5–79.5 °C). The mixture melting point with authentic **3i** was undepressed, but the mixture melting point with **1a** was <58–62 °C.

Similar treatment of **1d** in absolute ethanol yielded, after recrystallization from hexanes, 64% of phenyl *p*-toluenethiosulfonate (**3j**), mp 74–76 °C (lit.[7b] mp 78 °C).

Gas chromatographic analyses of the above reaction solutions (after 24 h at room temperature) indicated a single peak for the thiosulfonate product, with no trace of disulfide observed.

Attempted Sulfur Extrusion from *p*-Toluenesulfenic *p*-Toluenesulfonic Thioanhydride (1a). The procedure outlined

(16) Unless stated otherwise, chemical reagents were obtained from commercial 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 1602-cm^{-1} and 1028-cm^{-1} bands of a polystyrene film. Nuclear magnetic resonance spectra were measured with a Varian Associates T-60 spectrometer. Mass spectra were obtained on an AEI MS-902 or LKB 9000 mass spectrometer by using a direct insertion probe, while gas chromatographic mass spectral analyses were performed with 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). Elemental analyses were performed by Scandanavian Microanalytical Laboratories.

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here is typical of the attempted extrusion reactions described in the text in which **1a** was recovered unchanged. A solution of 200 mg of **1a** in 20 mL of solvent was stirred at room temperature. After 24 h, the solvent was evaporated in vacuo to quantitatively provide a crude solid whose infrared spectrum was identical with that of authentic **1a**. Recrystallization from *n*-hexane afforded 63% of recovered starting material, mp 72–74 °C (lit.[3f] mp 77.5–78.5 °C). The mixture melting point with authentic **1a** was 68–71 °C; the mixture melting point with **3i** was <59–65 °C.

Preparation of 4-(Methyl-*d*)benzenesulfenic 4-(Methyl-*d*)benzenesulfonic Thioanhydride (1f). (a) Toluene-α-*d*. A mixture of 48.8 g (2.0 mol) of magnesium turnings and 200 mL of anhydrous diethyl ether, in a 2-L, three-necked flask fitted with a mechanical stirrer, a condenser with a drying tube, and an addition funnel with a gas inlet tube, was flushed with nitrogen. A small amount (ca. 1.5 mL) of α-chlorotoluene was added and the reaction was initiated. A solution of 253.2 g (2.0 mol) of α-chlorotoluene in 1 L of dry ether was added over 45 min as the temperature was controlled by an ice bath. The reaction mixture was then refluxed for 15 min. After the mixture was cooled to 0 °C, 80 g (4.0 mol) of deuterium oxide (mininum isotopic purity 99.7%) was added dropwise at such a rate so as to maintain gentle refluxing. After the addition, the reaction mixture was refluxed for 15 min and cooled.

The reaction mixture was added, in small portions, to 600 mL of water and 200 mL of concentrated hydrochloric acid which had been cooled in an ice bath. The ether layer was decanted and 100 mL of ether was added and decanted. The combined ether layers were dried over anhydrous sodium sulfate and evaporated in vacuo, with a bath temperature of ca. 25 °C, to afford 280 mL of yellow liquid. Fractional distillation at atmospheric pressure gave, after a forerun of 120 mL of diethyl ether (bp ca. 35 °C), 107.95 g (58%) of toluene-α-*d* as a colorless liquid: bp 110–111 °C (lit.[20] bp 110.6 °C); NMR (neat) δ 7.05 (s, 5 H), 2.13 (t, 2 H, J_{HD} = 2 Hz).

(b) *p*-Toluenesulfonyl chloride-α-*d* was prepared in 31% yield from toluene-α-*d* essentially as described by Vogel:[21] mp 66–69.5 °C (lit.[20] mp 71 °C); NMR ($CDCl_3$) δ 7.73 (m, 4 H), 2.5 (t, 2 H, J_{HD} = 2 Hz).

Evaporation of the mother liquor from the above and fractional distillation by the procedure of Vogel[21] gave a 38% yield of a 7:3 mixture of *o*- and *p*-toluenesulfonyl chlorides: bp 140–142 °C (17 mm) (lit.[21] bp 126 °C (10 mm)); NMR ($CDCl_3$) δ 8.15–7.3 (m), 2.7 (t, J_{HD} = 2 Hz), 2.5 (t, J_{HD} = 2 Hz).

(c) *p*-Toluenethiol-α-*d* was prepared in 45% yield from *p*-toluenesulfonyl-α-*d* chloride according to the procedure of Vogel:[21] mp 41–44 °C (lit.[20] mp 44 °C); NMR ($CDCl_3$) δ 7.05 (m, 4 H), 3.3 (s, 1 H), 2.25 (t, 2 H, J_{HD} = 2 Hz).

(d) *p*-Toluenesulfenyl-α-*d* chloride was prepared in 74% yield from *p*-toluenethiol-α-*d* by the method of Emde:[22] bp 63–65 °C (0.55 mm) (lit.[17] bp 68–70 °C (0.5 mm)); NMR ($CDCl_4$) δ 7.35 (m, 4 H), 2.32 (t, 2 H, J_{HD} = 2 Hz).

(e) Potassium *p*-toluenethiosulfonate-α-*d* was prepared in 55% yield from *p*-toluenesulfonyl-α-*d* chloride as described by Boldyrev and co-workers.[23]

(f) 4-(Methyl-*d*)benzenesulfenic 4-(methyl-*d*)benzenesulfonic thioanhydride (1f) was prepared in 68% yield from potassium *p*-toluenethiosulfonate-α-*d* and *p*-toluenesulfenyl-α-*d* chloride as described for **1a**:[3f] mp 71–74 °C; mmp 72–76.5 °C; NMR (CCl_4) δ 8.2–7.0 (m, 8 H), 2.35 (m, 4 H); mass spectrum, parent ion at *m/e* 312, fragments at *m/e* 92, 124, 140, and 156. Integration of the NMR signals of **1f** and its precursors indicated a deuterium content of greater than 97%.

4-(Methyl-*d*)phenyl 4-(Methyl-*d*)benzenethiosulfonate (3k). This compound was prepared in 75% yield from **1f** by sulfur extrusion in methanol, as described earlier: mp and mmp 73–77 °C (lit.[19] mp 78.5–79.5 °C); NMR (CCl_4) δ 7.3 (m, 8 H), 2.4 (m, 4 H); mass spectrum, parent ion at *m/e* 280, fragments at *m/e* 92, 124, 140, and 156. The following relative ratios of peak intensities were observed: *m/e* 278 (0), 279 (0.09), 280 (1.00), 281 (0.18), 282 (0.09). NMR integration indicated a deuterium content of 98%.

Sulfur Extrusion of 1a Plus 1f/Crossover Experiment. A solution of 100 mg (0.32 mmol) of **1a** and 100 mg (0.32 mmol) of **1f** in 20 mL of absolute ethanol was stirred at room temperature for 24 h. A yellow semisolid precipitate was noted. The solvent was evaporated to provide an oil which crystallized on standing. Recrystallization from *n*-hexane followed by recrystallization from ethanol yielded 121 mg (68%) of thiosulfonate, mp 73–75.5 °C. Mass spectral analysis gave the following relative ratios of parent peak intensities: *m/e* 278 (0.52), 279 (1.00), 280 (0.64), 281 (0.20), 282 (0.08).

The mass spectrum of the undeuterated thiosulfonate **3i** had the relative ratios *m/e* 278 (1.00), 279 (0.20), 280 (0.10), 281 (0.03), and 282 (0). Therefore, the calculated relative ratios for complete crossover (based on the parent peak patterns for **3i** and **3k**) are 278 (0.48), 279 (1.00), 280 (0.65), 281 (0.17), and 282 (0.05).

Reaction of Triphenylarsine with 1a. To a solution of 306 mg (1.0 mmol) of triphenylarsine in 25 mL of methanol was added 310 mg (1.0 mmol) of *p*-toluenesulfenic *p*-toluenesulfonic thioanhydride (**1a**). After 20 h at room temperature, the reaction mixture was filtered to yield 155 mg of triphenylarsine sulfide, mp 166–168 °C. The filtrate, upon cooling in the freezer, yielded an additional 130 mg of crystals, mp 167–168 °C (lit.[10a] mp 164–165 °C), for a total yield of 285 mg (84%). The mother liquor was evaporated in vacuo, and the residue was crystallized from ethanol to yield 222 mg (80%) of *p*-tolyl *p*-toluenethiosulfonate (**3i**): mp 74–75 °C (lit.[19] mp 78.5–79.5 °C), mixture melting point with authentic **3i** 74.5–76 °C. When benzene or diethyl ether was used as reaction solvent in place of methanol, after 24 h at room temperature, the solvent was removed in vacuo and the residue was recrystallized from hexanes to yield two crops of triphenylarsine sulfide (62%) followed by two crops of **3i** (64%).

Attempted Preparation of Triphenylarsine Sulfide from Triphenylarsine and Sulfur. To a solution of 306 mg (1.0 mmol) of triphenylarsine in 25 mL of methanol was added 32 mg (1.0 mg-atom) of sulfur. After 4 days at room temperature, 30 mg of sulfur as a fine yellow powder was removed by filtration, and the filtrate was evaporated in vacuo to give 308 mg (100%) of triphenylarsine as a white solid: mp 58–59 °C (lit.[24] mp 61 °C), mixture melting point with authentic triphenylarsine 59–60.5 °C. Similar results were obtained when the reaction was conducted in refluxing carbon disulfide.

Attempted Desulfurization of *p*-Tolyl Trisulfide by Triphenylarsine. A solution of 139 mg (0.5 mmol) of *p*-tolyl trisulfide[25] and 153 mg (0.5 mmol) of triphenylarsine in 50 mL of anhydrous diethyl ether was kept at room temperature for 2 days, after which time no trace of triphenylarsine sulfide could be detected by TLC (silica gel, 8:2 hexane–chloroform).

Exchange Experiment between Thiosulfonates 3i and 3k. A mixture of equimolar amounts of **3i** and **3k** was recrystallized from ethanol to give the following relative intensities in the mass spectrum of the recrystallized product: *m/e* 278 (0.52), 279 (1.00), 280 (0.64). When recrystallized from acetonitrile the values were *m/e* 278 (0.54), 279 (1.00), and 280 (0.65). These results are both indicative of extensive exchange crossover. An ethanol solution of **3i** and **3k** also showed almost complete crossover by GC/MS after standing 24 h at room temperature.

The above procedure was repeated for two other recrystallization solvents. The results are, for anhydrous diethyl ether, *m/e* 278 (0.91), 279 (0.33), and 280 (1.00) and, for chloroform, *m/e* 278 (0.91), 279 (0.49), and 280 (1.00). As the calculated relative intensities for an equimolar mixture of **3i** and **3k** are *m/e* 278 (0.91), 279 (0.27), and 280 (1.00), these results are indicative of essentially no exchange between the thiosulfonates.

Phenyl Benzenethiosulfonate (3l). To a solution of 4.4 g (0.02 mol) of phenyl disulfide in 50 mL of CH_2Cl_2 and 50 mL of glacial acetic acid was added 5.1 g of a 30% solution of hydrogen peroxide. After 4.5 days of stirring at room temperature, an

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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

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