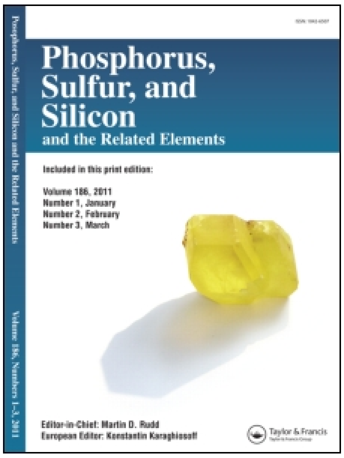

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REDOX REACTIONS OF ANTIMONY(III) O,O-DISUBSTITUTED PHOSPHORODITHIOATES WITH FERRIC CHLORIDE

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REDOX REACTIONS OF ANTIMONY(III) O,O-DISUBSTITUTED PHOSPHORODITHIOATES WITH FERRIC CHLORIDE

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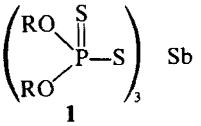
The reaction of antimony(III) *tris*-(O,O-diethylphosphorodithioate) with three equivalents of ferric chloride in ether solution has been found to give ferrous chloride, *bis*-(O,O-diethylthiophosphoryl) disulfide and dichloroantimony O,O-diethyl phosphorodithioate as the major products. However, a relatively low yield of *bis*-(O,O-diethylthiophosphoryl) trisulfide was also obtained. The structures of these products were established by independent syntheses. Several additional antimony(III) *tris*-(O,O-disubstituted phosphorodithioates) were prepared, and the major organic product obtained by reaction of each of these compounds with three equivalents of ferric chloride was the corresponding *bis*-(O,O-disubstituted thiophosphoryl) disulfide. A mechanism for this reaction has been suggested, and evidence in support of the mechanism has been presented.

The various antimony(III) *tris*-(O,O-dialkyl phosphorodithioates) are passivating agents used in petroleum refining. The results reported in this and in our previous papers indicate that such compounds undergo a variety of reactions with components of crude petroleum prior to the ultimate pyrolysis reactions which occur in the fluid catalytic cracking process.

INTRODUCTION

Reports have been published[1-9] that the addition of relatively small amounts of "Phil-Ad CA" to the crude feed entering a catalytic cracking unit results in passivation of contaminant metals (mainly nickel, vanadium and iron). The presence of these contaminant metals on the cracking catalyst brings about an increase in hydrogen and coke yields and a decrease in gasoline yield. The major benefits which have been realized by use of "Phil-Ad CA" are: (1) an increase in product value as a result of an improved distribution of cracked products; (2) an increase in fluid catalytic cracking capacity inasmuch as less coke and light gases are formed; and (3) an ability to use oil feeds having higher contaminant metal concentrations.

Since "Phil-Ad CA" is a solution in liquid hydrocarbons mainly of antimony(III) O,O-*bis*-(*n*-propyl) phosphorodithioate **2** (but also containing related compounds, **1**), and since almost nothing is known about the fundamental chemistry of such compounds, we have initiated a program designed to remedy this situation. As an obvious starting point for new research, we have determined the structure of the ethyl analog, **3**, by single crystal X-ray diffraction analysis.[10] The reason for the use of **3** in the structure determination rather than **2** is that **3** is a solid of melting point 56°C,[11] while **2** is a liquid even at 0°C.[12]



1

2 R = *n*-propyl

3 R = ethyl

We have found[10] that the coordination polyhedron of the antimony atom in antimony(III) *tris*-(O,O-diethyl phosphorodithioate) is a distorted capped octahedron with a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the antimony atom.

Both geometric and electronic effects may be involved in the passivation of contaminant metals by antimony. Antimony may form an alloy with the contaminant metals on an FCC catalyst, and this alloy may have much of the antimony segregated to the surface. For example, Sparks[13] has reported that annealing of an alloy of composition $Ni_{0.96}Sb_{0.04}$ at 725°C gives a stable, reproducible antimony enriched surface having a first monolayer with an antimony fraction of about 0.5. Also, Dreiling and Schaeffer[14] have demonstrated that a nickel-antimony alloy having surface enrichment of antimony is produced when nickel octoate, impregnated on a steam-aged Filtrol F-950 clay zeolite, is treated with antimony(III) *tris*-(O,O-di-*n*-propyl phosphorodithioate), **2**, and the system then subjected to several oxidation-reduction cycles at 500–650°C. Furthermore, Hudis, Perlman and Watson[15] have detected significant volume and electronic effects when antimony is added to nickel metal, indicating a strong interaction. Thus, a tentative conclusion can be reached that the metals end up as bimetallic (metal plus antimony) particles supported on the FCC catalyst, and that one element alters the catalytic activity of the other. The detailed chemical pathway whereby both the antimony in the additive and the contaminant metal in its compounds end up in the zerovalent states is not known, but thermolysis is almost certainly involved in the process. However, before this occurs, the antimony(III) O,O-dialkyl phosphorodithioates, **1**, undoubtedly undergo a variety of reactions with compounds found in crude petroleum. The purpose of our present research program is to explore such reactions. Some prototype reactions involving solvolysis were covered in a previous publication.[16]

The contaminant metals in crude petroleum exist in three possible forms: (1) as salts dissolved in water suspended in the petroleum; (2) as metallic soaps of aliphatic, aromatic, or naphthenic acids; and (3) as organometallic complexes (e.g. complexes with porphyrins).[17] Although we intend to investigate the reactions of compounds of type **1** with the metallic compounds in all of the forms cited above, we have chosen to begin with model reactions involving anhydrous ferric chloride.

RESULTS AND DISCUSSION

A series of antimony(III) *tris*-(O,O-dialkyl phosphorodithioates), **1**, was prepared by the general method[18–24] shown below:

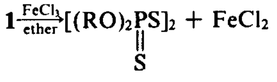
$$P_4S_{10} + 8\ ROH \xrightarrow[x,\ h]{T_1,\ ^\circ C} 4\ (RO)_2PS_2H + 2\ H_2S$$

4

$$3\ \mathbf{4} + SbCl_3 \xrightarrow[y,\ h]{T_2,\ ^\circ C} \mathbf{1} + 3\ HCl$$

The yields of products, reaction conditions, and physical properties of the products are presented in Table I.

When an ether solution of each of several antimony(III) *tris*-(O,O-dialkyl phosphorodithioates) was refluxed with three equivalents of ferric chloride, a *bis*-(O,O-dialkylthiophosphoryl) disulfide, **5**, and ferrous chloride were obtained.



$$\mathbf{1} \xrightarrow[ether]{FeCl_3} [(RO)_2\underset{\underset{S}{\|}}{P}S]_2 + FeCl_2$$

5

(R: methyl-, isopropyl-, *n*-propyl-, isobutyl-, *n*-pentyl-, phenyl-.)

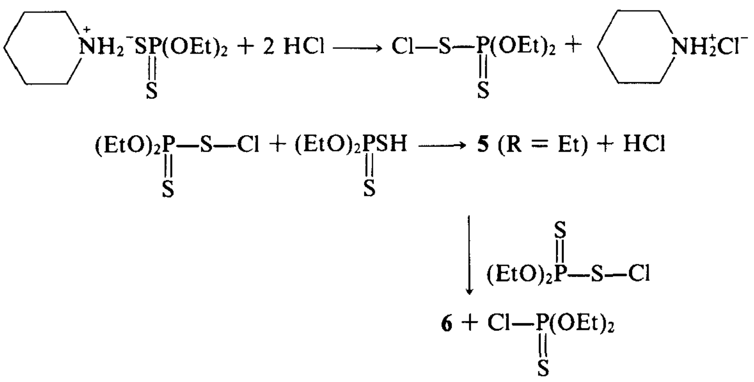
In addition to the products mentioned above, *bis*-(O,O-diethylthiophosphoryl) trisulfide (**6**) and dichloroantimony(III) O,O-diethylphosphorodithioate (**7**) were also found in the mixture resulting from the reaction of antimony(III) *tris*-(O,O-diethyl phosphorodithioate) with ferric chloride.

$$\mathbf{3} + FeCl_3 \longrightarrow \mathbf{5} + [(EtO)_2PS_2]_2S + FeCl_2 + [(EtO)_2PS_2]SbCl_2$$
$$(R = Et) \quad \mathbf{6} \qquad\qquad \mathbf{7}$$

In order to elucidate the structure of the compound **7** it was treated with two equivalents of O,O-diethylphosphorodithioic acid, **4** (R = Et), and antimony(III) *tris*-(O,O-diethyl phosphorodithioate), **3**, was obtained. Compound **7** was also synthesized in an independent manner by reaction of sodium O,O-diethyl phosphorodithioate with $SbCl_3$.

$$\mathbf{7} + 2\,\mathbf{4}\ (R = Et) \longrightarrow \mathbf{3} + 2\ HCl$$

The structure of the disulfide **5** (R = Et) and the structure of **6** were confirmed by independent syntheses,[25] as shown below:



In the other examples of the oxidation of **1** (R = Me, *i*-Pr, *n*-Pr, *i*-Bu, *n*-C_5H_{11}, Ph) by ferric chloride, only ferrous chloride and the respective *bis*-(O,O-disubstituted thiophosphoryl) disulfides (**5**) were isolated. The yields of **5** and **7** reported in the Experimental Section are based on the equation

$$\mathbf{1} + 2\ FeCl_3 \longrightarrow \mathbf{5} + 2\ FeCl_2 + Cl_2Sb[SP(S)(OR)_2].$$

However, except for **7**, no attempt was made to isolate the dichloroantimony(III) O,O-disubstituted phosphorodithioate formed in each reaction. When some of the compounds of type **1** were treated with $FeCl_3$ for a longer period of time, more than one equivalent of **5** was produced. Thus a competing overall reaction sequence is the following:

$$2\ \mathbf{1} + 6\ FeCl_3 \longrightarrow 3\ \mathbf{5} + 2\ SbCl_3 + 6\ FeCl_2$$

We have found that the disulfide **5** can also be formed by the addition of almost any oxidizing agent (e.g., Br_2 or H_2O_2) to an appropriate solution of the corresponding antimony(III) *tris*-(O,O-dialkyl phosphorodithioate), **1**.

It is known that halogens (Br_2, Cl_2) oxidize trialkyl- and triarylstibines to trialkyl- and triarylstibine dihalides, respectively.[26-27] Triarylstibines also undergo redox reactions with ferric chloride to give triarylstibine dichlorides.[28] Naturally, these re-

TABLE I

Preparation and properties of antimony *tris*-(O,O-disubstituted phosphorodithioates), **1**.

R	T_1, °C	x, *h*	T_2, °C	y, *h*	Yield, %	mp, °C	NMR ($CDCl_3$), δ (J, Hz)
methyl	25	1.0	25	2.0	53	96–97[a]	3.86 (d, $J_{P-H} = 16$)
ethyl	50	0.5	50	2.0	50	56–57[b]	1.38 (t, 18, J = 7), 4.18, 4.32 (overlapping quartets, 12)[c]
n-propyl	45	1.0	45	0.5	50	liq.[d]	1.00 (t, 18, J = 7.5), 1.50–2.10 (m, 12), 4.12 (overlapping triplets, 12, $J_{H-H} = 6.5$, $J_{P-H} = 10$)
iso-propyl	45	1.5	25	0.5	73	71–72[e]	1.37 (d, 36, J = 7), 4.91 (septet, 6, $J_{H-H} = 7$, $J_{P-H} = 7$)
iso-butyl	45	2.0	25	0.5	70	92–93[f]	0.95 (d, 36, J = 6.5), 1.79 (m, 6), 3.91 (d of d, 12, $J_{H-H} = 6.5$, $J_{P-H} = 2.5$)
n-pentyl	25	20.0	25	3.0	100	liq.[g]	0.75–1.15 (m, 18), 1.25–1.58 (m, 24), 1.58–2.00 (m, 12), 4.18 (d of t, 12, $J_{H-H} = 6.2$, $J_{P-H} = 10$)
n-hexyl	40	20.0	40	4.0	95	liq.[h]	0.68–1.07 (m, 18), 1.25–2.00 (m, 48), 4.16 (d of t, 12, $J_{H-H} = 6.0$, $J_{P-H} = 10$)
2-ethyl-1-hexyl	45	20.0	25	20.0	50	liq.[i]	0.67–1.10 (m, 36), 1.10–1.83 (m, 54), 4.12 (q, 12, $J_{H-H} = 7$, $J_{P-H} = 10$)
phenyl	60	20.0	25	20.0	40	89–90[j]	7.29 (s)
benzyl	55	5.0	25	20.0	20	88–89[k]	5.16 (d, 12, $J_{P-H} = 10$), 7.33 (s, 30)
2-phenyl-ethyl	45	1.0	45	20.0	35	liq.[l]	2.95 (t, 12, J = 6.5), 4.28 (d of t, 12, $J_{H-H} = 6.5$, $J_{P-H} = 10$), 7.20 (s, 30)

[a] *Anal.* Calcd. for $C_6H_{18}O_6P_3S_6Sb$: C, 12.15; H, 3.06; S, 32.43; P, 15.66. Found: C, 12.22; H, 3.14; S, 32.74; P, 15.38.

[b] A known compound; lit.[11] mp. 56°C.

[c] Ref. 10.

[d] *Anal.* Calcd. for $C_{18}H_{42}O_6S_6P_3Sb$: C, 28.39; H, 5.56; P, 12.20. Found: C, 28.23; H, 5.52; P, 11.82

[e] *Anal.* Calcd. for $C_{18}H_{42}O_6S_6P_3Sb$: C, 28.39; H, 5.56; P, 12.20; S, 25.26. Found: C, 28.39, H, 5.31; P, 11.94; S, 25.35.

[f] *Anal.* Calcd. for $C_{24}H_{54}O_6S_6P_3Sb$: C, 34.08; H, 6.44; P, 10.99; S, 22.75. Found: C, 34.01; H, 6.48; P, 10.77; S, 22.61.

[g] *Anal.* Calcd. for $C_{30}H_{66}O_6S_6P_3Sb$: C, 38.75; H, 7.15; P, 9.99. Found: C, 38.88; H, 7.17; P, 9.89.

[h] *Anal.* Calcd. for $C_{36}H_{78}O_6S_6P_3Sb$: C, 42.63; H, 7.75; P, 9.16. Found: C, 42.42; H, 8.15; P, 9.16.

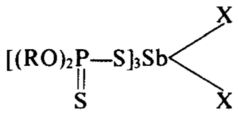
[i] *Anal.* Calcd. for $C_{48}H_{102}O_6S_6P_3Sb$: C, 48.76; H, 8.70; P, 7.86. Found: C, 48.57; H, 9.04; P, 7.58.

[j] *Anal.* Calcd. for $C_{36}H_{30}O_6S_6P_3Sb$: C, 44.77; H, 3.13; P, 9.62. Found: C, 44.61; H, 3.08; P, 9.44.

[k] *Anal.* Calcd. for $C_{42}H_{42}O_6S_6P_3Sb$: C, 48.05; H, 4.03; P, 8.85. Found: C, 48.29; H, 4.10; P, 8.67.

[l] *Anal.* Calcd. for $C_{48}H_{54}O_6S_6P_3Sb$: C, 50.84; H, 4.80; P, 8.19. Found: C, 51.10; H, 5.09; P, 8.17.

sults suggest that dichloroantimony(V) *tris*-(O,O-dialkyl phosphorodithioates), **8** (X = Cl), may constitute reasonable intermediates in the redox reactions under consideration.



8

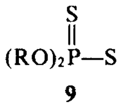
In an attempt to test this hypothesis, two equivalents of sodium methoxide were added to an ether solution of the possible product of reaction, **8**, (R = Et; X = Br) of antimony(III) *tris*-(O,O-diethyl phosphorodithioate), **3**, with bromine water at −78°C. The reddish color of bromine did not disappear until the temperature was allowed to rise to −65°C. Unfortunately, all attempts to isolate dimethoxyantimony(V) *tris*-(O,O-diethyl phosphorodithioate), **8**, (R = Et; X = MeO), failed, and the only product obtained was *bis*-(O,O-diethylthiosphosphoryl) disulfide, **5**, (R = Et).

In a second reaction, two equivalents of phenyllithium were added to an ether solution of the possible product, **8** (R = Et; X = Br), of reaction of antimony(III) *tris*-(O,O-diethyl phosphorodithioate), **3**, with bromine water at −65°C. Again, the attempt to isolate diphenylantimony(V) *tris*-(O,O-diethyl phosphorodithioate), **8** (R = Et; X = C_6H_5), failed; triphenylstibine and lithium O,O-diethyl phosphorodithioate were isolated instead.

Another possible mechanism for the formation of **5** from **1** by the action of $FeCl_3$ entails a prior ligand exchange reaction to form $SbCl_3$ and the appropriate Fe(III) *tris*-(O,O-dialkylphosphorodithioate),[29] which could then decompose to give **5** and a ferrous salt. However, Fe(III) *tris*-(O,O-diethylphosphorodithioate) is a known compound.[30] It is a black solid of mp 129°C., and it has sufficient stability to permit its Mössbauer spectrum,[31] magnetic moment,[32] and ultraviolet and visible spectra [33] to be taken. Also, a spectrophotometric analysis of the compound in CCl_4 solution has been developed.[34] Thus, even though the compound is known to undergo decomposition to **5** (R = Et) and Fe(II) salts in acid medium[34] and to undergo decomposition to unspecified products in a polar medium (methanol)[33] we do not believe that it represents a major intermediate in the formation of **5** (R = Et) from **3**. Also, a scheme involving this compound as an intermediate in the oxidation of **3** by $FeCl_3$ does not account for the formation of **7**.

Since it is known that the unshared pair of electrons of Sb(III) in its compounds coordinates readily with Fe(III) in its compounds,[35–38] another mechanism is presented in Figure 1.

A determination of the epr spectrum of radicals of the type **9** has recently been reported.[39] Unfortunately, our attempt to detect this radical by carrying out the redox reaction in the cavity of the epr spectrometer was thwarted by the presence of iron compounds in the reaction mixture, which masked the desired spectrum.



$$(RO)_2\overset{\overset{S}{\|}}{P}-S^{\cdot}$$

9

On the basis of this work and that reported previously on solvolysis reactions of **1**,[16] it is highly probable that the eventual pyrolysis reactions to provide zerovalent

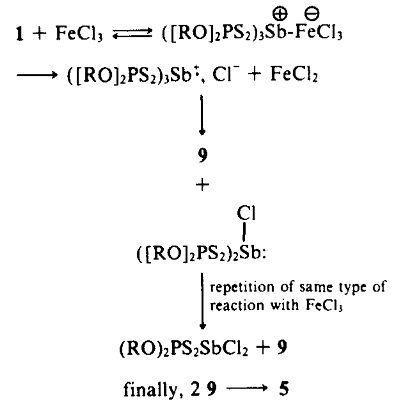


FIGURE 1† Possible Mechanism of Oxidation of **1** by $FeCl_3$.

antimony in the FCC process do not occur with **1** but rather with a variety of products which arise in reactions of **1** with components of crude petroleum.

EXPERIMENTAL SECTION

Preparation of Antimony(III) tris-*(O,O-Dialkyl Phosphorodithioates)*, **1**.

(1). *Antimony(III)* tris-*(O,O-Dimethyl Phosphorodithioate)*, **1** *(R = Me)*. To 100 mL of absolute methanol, maintained under an argon atmosphere, was added 40.0 g (0.18 mol) of phosphorus pentasulfide, and the mixture was maintained at room temperature with stirring until evolution of hydrogen sulfide ceased and a homogeneous solution resulted (about 1 h). To this solution was added 25.0 g (0.11 mol) of finely pulverized antimony trichloride, and the mixture was stirred for about 2 h, until evolution of hydrogen chloride stopped. A yellow precipitate was removed by filtration and the filtrate was concentrated under vacuum. The solid which precipitated from the concentrated filtrate was washed a few times with methanol and recrystallized from chloroform. There was obtained 28.5 g (0.053 mol, 54% yield) of antimony(III) *tris*-(O,O-dimethyl phosphorodithioate), **1** (R = Me), mp 96–97°C. The pmr spectrum taken in $CDCl_3$ solution shows a doublet at $\delta = 3.86$ ppm ($J_{P-H} = 16$ Hz).

Anal. Calcd. for $C_6H_{18}O_6P_3S_6Sb$: C = 12.15, H = 3.06, S = 32.43, P = 15.66., Found: C = 12.22, H = 3.14, S = 32.74, P = 15.38.

(2). *General Preparation of* **1**. Essentially the same procedure was used as described for the preparation of antimony(III) *tris*-(O,O-dimethyl phosphorodithioate. Details are provided in Table I.

Redox Reactions of Antimony(III) tris-*(O,O-Dialkyl Phosphorodithioates)*, **1**, *with Ferric Chloride and Related Reactions.*

(1) *Redox Reaction of Antimony(III)* tris-*(O,O-Diethyl Phosphorodithioate)*, **3**, *with Ferric Chloride.* To a solution of 8.12 g (0.012 mol) of antimony *tris*-(O,O-diethyl phosphorodithioate), **3**, in 100 mL of anhydrous ether, maintained under an argon atmosphere, was added 6.5 g (0.036 mol) of anhydrous ferric chloride, and the mixture was refluxed for two days. The light pink solid which had formed was collected by filtration and washed with ether several times. This solid gave an elemental analysis of 24.4% Fe and 35.12% Cl (Fe:Cl = 1:2).

The filtrate was refiltered through a silica gel column, which was also washed with methylene chloride. The filtrate was concentrated to produce a viscous residue (8.1 g) which was washed with 100 mL of Skelly F solvent. A brown solid which remained undissolved in the Skelly F solution was warmed with 50 mL of chloroform. An undissolved precipitate was removed by filtration, and the chloroform filtrate was concentrated to dryness. A white solid product which remained as a residue was recrystallized from methylene chloride-Skelly F solution (i.e., the solution being prepared by adding Skelly F solvent to the

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† It is understood, of course, that this is merely a convenient way of representing the reactions. It would be unduly clumsy to depict each antimony phosphorodithioate as a distorted octahedron.

methylene chloride solution to the cloud point). The yield of crystalline product, which proved to be dichloroantimony O,O-diethyl phosphorodithioate (**7**) was 1.96 g (0.0052 mol, 43%), mp 106–107°C; NMR ($CDCl_3$) δ 1.40 (t,6,J = 7), 4.25 (octet, 4, $J_{H—H} = 7$, $J_{P—H} = 9.5$).

Anal. Calcd. for $C_4H_{10}O_2PS_2Cl_2Sb$: C, 12.71; H, 2.67; Cl, 18.76. Found: C, 12.50; H, 2.55; Cl, 18.91.

The methylene chloride-Skelly F solution which was obtained from the recrystallization of the product of mp 106–107°C was combined with the 100 mL of Skelly F filtrate which had been obtained from washing the original viscous residue. The methylene chloride-Skelly F solution was concentrated to give a highly viscous residue. The residue was induced to crystallize from pentane at −78°C and gave 4.44 g (0.012 mol, 61%) of *bis*-(O,O-diethylthiophosphoryl) disulfide, **5** (R = Et), which is a liquid at room temperature. The refractive index was $n_d^{20} = 1.5572$ (Lit.[25] $n_d^{20} = 1.5600$); NMR ($CDCl_3$) δ 1.30 (t, 12, J = 5), 4.05 (octet, 8, $J_{H—H} = 5$, $J_{P—H} = 8$).

Anal. Calcd. for $C_8H_{20}O_4P_2S_4$: C = 25.94, H = 5.44, P = 16.72, S = 34.62. Found: C = 25.74, H = 5.64, P = 17.29, S = 34.31.

The pentane filtrate which was obtained from recrystallization of *bis*-(O,O-diethylthiophosphoryl) disulfide was concentrated to about half volume *in vacuo*. Crystals which had formed were collected by filtration and recrystallized from Skelly F solvent. The yield of *bis*-(O,O-diethylthiophosphoryl) trisulfide (**6**) was 0.32 g (0.008 mol, 22%) mp 70–71°C; NMR ($CDCl_3$) δ 1.39 (t, 12, J = 6.5), 4.31 (m, 8).

Anal. Calcd. for $C_8H_{20}O_4P_2S_5$: C = 23.87, H = 5.01, P = 15.39, S = 39.83., Found: C = 24.09, H = 5.27, P = 15.29, S = 39.31.

Reaction of Dichloroantimony(III) O,O-Diethyl Phosphorodithioate (**7**) *with O,O-Diethyl Phosphorodithioic Acid* (**4**, *R = Et*). To 1.5 g (0.008 mol) of O,O-diethyl phosphorodithioic acid (**4**, R = Et), maintained under an argon atmosphere, was added 0.94 g (0.0025 mol) of dichloroantimony(III) O,O-diethyl phosphorodithioate (**7**), and the mixture was stirred at room temperature overnight. Methylene chloride (15 mL) was added, and the mixture was stirred for another hour. The reaction mixture was concentrated to remove the methylene chloride, and 20 mL of Skelly F solvent was added to the residue. Excess dichloroantimony(III) O,O-diethyl phosphorodithioate was removed by filtration, and the filtrate was cooled in the refrigerator. A precipitate which had formed (1.35 g, 80%) was recrystallized from Skelly F solvent. Its mp was 56.5–57°C, also in admixture with authentic antimony(III) *tris*-(O,O-diethyl phosphorodithioate), **3**. The NMR and IR spectra were identical with those of antimony *tris*-(O,O-diethyl phosphorodithioate), **3**.

Reaction of Sodium O,O-Diethyl Phosphorodithioate with $SbCl_3$. To a solution of 1.46 g (0.007 mol) of sodium O,O-diethyl phosphorodithioate in 50 mL of anhydrous tetrahydrofuran, maintained under an argon atmosphere, was added 0.8 g (0.0035 mol) of anhydrous antimony trichloride, and the mixture was stirred overnight at room temperature. The precipitate which had formed was removed by filtration, and the filtrate was concentrated to dryness *in vacuo*. Ten mL of methylene chloride was added to the oily residue, and pentane was added to the solution to the cloud point. The solution was cooled, and there was obtained 0.52 g (0.0013 mol, 37%) of dichloroantimony(III) O,O-diethyl phosphorodithioate (**7**), mp 101–102°C, also in admixture with the sample obtained in the redox reaction. The NMR and IR spectra of the two samples were identical.

Preparation of bis-(*O,O-Diethylthiophosphoryl*) *Disulfide* (**5**, *R = Et*) *and* bis-(*O,O-Diethylthiophosphoryl Trisulfide* (**6**). To a solution of 4.46 g (0.021 mol) of sodium O,O-diethyl phosphorodithioate in 15 mL of pentane, maintained under an argon atmosphere, was added 0.86 g (0.005 mol) of bromine, and the mixture was stirred for 3 h at room temperature. A small additional amount of sodium O,O-diethyl phosphorodithioate was added, and the mixture was stirred for an additional hour until the color of bromine disappeared. The reaction mixture was concentrated to dryness *in vacuo*, and 50 mL of methylene chloride was added to the residue. The mixture was filtered, and the filtrate was concentrated to dryness. To the residue was added 30 mL of pentane at room temperature, and the pentane solution was cooled at −25°C. A white precipitate which had formed was collected by filtration and recrystallized from Skelly F solvent to provide 0.17 g (0.0005 mol, 4.7%) of the trisulfide **6**, mp 72–73°C. The filtrate was cooled to −78°C and the pentane layer was decanted from a heavier oil. This process was repeated a few times to purify the disulfide **5** (R = Et). The yield was 0.85 g (0.0023 mol, 21%). The identities of both products with those obtained previously and with those obtained by the method of Almasi and Paskucz[25] were verified by comparisons of infrared (neat) and NMR (in $CDCl_3$ solution) spectra.

General Procedure for Reaction of **1** *with $FeCl_3$.* To a solution of 0.011 mol of **1** in 70 mL of anhydrous ether, maintained under an argon atmosphere, was added 4.4 g (0.027 mol) of anhydrous $FeCl_3$, and the mixture was refluxed for 24 h. An inorganic salt ($FeCl_2$ complexed with organic material) which had formed was removed by filtration, and the filtrate was concentrated to dryness. Methylene chloride (150 mL) was added to the residue. The disulfides **5** were isolated from the methylene chloride solutions in high yields.

(a) bis-(*O,O-Dimethylthiophosphoryl) Disulfide* (**5**, *R* = *Me*), mp 53–55°C; NMR ($CDCl_3$) δ 3.87 (d, $J_{P—H}$ = 16.5).

Anal. Calcd. for $C_4H_{12}O_4P_2S_4$: C = 15.28, H = 3.85, P = 19.71., Found: C = 15.40, H = 4.05, P = 19.49.

(b) bis-(*O,O-Di-*n*-propylthiophosphoryl) Disulfide* (**5**, *R* = n-*Pr*), liquid, NMR ($CDCl_3$) δ 1.00 (t, 12, J = 5.5), 1.73 (sextet, 8, J = 5.5), 4.18 (m, 8).

Anal. Calcd. for $C_{12}H_{28}O_4P_2S_4$: C = 33.78, H = 6.62., Found: C = 33.68, H = 6.60.

(c) bis-(*O,O-di-isopropylthiophosphoryl) Disulfide* (**5**, *R* = i-*Pr*), mp 95–96°C; NMR ($CDCl_3$) δ 1.35 (d, 24, J = 6.1), 4.89 (overlapping septets, 4, $J_{H—H}$ = 6.1, $J_{P—H}$ = 6.1).

Anal. Calcd. for $C_{12}H_{28}O_4P_2S_4$: C = 33.78, H = 6.62, P = 14.52, S = 30.07., Found: C = 33.58, H = 6.62, P = 14.72, S = 30.13.

(d) bis-(*O,O-diisobutylthiophosphoryl) Disulfide* (**5**, *R* = i-*Bu*), a yellow liquid n_D^{20} 1.5721; NMR ($CDCl_3$) δ 0.97 (d, 24, J = 6.5), 2.02 (septet, 4, J = 6.5), 3.95 (q, 8, $J_{H—H}$ = 6.5, $J_{P—H}$ = 2.5).

Anal. Calcd. for $C_{16}H_{36}O_4P_2S_4$: C = 39.81, H = 7.52, P = 12.83, S = 26.57., Found: C = 40.09, H = 7.67, P = 12.64, S = 26.81.

(e) bis-(*O,O-di-*n*-pentylthiophosphoryl) Disulfide* (**5**, *R* = n-C_5H_{11}), a yellow liquid, NMR ($CDCl_3$) δ 0.74–1.16 (m, 12), 1.20–1.58 (m, 16); 1.60–2.02 (m, 8), 4.19 (doft, 8, $J_{H—H}$ = 9.5, $J_{P—H}$ = 9.5).

Anal. Calcd. for $C_{20}H_{44}O_4P_2S_4$: C = 44.58, H = 8.23, P = 11.50, S = 23.81., Found: C = 44.54, H = 8.43, P = 10.98, S = 23.56.

(f) bis-(*O,O-Diphenylthiophosphoryl) Disulfide* (**5**, *R* = C_6H_5), originally a waxy solid. The light yellow solid was recrystallized from ether, and a white solid was obtained, mp 77.5–78.5°C; NMR ($CDCl_3$) δ 7.18 (s).

Anal. Calcd. for $C_{24}H_{20}O_4P_2S_4$: C = 51.23, H = 3.58, P = 11.00., Found: C = 51.10, H = 3.59, P = 11.07.

Infrared Spectra. All infrared spectra have been taken as a film on a KBr disc. The data are available to anyone who submits a request to the authors. The characteristic absorption peaks attributable to P = S (750–550 cm^{-1}, s, variable), P—O—C (1060–905 cm^{-1}, s; 875–730 cm^{-1}, s; 1240–1085 cm^{-1}, variable), P—S—S (520–400 cm^{-1}, s or m) groups are apparent in the appropriate compounds.[40]

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