

methyl-2-phenylethyl)aziridine, 72174-76-6; 2-methyl-1-phenyl-2-propanamine, 122-09-8; *N*-(2-methoxyethyl)-2-methyl-1-phenyl-2-propanamine-HCl, 72174-77-7; *N,N'*-bis(1,1-dimethyl-2-phenylethyl)-1,2-ethanediamine, 72174-78-8; spiro[cyclopropane-1,1'-indene], 19770-38-8; indene, 95-13-6; 1-methyl-2-phenylaziridine, 4164-25-4; *N*-benzylidenemethanamine, 622-29-7; methanamine, 74-89-5; 1-*tert*-butyl-2-phenylaziridine, 18366-49-9; *tert*-butylamine, 75-64-9; 1-(1,1-dimethyl-2-phenylethyl)-2-phenylaziridine, 72174-79-9; 1-(*p*-tolylsulfonyl)-2-phenylaziridine, 24395-14-0; *p*-toluene-sulfonamide, 70-55-3; 2,3,3a,4,5,6-hexahydro-3-phenylspiro[1*H*-indole-1,1'-pyrrolidinium] fluoborate, 72174-81-3; pyrrolidine enamine of cyclohexanone, 1125-99-1; 1-phenyl-1-(2-phenylcyclopropyl)-*N,N*-dimethylmethaniminium fluoborate, 72174-83-5; *N,N*-dimethyl-1-phenylethylamine, 14548-16-4; 1-(4,5-dihydro-4-phenyl-3-furanyl)-1-ethanone, 5831-65-2; 2,3-butanedione, 431-03-8; ethyl 4,5-dihydro-2-methyl-4-phenyl-3-furancarboxylate, 19225-61-7; ethyl 1-acetyl-2-phenylcyclopropanecarboxylate, 72174-84-6; ethyl acetoacetate, 141-97-9; ethyl 4,5-dihydro-2,4-diphenyl-3-furancarboxylate, 34878-89-2; ethyl 1-benzoyl-2-phenylcyclopropanecarboxylate, 39626-45-4; ethyl benzoylacetate, 94-02-0; *trans*-1-nitro-2-phenylcyclopropane, 15267-27-3; nitromethane, 75-52-5; 3-methyl-4-phenylisoxazoline 2-oxide, 60239-09-0; *cis*-1-methyl-1-nitro-2-phenylcyclopropane, 72174-85-7; *trans*-1-methyl-1-nitro-2-phenylcyclopropane, 72174-86-8; nitroethane, 79-24-3; 3-ethyl-4-phenylisoxazoline 2-oxide, 72174-87-9; 1-ethyl-1-nitro-2-phenylcyclopropane, 72174-88-0; 1-nitropropane, 108-03-2; 3-ethyl-4-

phenylisoxazole, 72174-89-1; 3-(methoxycarbonyl)-4-phenylisoxazoline 2-oxide, 72174-90-4; methyl nitroacetate, 2483-57-0; (+)-3-(methoxycarbonyl)-4-phenylisoxazoline 2-oxide, 72174-91-5; dimethyl 2-phenyl-1,1-cyclopropanedicarboxylate, 3709-20-4; dimethyl malonate, 108-59-8; (+)-(1*S*,2*R*)-methyl 1-cyano-2-phenylcyclopropanecarboxylate, 31002-43-4; (1*S*,2*R*)-ethyl 1-cyano-2-phenylcyclopropanecarboxylate, 72204-01-4; 2-phenyl-1,1-cyclopropanedicarboxylate, 3709-34-0; methyl cyanoacetate, 105-34-0; ethyl cyanoacetate, 105-56-6; (1*R*,2*R*)-1,2-diphenyl-1-cyclopropanecarbonitrile, 72204-02-5; phenylacetone, 140-29-4; 1-phenylspiro[2.4]hepta-4,6-diene, 13189-30-5; cyclopentadiene, 542-92-7; *trans*-2-phenylspiro[cyclopropane-1,1'-indene], 66374-17-2; dimethyl 2,2-diphenyl-1,1-cyclopropanedicarboxylate, 72174-92-6; 2,2-diphenylspiro[cyclopropane-1,1'-[1*H*]indene], 72174-93-7; dimethyl 2,2-dimethyl-1,1-cyclopropanedicarboxylate, 18795-95-4; methyl 1-benzoyl-2,2-dimethylcyclopropanecarboxylate, 72174-94-8; 2,2-dimethylspiro[cyclopropane-1,1'-[1*H*]indene], 60584-81-8; diethyl 2-*p*-tolyl-1,1-cyclopropanedicarboxylate, 72174-95-9; diethyl malonate, 105-53-3; diethyl 2-furanyl-1,1-cyclopropanedicarboxylate, 72174-96-0; diethyl 2,2-dimethyl-1,1-cyclopropanedicarboxylate, 16783-05-4; diethyl 2-methyl-2-phenyl-1,1-cyclopropanedicarboxylate, 72174-97-1.

**Supplementary Material Available:** Analytical and spectral data (8 pages). Ordering information is given on any current masthead page.

## Triphenylphosphine Decomposition of Sulfenyl Thiocarbonates<sup>1</sup>

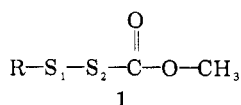
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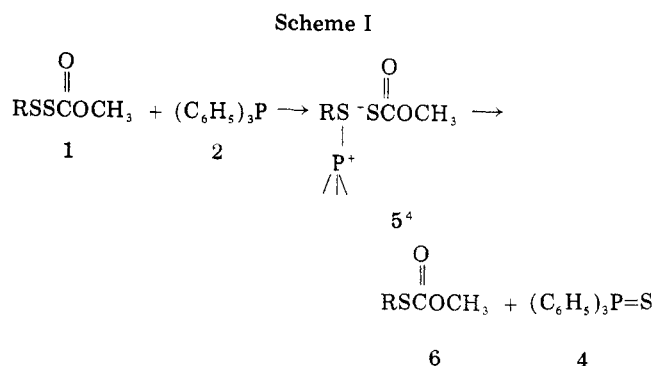
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Several sulfenyl thiocarbonates (RSSCO<sub>2</sub>CH<sub>3</sub>) have been decomposed with triphenylphosphine. In the case of R = alkyl, desulfurization takes place to give the *S*-alkyl thiocarbonate while in the case of R = aryl, a phosphonium salt is likely formed which on chromatographic workup on silica gel is converted to a thiol and triphenylphosphine oxide and sulfide. A mechanistic interpretation is offered.

Sulfenyl thiocarbonates (1, RSSCO<sub>2</sub>CH<sub>3</sub>) are a stable class of compounds which has experienced relatively little study.<sup>1,2</sup> As part of our program involved with phosphine



decompositions of various sulfur derivatives,<sup>3</sup> we felt it was of interest to examine the title compounds (Table I). In principle, there are three reasonable decomposition pathways involving triphenylphosphine (2) attack on oxygen or either sulfur atom. We have found that the main pathway involves attack at S<sub>1</sub> (Scheme I). When sulfenyl thiocarbonate 1a (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) was treated with 1 equiv of triphenylphosphine (2) in benzene and the products were chromatographed<sup>5</sup> on silica gel, benzyl mercaptan



(21%), methyl *S*-benzyl thiocarbonate 6a (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 78%), triphenylphosphine sulfide (4, 76%), and triphenylphosphine oxide (24%) were isolated. Parallel results were obtained for 1b (R = *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) (Table II). These products can best be accounted for by the pathway shown in Scheme I. Decomposition of any unreacted phosphonium salt 5 on the silica column would explain the

(1) Organic Sulfur Chemistry. Part 37. For part 36, see D. N. Harpp and A. Granata, *J. Org. Chem.*, **44**, 4144 (1979).

(2) G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970); S. J. Brois, J. F. Pilot, and M. W. Barnum, *J. Am. Chem. Soc.*, **92**, 7629 (1970); R. G. Hiskey, N. Muthukumaraswamy, and R. Vunnam, *J. Org. Chem.*, **40**, 950 (1975); D. N. Harpp and A. Granata, *Tetrahedron Lett.*, 3001 (1976); K. Nokihara and H. Berndt, *J. Org. Chem.*, **43**, 4893 (1978).

(3) D. N. Harpp, J. Adams, J. G. Gleason, D. Mullins, and K. Steliou, *Tetrahedron Lett.*, 3989 (1978), and references cited therein.

(4) C. N. Murphy and G. Winter, *Aust. J. Chem.*, **26**, 755 (1973).

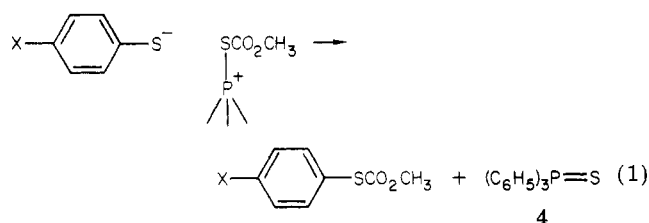
(5) When the reaction was carried out and the residue distilled directly, a 78% yield of benzyl methyl sulfide was obtained (Table II). That compound 6a is the precursor of benzyl methyl sulfide was independently demonstrated (Experimental Section). This thermal degradation has been studied; see J. L. Kice, R. A. Bantsch, M. A. Darkleff and S. L. Schwartz, *J. Am. Chem. Soc.*, **87**, 1734 (1965).

Table I. Preparation of Aryl- and Alkylsulfenyl Methyl Thiocarbonates

RSH + ClSCO <sub>2</sub> CH <sub>3</sub> → RSSCO <sub>2</sub> CH <sub>3</sub>							
R	bp, °C (mm)	yield %	<sup>1</sup> H NMR, δ			IR, cm <sup>-1</sup>	
1a	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> <sup>a</sup>	140 (3)	96	7.1 (s, 5 H), 3.9 (s, 2 H), 3.75 (s, 3 H)			3020, 2940, 1730, 1700, 1140
1b	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> <sup>a</sup>	semisolid	97	7.1 (s, 4 H), 3.9 (s, 2 H), 3.7 (s, 3 H)			3010, 2940, 1735, 1705, 1140
1c	C <sub>6</sub> H <sub>5</sub> <sup>a</sup>	120 (1.5)	98	7.6–7.2 (m, 5 H), 3.75 (s, 3 H)			3040, 2940, 1735, 1710, 1140
1d	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> <sup>b</sup>	oil	98	7.8–6.8 (m, 4 H), 3.9 (s, 3 H)			3160, 2945, 1735, 1710, 1145
1e	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <sup>c</sup>	oil	95	7.35 (m, 4 H), 3.85 (s, 3 H)			2940, 1735, 1710, 1140

<sup>a</sup> Correct C, H, and S combustion analysis. <sup>b</sup> Mass spectrum *m/e* 217.9881 (P<sup>+</sup>), calcd 217.9872. <sup>c</sup> Mass spectrum *m/e* 233.9582 (M<sup>+</sup>), calcd 233.9575.

presence of thiol and triphenylphosphine oxide.<sup>6</sup> Although no information appears to be available on the *pK<sub>a</sub>* of ROC(O)SH, it is reasonable to assume that it would be considerably lower than that of an alkyl mercaptan (*pK<sub>a</sub>* = ~10). The *pK<sub>a</sub>* value for thiolacetic acid is ca. 3.4<sup>7a</sup> and that of *O*-ethylxanthic acid (CH<sub>3</sub>CH<sub>2</sub>OCS<sub>2</sub>H) is 1.6.<sup>7b</sup> Thus, it is likely that the anion of **5** is displaced as displayed in Scheme I. It follows that no sulfenyl thiocarbonate (**6**) should be formed when an *S*-aryl sulfenyl thiocarbonate such as **1c** (R = C<sub>6</sub>H<sub>5</sub>) is treated with triphenylphosphine; the main product should be salt **5**. This salt would be expected to give substantial amounts of thiol and triphenylphosphine oxide when chromatographed over silica gel. When the experiment was carried out, a near quantitative yield of phenyl mercaptan was obtained along with an 80% yield of triphenylphosphine oxide. Only a trace of triphenylphosphine sulfide was noted. When the (*p*-fluorophenyl)sulfenyl thiocarbonate **1d** (R = *p*-FC<sub>6</sub>H<sub>4</sub>) was treated with phosphine **2**, a 90% yield of the thiol was obtained along with 94% of triphenylphosphine oxide and 6% triphenylphosphine sulfide (**4**). For **1e** (R = *p*-ClC<sub>6</sub>H<sub>4</sub>) 84% thiol was observed with 83% oxide and 15% sulfide. Presumably, in the cases of the *p*-halo-substituted phenyl derivatives, triphenylphosphine (**2**), to a limited extent, is attacking the carbonyl sulfur, displacing the appropriate mercaptide ion which collapses to give triphenylphosphine sulfide. In the case of the aryl derivatives (eq 1), as X



becomes increasingly electron-attracting a greater degree of attack takes place at the carbonyl sulfur. This would appear due to the increased leaving ability of the displaced aryl mercaptide (lower *pK<sub>a</sub>*) when X is changed from H to F to Cl.<sup>8</sup>

(6) (a) Alkyl chlorocarbonyl disulfides [RSSC(O)Cl] have been desulfurized by (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P, giving alkyl chlorides, COS, and mainly triphenylphosphine sulfide; see D. L. J. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Commun.*, 773 (1972). The formation of a small amount of triphenylphosphine oxide could be explained by an alternative pathway to any mentioned here; however, if this pathway were operative here, a thionocarbonate [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SC(S)OCH<sub>3</sub>] would have been simultaneously formed with triphenylphosphine oxide. None was detected; thus pathway I is likely not operative. Further, while triphenylphosphine has a strong affinity for oxygen, in sulfenic sulfonic thioanhydrides (RSSO<sub>2</sub>R), sulfur is removed before oxygen on treatment with triphenylphosphine (see ref 3h of ref 3). (b) When the products of the reaction of **1c** with **2** were chromatographed over alumina, no thiol could be isolated.

(7) (a) M. R. Compton in "The Chemistry of the Thiol Group", Part 1, S. Patai, Ed., Wiley-Interscience, New York, 1974, p 402; (b) F. G. Bordwell, Ed., "Organic Chemistry", Macmillan, New York, 1963, p 869.

(8) The *pK<sub>a</sub>* of these thiols decreases from phenyl (8.6) to *p*-fluorophenyl (8.1) to *p*-chlorophenyl (7.8): B. Dmuchovsky, F. B. Zienty, and J. Vredenburg, *J. Org. Chem.*, 31, 865 (1966).

In summation, we feel the product distribution can best be explained by the reaction in Scheme I. In general, the better leaving ability of the anion of **5** (as opposed to a mercaptide) would appear to be the important governing factor in this reaction.

### Experimental Section<sup>9</sup>

**Benzylsulfenyl Methyl Thiocarbonate (1a).** The preparations of **1a–e** were all carried out as for **1a**; hence only this experimental preparation will be given (see Table I for data for **1b–e**).

Benzyl mercaptan (8.95 g, 0.068 mol) in 10 mL of methanol was added dropwise at 0 °C to (carbomethoxy)sulfenyl chloride<sup>2</sup> (10.0 g, 0.08 mol) in 10 mL of methanol. The mixture was allowed to reach room temperature and stirred for 3 h. The volatiles were evaporated, leaving a yellowish oil which was purified by distillation at 140 °C (3 mm): 14.0 g (96%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (s, 5 H), 3.9 (s, 2 H), 3.75 (s, 3 H); IR (neat) 3020, 2940, 1730, 1700, 1140 cm<sup>-1</sup>. Anal. Calcd: C, 50.44; H, 4.70; S, 29.93. Found: C, 50.63; H, 4.51; S, 29.53.

**Benzyl Methyl Sulfide.** Benzylsulfenyl methyl thiocarbonate (**1a**) (4.0 g, 0.019 mol) was placed in a dried, round-bottom flask equipped with a dropping funnel. The compound was cooled to 0 °C, and a solution of triphenylphosphine (4.9 g, 0.019 mol) previously dissolved in benzene (10 mL) was added dropwise. The reaction was allowed to reach room temperature and stirred overnight. The volatiles were evaporated and the residue was distilled at 68–69 °C (5 mm) to give benzyl methyl sulfide: 2.0 g (78%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.3 (s, 5 H), 3.83 (s, 2 H), 2.95 (s, 3 H); IR (neat) 3010, 2900, 1600, 1490, 1450, 700 cm<sup>-1</sup>; mass spectrum *m/e* 138, 123, 91, 77; *n*<sub>D</sub><sup>20</sup> 1.5645 (lit.<sup>10</sup> *n*<sub>D</sub><sup>20</sup> 1.5645).

**Reaction of Benzylsulfenyl Methyl Thiocarbonate with Triphenylphosphine. Isolation of *S*-Benzyl Methyl Thiocarbonate (6a).**<sup>11</sup> Triphenylphosphine (2.22 g, 8.6 mmol) was dissolved in benzene (7 mL) and added dropwise to benzylsulfenyl methyl thiocarbonate (**1a**; 1.84 g, 8.6 mmol). During the addition, the reaction was kept between 0 and 10 °C. The reaction was allowed to reach room temperature and stirred overnight; the benzene was evaporated and the residue chromatographed over

(9) Chemical reagents were obtained from commercial sources and were used directly. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected; boiling points are also uncorrected. A Carl Zeiss Model 28241 refractometer was employed for refractive indices. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer calibrated by means of the 1601-cm<sup>-1</sup> band of polystyrene. Nuclear magnetic resonance spectra of protons were taken on a Varian Associates T-60 spectrometer. Low- and high-resolution mass spectra were obtained on an AEI-MS-902 spectrometer by direct insertion. TLC was carried out on Eastman Kodak chromatogram sheets with a fluorescent indicator; gas chromatography (GC) was performed on a F & M Model 5750 research chromatograph (Hewlett-Packard) with a Honeywell recorder. The columns were stainless steel (6 ft × 1/8 in.) packed with either 10% diethylene glycol succinate on Chromosorb W/AW-DMSC (LAC column) or 10% SE-30 Ultraphase silicon gum rubber on Chromosorb W/AW-DMSC (SE-30 column). Elemental analyses of new compounds were by the Microanalytical Laboratory of Kemisk Laboratorium II of the H. C. Ørsted Institute, Copenhagen, Denmark.

(10) C. J. Pouchert, "The Aldrich Library of Infrared Spectra", 2nd ed., Aldrich Chemical Co., Milwaukee, WI, 1977.

(11) All mercaptans and triphenylphosphine oxide and sulfide were identified by comparison with <sup>1</sup>H NMR and IR spectra of authentic samples.

Table II. Decomposition of Aryl- and Alkylsulfenyl Methyl Thiocarbonates with Triphenylphosphine

		RSSCO <sub>2</sub> CH <sub>3</sub> + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P → products				
		products, %				
	R	RSH	RSCO <sub>2</sub> CH <sub>3</sub>	RSCH <sub>3</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P=O	(C <sub>6</sub> H <sub>5</sub> )P=S
1a	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	21	78	78 <sup>a</sup>	24	76
1b	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	<i>b</i>	70		30	69
1c	C <sub>6</sub> H <sub>5</sub>	99			99	1
1d	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	90			94	6
1e	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	84			83	15

<sup>a</sup> Obtained by distillation of reaction mixture. <sup>b</sup> Not isolated.

silica. The first fraction, which was eluted with chloroform/hexane (1:4), yielded an oil upon evaporation which was identified as benzyl mercaptan: 0.27 g (21%); NMR (CDCl<sub>3</sub>) δ 7.3 (s, 5 H), 3.7 (d, 2 H), 1.7 (t, 1 H). The GC and <sup>1</sup>H NMR analyses of this fraction corresponded exactly to those of a known sample. The second fraction, which was eluted with chloroform/hexane (1:3), yielded a yellowish oil: 1.24 g (78%); NMR (CDCl<sub>3</sub>) δ 7.4 (s, 5 H), 4.15 (s, 2 H), 3.85 (s, 3 H); IR (neat) 3020, 2940, 1710, 1600, 1500, 820, 700 cm<sup>-1</sup> (lit.<sup>5</sup> C=O stretching for aryl/alkyl thiocarbonates 1705–1720 cm<sup>-1</sup>); mass spectrum, parent peak at *m/e* 182.0396 (calcd for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>S, *m/e* 182.0402). This compound was identified as *S*-benzyl methyl thiocarbonate (6a) and was pure by gas chromatography. The third fraction was eluted with chloroform/hexane (1:1) to give triphenylphosphine sulfide: 1.9 g (76%); mp 158–160 °C (lit.<sup>12</sup> mp 158–160 °C). The fourth fraction was eluted with chloroform/hexane (3:1). It yielded triphenylphosphine oxide: 0.5 g (24%); mp 147–152 °C (lit.<sup>13</sup> mp 152–153 °C).

**Reaction of *S*-*p*-Chlorobenzyl Methyl Thiocarbonate with Triphenylphosphine.** This reaction was performed as the previous one. The starting materials were (*p*-chlorobenzyl)sulfenyl methyl thiocarbonate (1b; 5.0 g, 0.02 mol), triphenylphosphine (5.27 g, 0.02 mol), and benzene (20 mL). The product thiocarbonate was obtained as a colorless liquid after purification by chromatography (silica, chloroform/hexane, 1:3): 3.07 g (70%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (s, 4 H), 3.95 (s, 2 H), 3.7 (s, 3 H); IR (neat) 3000, 2950, 1715, 1600, 1500, 1150, 825, 680 cm<sup>-1</sup>; mass spectrum *m/e* 216.0017 (P<sup>+</sup>) (calcd for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>SCl, *m/e* 216.0015). Triphenylphosphine sulfide, 4.1 g (69%), and triphenylphosphine oxide, 1.85 g (30%), were isolated.

**Thermal Decomposition of *S*-Benzyl Methyl Thiocarbonate (6a). Preparation of Benzyl Methyl Sulfide.** *S*-Benzyl methyl thiocarbonate (6a; 0.70 g, 3.8 mmol) was placed in a flask equipped with a thermometer and an adapter connected to an aqueous solution of calcium hydroxide. The container was immersed in an oil bath preheated to 90 °C. When the temperature of the thiocarbonate reached 70 °C, a gas started to evolve and was bubbled through the solution of calcium hydroxide giving rise to a milky precipitate. The reaction temperature kept rising until it was in equilibrium with the bath temperature; the thiocarbonate decomposition was monitored by GC. The evolution of gas stopped after 45 min, and no more starting material was detected by GC. A yellowish oil was left as residue in the flask and was identified by GC as pure benzyl methyl sulfide, 0.52 g (100%, crude yield).

**Reaction of Phenylsulfenyl Methyl Thiocarbonate (1c) with Triphenylphosphine.** Starting materials were phenylsulfenyl methyl thiocarbonate (1c; 5.0 g, 0.025 mol), triphenylphosphine (6.55 g, 0.025 mol), and benzene (40 mL). A thin-layer chromatogram (silica, chloroform/hexane, 1:3) was taken of the residue after the evaporation of benzene. It showed the presence

of three compounds. The residue was chromatographed over silica. The first fraction (chloroform/hexane, 1:3) was a yellowish liquid with a strong unpleasant smell: 2.49 g (99.5%); NMR (CDCl<sub>3</sub>) δ 7.00 (s, 5 H), 3.35 (s, 1 H). GC analysis of this compound showed a peak with the same retention time of a pure sample of benzenethiol. The second fraction (chloroform/hexane, 1:1) yielded white crystals: 1.33 g (20%); mp 145–150 °C. This fraction was identified by GC as a mixture of triphenylphosphine sulfide (ca. 1%) and triphenylphosphine oxide (ca. 19%). The third fraction yielded white crystals (5.55 g, 80%); mp 153–156 °C and was identified as triphenylphosphine oxide.

**Reaction of *p*-Fluorophenylsulfenyl Methyl Thiocarbonate (1d) with Triphenylphosphine.** The starting materials were *p*-fluorophenylsulfenyl methyl thiocarbonate (1d; 2.0 g, 9.2 mmol), triphenylphosphine (2.41 g, 9.2 mmol), and benzene (20 mL). Three fractions were collected by using the same eluents as in the previous experiment. The first fraction was a yellowish liquid (0.145 g, 90%) and was identified by GC as *p*-fluorophenyl mercaptan. The second fraction was triphenylphosphine sulfide (0.24 g, 6%); mp 160–162 °C. The third fraction was 2.4 g (94%) of triphenylphosphine oxide, mp 152–155 °C.

**Reaction of Phenylsulfenyl Methyl Thiocarbonate (1c) with Triphenylphosphine (Alumina Chromatography).** This reaction was performed as the previous one. Starting materials were phenylsulfenyl methyl thiocarbonate (1c) (2.0 g, 0.01 mol), triphenylphosphine (2.62 g, 0.01 mol), and benzene (25 mL). The residue obtained after the evaporation of benzene was chromatographed over alumina. Again, three fractions were obtained by using the same eluents as before. The first fraction, which was a light yellow oil showing one product by TLC gave four peaks by GC. Only one of these products was identified (diphenyl disulfide). The second fraction consisted of 33% triphenylphosphine sulfide. Fraction three was 2.1 g (67%) of triphenylphosphine oxide.

**Reaction of (*p*-Chlorophenyl)sulfenyl Methyl Thiocarbonate (1e) with Triphenylphosphine.** Starting materials were *p*-chlorophenylsulfenyl methyl thiocarbonate (1e; 2.0 g, 8.6 mmol), triphenylphosphine (2.25 g, 8.6 mmol), and benzene (20 mL). The residue, after the evaporation of benzene, was chromatographed over silica. Three fractions were collected by using the same eluents as in the previous experiment. The first fraction was a colorless liquid which crystallized on standing (0.94 g, 84%); mp 48 °C and was identified as *p*-chlorobenzenethiol. The second fraction was triphenylphosphine sulfide, 0.40 g (15%), and the third fraction was triphenylphosphine oxide, 2.0 g (83%).

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada and the Department of Education of Quebec for financial support of this work.

**Registry No.** 1a, 61775-34-6; 1b, 72050-05-6; 1c, 61775-35-7; 1d, 72050-06-7; 1e, 67318-38-1; 2, 603-35-0; 4, 3878-45-3; 6a, 72050-07-8; 6b, 72050-08-9; benzyl mercaptan, 100-53-8; benzenethiol, 108-98-5; *p*-fluorophenyl mercaptan, 371-42-6; *p*-chlorophenyl mercaptan, 106-54-7; triphenylphosphine oxide, 791-28-6; (carbomethoxy)sulfenyl chloride, 26555-40-8; benzyl methyl sulfide, 766-92-7.

(12) G. A. Olah and D. Hehemann, *J. Org. Chem.*, 42, 2190 (1977).

(13) H. R. Hays and D. J. Peterson in "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Eds., Wiley-Interscience, New York, 1972, p 431.