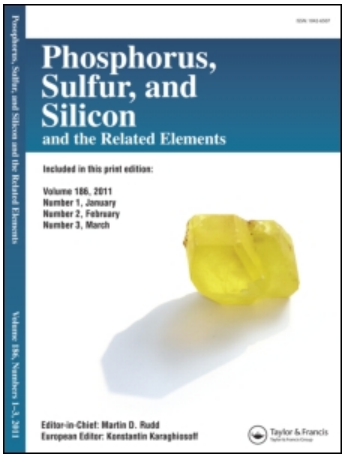

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SOLVOLYSIS REACTIONS OF ANTIMONY (III) O,O-DISUBSTITUTED PHOSPHORODITHIOATES

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SOLVOLYSIS REACTIONS OF ANTIMONY (III) O,O-DISUBSTITUTED PHOSPHORODITHIOATES

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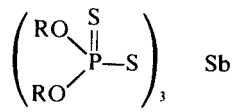
Antimony (III) *tris*-(O,O-di-*p*-tolyl phosphorodithioate) (**4**) has been found to undergo solvolysis in ethanol to give antimony triethylate and O,O-di-*p*-tolyl phosphorodithioic acid (**5**). Both **4** and antimony (III) *tris*-(O,O-diethyl phosphorodithioate) (**3**) undergo solvolysis reactions with diethylamine to give the respective diethylammonium O,O-disubstituted phosphorodithioates and complex oxidation products. Compounds **3** and **4** are similar to passivation agents used in petroleum refining, and the results suggest that such compounds can undergo solvolysis at antimony with various components of crude petroleum prior to the ultimate pyrolysis reactions.

INTRODUCTION

Studies have been initiated on the fundamental chemistry of a type of compound which has been found to bring about passivation of contaminant metals in the cracking of crude petroleum. The contaminant metals, such as nickel, vanadium and iron, which are present in crude hydrocarbon feedstocks, are known to have detrimental effects on the performance of the catalyst used in the fluid catalytic cracking (FCC) process. The detrimental effects are attributable to the deposition on the catalyst of these contaminant metals contained within the charge stock which result in an increase in hydrogen and coke yields and a decrease in the gasoline yield. Scientists employed by the Phillips Petroleum Company have reported[1–8] that the use of "Phil-Ad-CA" in relatively small amounts in the cracking process has resulted in (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 results, and (3) an ability to use oil feeds having relatively high contaminant metal concentrations.

"Phil-Ad-CA" is an organoantimony compound having the general formula **1**



1

2 R = *n*-propyl
3 R = ethyl

wherein the R groups, which can be the same or different, are alkyl groups each containing from 1 to about 18 carbon atoms, the overall number of carbon atoms per molecule being 6 to about 90. However, the major component of "Phil-Ad-CA" is the compound **2** in which R = *n*-propyl.

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[9] 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[10] 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[11] 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.

As an obvious starting point for new research in this area, we have recently determined[12] the structure of the ethyl analog, **3**, by single crystal X-ray diffraction analysis. 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,[13] while **2** is a liquid even at 0°C.[14]

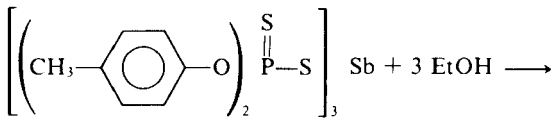
We have found[12] that the coordination polyhedron of the antimony atom in antimony *tris*-(O,O-diethyl phosphorodithioate), **3**, is a distorted capped octahedron with a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the antimony atom.

RESULTS AND DISCUSSION

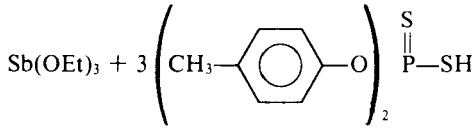
As mentioned above, antimony is eventually deposited on the FCC catalyst so as to passivate the contaminating metals. However, before this occurs, the antimony (III) O,O-dialkyl phosphorodithioates (**1**) undoubtedly undergo a variety of reactions with compounds found in crude petroleum. The purpose of our present research program is to explore such reactions. Some of those involving solvolysis are covered in this paper.

Crude petroleum contains numerous compounds that are potentially capable of undergoing solvolysis reactions with antimony (III) *tris*-(O,O-dialkyl phosphorodithioates), **1**. These include mercaptans, pyrrole, indole, carbazole, carboxylic acids and phenols.[15,16] At least two different types of solvolysis reactions can be envisioned, one involving substitution at phosphorus, and the other at antimony. Either of these types of reaction could be of the $S_{N}1$ or $S_{N}2$ type, with possible additional complications owing to the formation of unstable hypervalent intermediates.

Actually, no reaction at all occurred when **3** and *p*-cresol were brought together at moderate temperatures. The NMR spectrum of the reaction mixture was that of a mixture of the unchanged reagents. Solvolysis was found to take place, however, when antimony (III) *tris*-(O,O-di-*p*-tolyl phosphorodithioate) (**4**) was caused to react with ethanol. This resulted in the formation of antimony triethylate and O,O-di-*p*-tolyl phosphorodithioic acid (**5**). These are the products expected for solvolysis at antimony.



4



5

In the initial experiments, a ratio of one equivalent of compound **4** to six equivalents of ethanol was used, with hexane present as the solvent. These reactions were largely unsuccessful because they always resulted in the formation of a decomposition product during workup, as evidenced by the appearance of a sharp peak in the NMR spectrum of the reaction mixture at $\delta 0.1$ ppm. Thus, other reactions were carried out with no hexane present. Solvolysis was allowed to take place in excess ethanol. After the reaction mixture had been heated for two hours, two liquid layers formed. The NMR spectrum of the major (upper) layer suggested that it consisted essentially of a solution of $Sb(OEt)_3$ in ethanol. A quartet at about $\delta 3.70$ and a triplet at about $\delta 1.22$ corresponded fairly closely with the same peaks of absolute ethanol, but the singlet for the proton of the hydroxyl group was shifted downfield from about $\delta = 2.58$ in absolute ethanol to about $\delta = 4.18$ in the reaction solution. A more complete explanation of the phenomena involved in this spectrum will be presented later. There was also evidence of the presence of very small amounts of **4** and O,O-di-*p*-tolyl phosphorodithioic acid (**5**). All NMR spectra were taken in $CDCl_3$ solution.

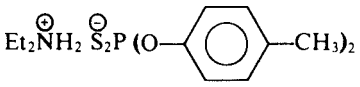
The NMR spectrum of the relatively small oily layer showed it to consist mainly of a mixture of ethanol, $Sb(OEt)_3$, O,O-di-*p*-tolyl phosphorodithioic acid (**5**) and the starting material, compound **4**. The quartet of ethanol appeared at about $\delta = 3.70$ and the triplet at about $\delta = 1.22$. A broad, ill-defined quartet of antimony triethylate appeared at about $\delta = 4.07$ and its triplet at about $\delta = 1.30$, where it overlapped partially with that of ethanol. The *p*-methyl protons of compound **4** appeared as a doublet ($J = 2$ Hz)[21] at about $\delta = 2.30$, while the *p*-methyl protons of the dithioic acid appeared as an overlapping doublet ($J = 2$ Hz) at about $\delta = 2.33$). The phenyl protons of both compounds overlapped at about $\delta = 7.18$–7.22. The hydroxyl proton of the ethanol and the acidic proton of the dithioic acid, owing to rapid exchange, appeared as a singlet at about $\delta = 1.88$. A solution of the dithioic acid, **5**, in ethanol showed the same pronounced upfield shift for these protons.

The reaction was then allowed to continue for another 50 min., whereupon a homogenous ethanol solution and an insoluble precipitate (which coated the walls of the flask) were observed. As shown in its NMR spectrum, the clear ethanol solution contained mainly antimony triethylate, again with a very small amount of **5** present also. Owing to rapid chemical exchange of ethoxyl groups between ethanol and $Sb(OEt)_3$, this spectrum contained a single quartet at about $\delta = 3.70$ and a single triplet at about $\delta = 1.20$. The singlet for the proton of the hydroxyl group of ethanol appeared at about $\delta = 3.90$.

An authentic sample of antimony triethylate was prepared by the method of Kijma and Takahashi,[17] and the NMR spectrum of the neat liquid showed a quartet at about $\delta = 4.07$ and a triplet at about $\delta = 1.30$. Solutions of authentic $Sb(OEt)_3$ in ethanol at two different concentrations were prepared. The first, consisting of

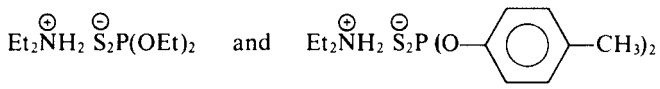
two parts by volume of ethanol to one part of $Sb(OEt)_3$, gave an NMR spectrum which consisted of a quartet at about $\delta = 3.96$ and a triplet at about $\delta = 1.20$. The hydroxyl proton appeared at about $\delta = 4.90$. The second solution contained equal volumes of ethanol and authentic $Sb(OEt)_3$, and its NMR spectrum showed a quartet at about $\delta = 3.78$ and a triplet at about $\delta = 1.20$. In this solution, the proton of the hydroxyl group appeared at about $\delta = 3.80$. These results confirm the existence of a relatively rapid exchange of ethoxyl groups between ethanol and antimony triethylate. However, when the concentrations of ethanol and antimony triethylate are low, and the medium is relatively non-polar, as in the oil globule described previously, the rate of exchange is lowered sufficiently to allow both compounds to exhibit their characteristic quartets and triplets, respectively.

When either **3** or **4** was caused to react with diethylamine, a salt and decomposition products were obtained. In the case of compound **3**, the salt obtained was identified as $Et_2\overset{\oplus}{N}H_2\ \overset{\ominus}{S}_2P(OEt)_2$ (diethylammonium O,O-diethyl phosphorodithioate), which was characterized by microanalysis, IR and NMR spectra. The salt was also synthesized in an unambiguous manner. The salt obtained by the corresponding reaction of compound **4** is



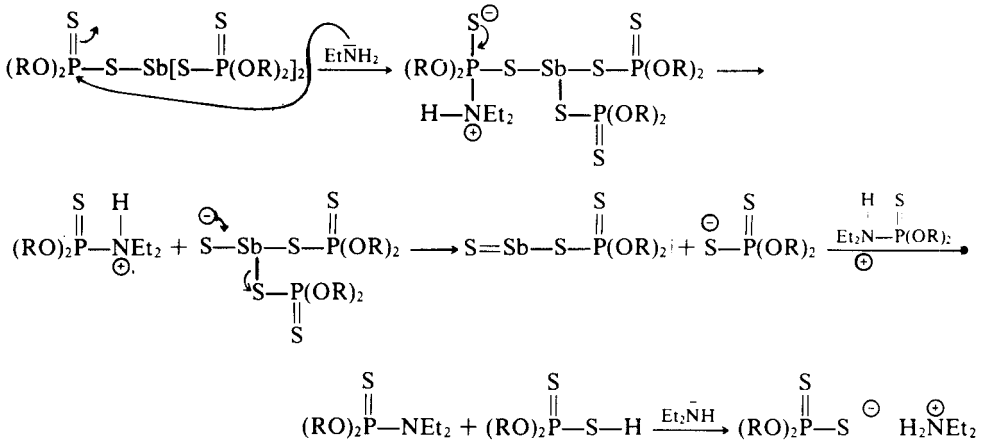
which was characterized by microanalysis, IR spectrum and NMR spectrum. It was also synthesized by an unambiguous method.

There are several plausible mechanisms which can be proposed for the formation of



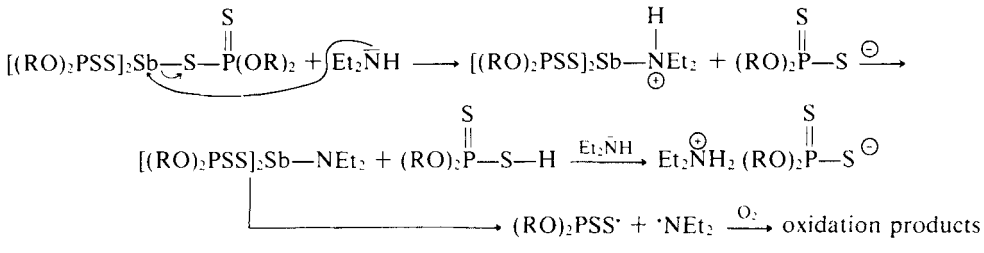
by reaction of **3** and **4**, respectively, with diethylamine.

MECHANISM I† Substitution at phosphorus:



†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.

MECHANISM II† Substitution at antimony.



†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.

Variations of these mechanisms involving $S_{N}1$ or $S_{N}2$ processes and possibly with formation of unstable hypervalent phosphorus or antimony compounds can also be envisioned.

Owing to the fact that compounds of the type $(RO)_2\overset{S}{\overset{\|}{P}}—NEt_2$ are well-known and stable, and, since no such compounds were isolated despite repeated attempts to do so (see experimental section), it is probable that substitution at phosphorus (Mechanism I and its conceivable variations) is not operative. On the other hand, the Sb—N bond is known to be extremely vulnerable at attack by oxygen,[18,19] and poorly defined products were obtained which appeared to have the composition of $[(RO)_2PSS]_2(O)_x$ and $(Et_2N)_2(O)_x$ or $[(RO)_2PSS]_2(O)_x[NEt_2]_2$. In particular, for the reaction of **4** with diethylamine, a product or mixture of products was isolated which, on the basis of elemental analyses, appeared to have the composition approximating $C_{36}H_{48}O_{11}P_2S_4N_2$. Thus, as in the solvolysis reaction of **4** with ethanol, the reactions of **3** and **4**, respectively, with diethylamine appear to involve nucleophilic substitution at antimony. The available evidence does not permit any decision to be made as to whether these solvolysis reactions are of the $S_{N}1$(Sb) or $S_{N}2$(Sb) type.

Since ethanol and diethylamine are not major components of crude petroleum (if present at all),[15] the solvolysis reactions described above are not those which occur when **1** is added to crude petroleum. However, these examples indicate the possibility of related reactions involving known components of petroleum taking place in the FCC process, and also that these solvolyses would probably occur at antimony rather than at phosphorus.

EXPERIMENTAL

Antimony tris-(*O,O-diethyl phosphorodithioate*) (**3**) This compound was prepared as described previously.[12]

Antimony tris-(*O,O-di*-p-*tolyl phosphorodithioate*) (**4**) A mixture of 402 ml of *p*-cresol and 100 g of phosphorus pentasulfide was heated and stirred at an oil bath temperature of 120–130°C for 4 hours under Argon, which gave rise to a yellow solution. The yellow solution was cooled and a white crystalline solid was obtained. It was recrystallized from a mixture of benzene and hexane (1:1), giving 184.9 g or O,O-di-*p*-tolyl phosphorodithioic acid (**5**), mp 52–54°C; nmr ($CDCl_3$) δ2.33 (d, 6, $J = 2$),[21] 3.3 (s, 1), 7.22 (s, 8). The compound was dissolved in a hexane and benzene solution (1:1), and 45.6 g of $SbCl_3$ was added. The mixture was stirred at room temperature under Argon for 4 hours, during which period a yellow solution was formed. The solvents were partially removed by evaporation *in vacuo*, and the resid-

ual yellow solution was cooled and induced to crystallize from a mixture of benzene and hexane (1:1). The yellow crystals amounted to 21.4 g (4.5% yield) of **4** and had a mp of 90–91°C; nmr ($CDCl_3$) δ2.30 (d, 18, $J = 2$),[21] 7.18 (s, 24); i.r.(KBr) 3030 (m), 2919 (m), 2850 (m), 1880 (w), 1590 (m), 1495 (s), 1371 (w), 1210 (s), 1180 (s), 1150 (s), 1098 (m), 1015 (m), 930 (s), 900 (s), 812 (s), 721 (s), 711 (s), 691 (m), 630 (s), 509 (s), 466 (m), 450 (w), 439 (w), 412 (w), 390 (w), 331 (w), 280 (m) cm^{-1}.

Anal. Calcd. for $C_{42}H_{42}P_3S_6SbO_6$: C, 48.05; H, 4.03; P, 8.85. Found: C, 47.85; H, 4.47; P, 8.72.

Reaction of Antimony (III) tris-(*O,O-di*-p-*tolyl phosphorodithioate*) (*compound* **4**) *with ethanol* A 5.0 g quantity of compound **4** and 50 ml of anhydrous ethanol were stirred under Argon at a temperature of 50–60°C for 5 hours. Aliquots were withdrawn at various time intervals and examined by NMR spectroscopy in $CDCl_3$ solution as described in the Discussion.

Antimony triethylate A mixture of 49 ml of anhydrous hexane and 10.2 ml of anhydrous ethanol was added, with cooling at a temperature of 12–15°C, to 10.0 g of $SbCl_3$. Then a mixture of 16 ml of anhydrous diethylamine and 12 ml of anhydrous hexane was added. There was an immediate formation of a cloudy solution. The mixture was allowed to reflux for two hours and then was filtered. A large amount of white solid and a colorless filtrate were obtained. The filtrate was vacuum distilled at a pressure of 15 mm at room temperature. The NMR spectrum of the residual pale yellow liquid was taken in $CDCl_3$ solution and is described in the Discussion. The NMR spectra of various mixtures of antimony triethylate with absolute ethanol in $CDCl_3$ solution were also taken and are described in the Discussion.

Reaction of Antimony tris-(*O,O-diethyl phosphorodithioate*) (*compound* **3**) *with diethylamine* A ratio of one equivalent of compound **3** to six equivalents of diethylamine was used. Specifically, a 15.0 g quantity of compound **3** was dissolved in 20 ml of benzene at room temperature under Argon. Then absolute diethylamine was added to the solution. The reaction mixture was stirred overnight, and it changed from yellow to a mustard color. After a second day of stirring, the mustard color changed to brown, and the solution was allowed to stir for another five hours. The brown solution became cloudy during this period. The mixture was allowed to stir for yet another day, which resulted in the formation of an orange, resinous viscous solution. A large amount of anhydrous ether was added to the mixture, and it was then filtered; 13.3 g of a brown-orange residue was obtained; decomposition point 105°C. The orange residue was partially soluble in water, methanol and acetone. It was slightly soluble in hot methanol. It gave off H_2S when treated with hot water and 10% hydrochloric acid. It was completely insoluble in Skelly F solvent and ethyl acetate.

Anal. Calcd. for material of general composition $C_{24}H_{60}P_3S_6N_3O_6Sb_2$: C, 28.38; H, 5.96; N, 4.14; P, 9.14. Found: C, 27.88; H, 6.67; N, 4.40; P, 8.50.

The various mother liquors were concentrated to dryness, and the residues were subjected to column chromatography under various conditions. No pure product was obtained.

Another experiment in which one equivalent of compound **3** was treated with six equivalents of diethylamine was carried out; a 15.0 g quantity of compound **3** was dissolved in 20 ml of benzene. This solution was stirred under Argon at a temperature of −10°C. Then, 2.3 ml of absolute diethylamine was added gradually, and the temperature was allowed to rise to 0°C. The reaction was allowed to continue for two hours, and a yellow solution was obtained. Removal of benzene *in vacuo* resulted in the formation of a brown solid. Ethyl acetate was added to the brown solid, and the mixture was then filtered. A small amount (0.7 g) of white residue (A) and a yellow-brown filtrate (B) were obtained.

The creamy white residue (A) had a decomposition point of around 120°C and was mainly inorganic. It was insoluble in hexane, chloroform, ethyl acetate, acetone and water. Analysis: Found: C, 7.26; H, 1.53; N, 0.39; S, 18.49; P, 4.14.

The yellow-brown filtrate (B) was allowed to pass through Florisil and both the Florisil and light yellow-brown solution were retained for further treatment.

The ethyl acetate solution remaining after the Florisil treatment, was concentrated *in vacuo*. The resulting yellow-brown residual solid was dissolved in ethyl acetate and was treated with activated carbon, giving a yellow solution. Then the ethyl acetate was removed *in vacuo* giving approximately 2 g of a yellow solid, mp 52–54°C. Its NMR spectrum was the same as that of the starting material **3**. A mixture mp test with **3** showed no depression.

The yellow colored compound that had been absorbed on the Florisil was extracted with methylene chloride. The methylene chloride was then removed *in vacuo*, which gave a yellow residual solution. Crystals were obtained from this solution and were subjected to fractional crystallization from ethyl acetate. There was obtained 0.1 g of diethylammonium O,O-diethyl phosphorodithioate,[20] mp 88–90°C; nmr ($CDCl_3$) δ1.3 (t, 6, $J = 9$), 1.5 (t, 6, $J = 8$), 3.25 (q, 4, $J = 9$), 3.8–4.3 (overlapping quartets, 4); ir(KBr) 2700–3000 (6 peaks, s), 2460 (m), 2360 (w), 1575 (w), 1435–1470 (3 peaks, m), 1390 (m), 1340 (w), 1260 (m), 1095 (m), 1050 (s), 1025 (s), 940 (s), 770 (s), 665 (s), 550 (m) cm^{-1}.

Anal. Calcd. for $C_8H_{22}O_2PS_2N$: C, 37.05; H, 8.55; N, 5.34; P, 11.94. Found: C, 37.33; H, 9.05; N, 5.43; P, 12.19.

Repeated attempts at fractional crystallization and column chromatography of the materials from the various mother liquors gave only additional **3** and diethylammonium O,O-diethyl phosphorodithioate. No products which would have resulted by attack of diethylamine on phosphorus were isolated.

Diethylammonium O,O-diethyl phosphorodithioate A 53.3 g batch of phosphorus pentasulfide was stirred in 56.0 ml of absolute ethanol under Argon for an hour until all of the pentasulfide had dissolved. The solution was maintained at less than 50°C, and 50 ml of absolute diethylamine was added gradually under Argon at room temperature. The mixture was stirred for an hour. (The reaction was vigorous with evolution of heat). A mixture of yellow and white solids formed. Ethyl acetate was added to the mixture, the white, crystalline solid being moderately soluble, and the yellow solid being very soluble. The mixture was then filtered, and the white crystalline diethylammonium O,O-diethyl phosphorodithioate obtained had a mp of 88–89°C. A mixture mp test with the samples obtained previously showed no depression, and its ir and nmr spectra were identical with those of the samples obtained previously.

Reaction of Antimony tris-(*O,O-di*-p-*tolyl phosphorodithioate*) (*compound* **4**) *with diethylamine* An 8.0 g portion of compound **4** was stirred in 90 ml of anhydrous hexane under Argon at a temperature of approximately −5°C. Then, 2.4 ml of anhydrous diethylamine was added slowly, and the reaction was allowed to take place for an hour. The reaction mixture was filtered. A colorless filtrate (A) and a pale yellow residue (B) were obtained.

The pale yellow residue (B) was treated with acetone and then the resulting mixture was filtered. A 0.5 g sample of a creamy solid (C) and a yellow filtrate (D) were obtained. The creamy solid (C) had a decomposition point of 145°C and was mainly inorganic.

Acetone was removed by evaporation of the yellow filtrate (D), which gave a yellow-orange solid (E). Ethyl acetate was added to the solid (E) and the mixture was filtered; 1.6 g of an orange solid (F), decomposition point 155°C, was obtained together with a yellow filtrate (G). The solid (F) was washed with additional portions of ethyl acetate, but it could not be recrystallized from any of the common solvents.

Anal. Calcd. for material of general composition $C_{36}H_{48}O_{11}P_2S_4N_2$: C, 49.42; H, 5.53; P, 7.31; S, 14.65; N, 3.20. Found: C, 48.01; H, 5.67; P, 6.55; S, 13.27; N, 2.92.

The various filtrates (A, G) and wash solution were concentrated and the residues subjected to column chromatography under a variety of conditions, but no pure compounds could be isolated.

In another experiment, the ratio of compound **4** to diethylamine was 1:3. First of all, 8.0 g of compound **4** was stirred with 30 ml of anhydrous benzene under Argon at a temperature between 2°C and −2°C. Then 2.4 ml of diethylamine was added slowly. There was an immediate formation of a heterogenous yellow mixture. This was filtered and gave a yellow filtrate (A) and a white, powdery residue (B). The filtrate (A) was concentrated to dryness and the residue subjected to fractional crystallization from acetone. There was obtained 1.5 g of starting material **4**, mp 90–91°C, also in admixture with an authentic sample of **4**.

The white, powdery product (B) was mixed with chloroform. The chloroform extract was then removed by filtration, giving a white, shiny, powdery residue (C) and a colorless filtrate (D).

Acetone was added to the residue (C). The mixture was filtered. When the colorless filtrate was cooled, diethylammonium O,O-di-*p*-tolyl phosphorodithioate, mp 205–210°C, crystallized. This was recrystallized from acetone four times; 0.15 g of colorless crystals was collected, mp 208–213° (dec.); nmr ($CDCl_3$) δ 1.15 (t, 6, $J = 7$), 2.2 (s, 6), 3.0 (q, 4, $J = 7$), 7.15 (s, 8); ir(KBr) 2640–3110 (8 peaks, s), 2480 (w), 1875 (w), 1605 (m), 1590 (m), 1505 (s), 1460 (s), 1420 (s), 1390 (m), 1380 (m), 1250–1340 (5 peaks, w), 1220 (s), 1200 (s), 1160 (s), 1100 (m), 1060 (m), 1040 (m), 1020 (s), 930 (m), 900 (s), 815 (s), 790 (s), 760 (m), 710 (s), 690 (s), 660 (s), 630 (s), 555 (s), 530 (m), 520 (s), 480 (m), 465 (s), 440 (m), 400 (m), 345 (m) cm^{-1}.

Anal. Calcd. for $C_{18}H_{26}O_2PS_2N$: C, 56.37; H, 6.83; N, 3.65; P, 8.1. Found: C, 56.34; H, 6.86; N, 3.60; P, 7.85.

Concentration of the chloroform solution (D) afforded an additional 0.06 g of diethylammonium O,O-di-*p*-tolyl phosphorodithioate.

Independent synthesis of N,N-diethylammonium O,O-di-p-*tolyl phosphorodithioate* A 28.6 g quantity of O,O-di-*p*-tolyl phosphorodithioic acid was dissolved in 75 ml of anhydrous benzene at a temperature between 0°C to −2°C under Argon. Then, 9.7 ml of anhydrous diethylamine was added, and the reaction mixture was stirred for an hour. A mixture of chloroform and ethyl acetate (1:1) was added to the white heterogeneous mixture, and it was then filtered. A white residue and a colorless filtrate were obtained.

Concentration of the filtrate to dryness gave a solid residue. A small portion of this was subjected to fractional crystallization from acetone. Pure N,N-diethylammonium O,O-di-*p*-tolyl phosphorodithioate was obtained as the more soluble component of the mixture, mp 208–213°C (dec.), also in admixture with the sample obtained previously. The nmr and ir spectra of this compound were identical with those of the sample isolated previously.

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