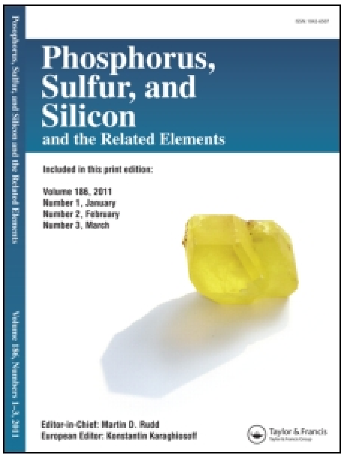

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article McEwen, W. E. , Woo, E. J. and Kalbacher, B. J.(1982) 'NUCLEOPHILIC SUBSTITUTION REACTIONS ON ANTIMONY(III) 0,0-DISUBSTITUTED PHOSPHORODITHIOATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 1, 35 — 40

To link to this Article: DOI: 10.1080/03086648208078980

URL: http://dx.doi.org/10.1080/03086648208078980

Phosphorus and Sulfur, 1982, Vol. 13, pp. 35–40
0308-664X/82/1301-0035/$06.50/0

NUCLEOPHILIC SUBSTITUTION REACTIONS ON ANTIMONY(III) 0,0-DISUBSTITUTED PHOSPHORODITHIOATES

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(*Received December 19, 1981; in final form January 20, 1982*)

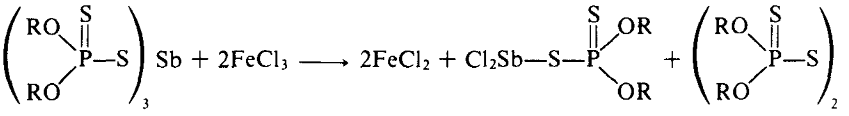
Antimony(III) *tris*(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu) has been found to undergo a nucleophilic displacement reaction with sodium 1-propanethiolate to give antimony(III) *tris*-(1-propanethiolate), **4**, and sodium 0,0-diisobutyl phosphorodithioate (**8**, R = *i*-Bu). Reaction of **1** (R = *i*-Bu) with phenyllithium gave triphenylstibine and lithium 0,0-diisobutyl phosphorodithioate. Similar reactions of various compounds of type **1** with the sodium salts of carboxylic acids and with the sodium salt of pyrrole were also found to occur. Furthermore, antimony *tris*(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), was found to undergo solvolysis with *n*-propyl mercaptan to give **4** and 0,0-diisobutyl phosphorodithioic acid **5**. Compounds of type **1** are used as passivating agents in petroleum refining, and reactions of the types described for **1** with *n*-propyl mercaptan and with the salts of carboxylic acids probably occur when "Phil-Ad CA" is added to the feedstock of a fluid catalytic cracking unit.

INTRODUCTION

Fluid catalytic cracking (FCC) of heavy residual oils which contain contaminant metals (primarily compounds of iron, nickel and vanadium) leads to deposition of these metals on the catalyst. This catalyzes the formation of hydrogen and coke, and decreases the yields of more valuable products. When the heavy residual oils also have a high sulfur content, hydrodesulfurization prior to the FCC process not only decreases the sulfur content, but also reduces the concentration of contaminant metals to a more manageable level. However, even with the lower concentration of contaminant metals in the hydrotreated feedstock, passivation with antimony *tris*-(0,0-dialkyl phosphorodithioates), **1**, in the FCC process provides a significant increase in the yield of gasoline, with a concomitant decrease in the yields of hydrogen and coke.[1–9]

Although the detailed mechanism of passivation of contaminant metals by introduction of **1** into the crude or hydrotreated feedstock is not known, it is thought that antimony may form an alloy with contaminant metals on the FCC catalyst, and that this alloy may have much of the antimony segregated to the surface. The evidence for this concept has been summarized in previous papers.[1,2,9,10] Although the available evidence indicates that the contaminant metals end up as bimetallic (metal plus antimony) particles on the surface of the FCC catalyst, with one element altering the catalytic activity of the other, the manner in which both the antimony in the additive and the contaminant metals in their compounds end up in the zerovalent states is not known.

Although thermolysis is almost certainly involved in the ultimate conversion of the antimony and contaminant metals in their respective compounds to the zerovalent state, evidence has already been uncovered that the passivating agents, **1**, probably undergo a variety of reactions with components of crude petroleum before the ultimate pyrolysis reactions occur. For example, we have found that compounds of type **1** undergo reaction with ferric chloride, even at room temperature, to give ferrous chloride, dichloroantimony 0,0-dialkylphosphorodithioates, **2**, and 0,0-dialkylthiophosphoryl disulfides, **3**, as the major products.[11]

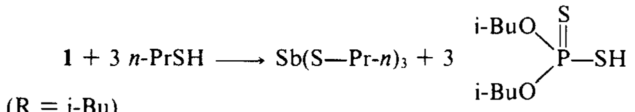


1 **2** **3**

Solvolysis reactions at antimony have also been shown to occur.[10] However, these reactions did not involve actual components of crude petroleum, and therefore we have continued such work to find more pertinent examples of such reactions.

RESULTS AND DISCUSSION

Crude petroleum contains numerous compounds that are potentially capable of undergoing solvolysis reactions with **1**. These include mercaptans, pyrrole, indole, carbazole, carboxylic acids and phenols.[12,13] We have now found that antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), undergoes facile reaction with *n*-propyl mercaptan in hexane solution to give antimony *tris*-(1-propanethiolate), **4**, and 0,0-diisobutyl phosphorodithioic acid, **5**.

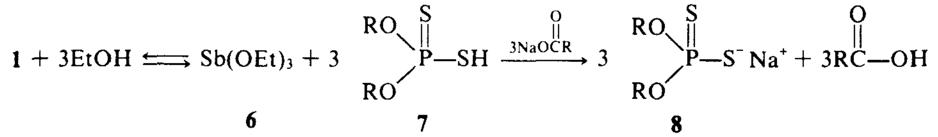


4 **5**

We have also found that antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), undergoes reaction with the sodium salt of *n*-propyl mercaptan, also in hexane, to give **4** plus sodium 0,0-diisobutyl phosphorodithioate (the sodium salt of **5**). Although the results clearly indicate that solvolysis by *n*-propyl mercaptan and nucleophilic displacement by the *n*-propyl mercaptide ion take place at antimony rather than at phosphorus,[10] the detailed mechanisms of reaction are not known. These mechanisms will be studied intensively at some future time. A brief discussion of possible nucleophilic substitution mechanisms has been provided previously,[10] but the occurrence of a radical chain reaction is another possibility which should be evaluated at some future time for the reactions of thiols with **1**.

No reaction occurs when compounds of type **1** are refluxed in acetic acid. The fact that these compounds are recovered quantitatively from the acetic acid solutions indicates that none of the possible variations of the S_N1(Sb) mechanism[10] are operative in this system.

When a tetrahydrofuran solution of antimony *tris*-(0,0-diethyl phosphorodithioate), **1** (R = Et), was refluxed for 12 hours with three equivalents of sodium acetate, sodium 0,0-diethyl phosphorodithioate, **8** (R = Et) was obtained in 15% yield, together with mixed antimony sulfides. Almost half of the starting material, **1** (R = Et), was recovered unchanged. In a similar experiment with sodium benzoate in place of sodium acetate, no sodium 0,0-diethyl phosphorodithioate, **8** (R = Et), was obtained. Thus, **1** (R = Et) shows almost no tendency to undergo any of the possible variations of the $S_N2(Sb)$ mechanism[10] with weak bases, such as acetate and benzoate ions. Higher yields (50–60%) of sodium 0,0-diethyl phosphorodithioate, **8** (R = Et), were obtained when **1** (R = Et) was refluxed in a solution of either sodium acetate or sodium benzoate in absolute ethanol. However, these results are probably a reflection of the known solvolysis of compounds of type **1** in ethanol to form antimony triethylate, **6**, and the appropriate 0,0-dialkyl phosphorodithioic acid, **7**. Neutralization of **7** by the sodium salt of the carboxylic acid affords **8**.



$$1 + 3EtOH \rightleftarrows Sb(OEt)_3 + 3\,(RO)_2P(=S)SH \xrightarrow{3NaOC(=O)R} 3\,(RO)_2P(=S)S^-Na^+ + 3RC(=O)OH$$

6 **7** **8**

We next turned our attention to possible nucleophilic displacement reactions involving strong anions. In particular, we wished to determine whether attack at phosphorus might occur in competition with attack at antimony. The reaction of an excess of phenyllithium with antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), in benzene-ether solution led to the isolation of triphenylstibine in 60% yield. No triphenylphosphine could be found in the reaction mixture. Thus, some variation of the $S_N2(Sb)$ mechanism[10] appears to be operative in this reaction. Also, it is obvious that, with a wide range of nucleophiles, attack at antimony occurs much more readily than attack at phosphorus in compounds of type **1**. Perhaps antimony back-donates its electrons to the PS_2-bidentate ligand and causes phosphorus to become less reactive towards nucleophilic attack.[14]

No reaction occurred when compounds of type **1** were refluxed in pyrrole, a known component of crude petroleum.[12,13] However, when **1** (R = Et, *i*-Bu, or *i*-Pr) was heated with three equivalents of the sodium salt of pyrrole in tetrahydrofuran, high yields of **8** (R = Et, *i*-Bu, or *i*-Pr, respectively) were obtained. Although *tris*-(N-pyrrolyl)-stibine could not be isolated in any of these reactions, this is not surprising inasmuch as the Sb—N bond is known to be exceptionally vulnerable to attack by oxygen,[15,16] and it is probably unstable towards water also. It is known that antimony trialkoxides, $Sb(OR)_3$ can be obtained by alcoholysis of *tris*-(dialkylamino)stibines, $Sb(NR_2)_3$, in the presence of base.[17] Unfortunately, attempts to provide indirect evidence for the formation of *tris*-(N-pyrrolyl)stibine by addition of anhydrous ethanol to the reaction mixture failed. No antimony triethoxide, **6**, could be detected.

The fact that 100% yields of **8** were obtained in these reactions provides additional evidence that nucleophilic substitution occurs exclusively at antimony in compounds of type **1**. Furthermore, the facts that the yield of **8** was 33%, with recovery of 67% of **1** when one equivalent of pyrrolylsodium was employed, and that the yield of **8** was 67%, with recovery of 33% of **1**, when two equivalents of pyrrolylsodium were employed, provide proof that the displacement of the first 0,0-diaklyl phosphorodithioate anion from **1** is less rapid than the displacement of the second phosphorodithioate anion, which, in turn, is less rapid than the displacement of the third phosphorodithioate anion. These facts will be of importance when the complete mechanism of reaction is understood. However, we are not able to propose a definitive mechanism at the present time. It should be kept in mind that the structures of compounds of type **1** are distorted capped octahedra with a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the antimony atom.[18] Also, the mechanisms might involve antimony in a hypervalent state at some stage, and are possibly quite complex.

EXPERIMENTAL

Antimony tris-*(0,0-Dialkyl Phosphorodithioates)*, **1**. These compounds were prepared and purified as described in a previous paper.[11]

Reaction of Antimony tris-*(0,0-Diisobutyl Phosphorodithioate)*, **1** *(R =* i-*Bu), with* n-*Propyl Mercaptan.* To a solution of 4.4 g (0.0047 mol) of antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), in 100 ml. of dry hexane was added 2 ml (0.022 mol) of *n*-propyl mercaptan. The reaction mixture was refluxed for one hour and then cooled to room temperature. The hexane solution was washed with 40 ml. of 2.5% NaOH solution and then with 40 ml of water. The hexane solution was dried over anhydrous magnesium sulfate and concentrated under a high vacuum. The residue was distilled at 55–60°C (0.1 torr.) and gave 1.55 g (0.0044 mol, 93%) of colorless Sb(S—Pr-*n*)$_3$, **4**, NMR ($CDCl_3$) δ 1.5 (t, 9, J = 6.5), 1.41–2.07 (m, 6), 2.95 (t, 6, J = 7.5); i.r. ($CHCl_3$) 3080 (s), 3050 (s), 3000 (s), 1640 (w), 1500 (m), 1420 (m), 1380 (w), 1330 (m), 1121 (w), 1061 (w), 926 (w), 900 (s) cm.$^{-1}$

Anal. Calcd. for $C_9H_{21}S_3Sb$: C = 31.12, H = 6.02, S = 27.72., Found: C = 31.24, H = 5.98, S = 27.74.

The aqueous NaOH solution was neutralized with 10% HCl solution and then extracted with 50 ml of pentane. The pentane solution was dried over anhydrous magnesium sulfate for one hour. Sodium hydride (0.5 g) was added to the pentane solution, and a white solid which had formed was collected and washed with 50 ml of pentane. The white solid was recrystallized from tetrahydrofuran-hexane solution and gave 0.18 g (0.0007 mol, 5%) of sodium 0,0-diisobutyl phosphorodithioate, **8** (R = *i*-Bu), m.p. 55°C; NMR (D_2O) δ 0.90 (d, 12, J = 7.5), 1.7–2.1 (m, 2), 3.68 (d of d, 4, $J_{H\text{-}H}$ = 8, $J_{P\text{-}H}$ = 6).

Antimony(III) tris-*(1-Propanethiolate)*, **4**. Antimony trichloride, 20 g (0.09 mol), was suspended in 50 ml of anhydrous hexane containing 25 ml of *n*-propyl mercaptan. The solution was placed in an ice-water bath. To this cold solution, maintained under an argon atmosphere, was added 32.0 ml (0.30 mol) of dry diethylamine. A white solid formed during the addition of the diethylamine. The resulting mixture was refluxed for two hours. The mixture was filtered, and the filtrate was concentrated. The residue was distilled at 56–60°C (0.1 torr.) and gave 10 g (0.03 mol, 33%) of antimony *tris*-(1-propanethiolate), **4**. The NMR spectrum (in $CDCl_3$ solution) and ir spectrum (in $CHCl_3$ solution) were identical with those of the sample of antimony *tris*-(1-propanethiolate), **4**, mentioned previously.

Sodium 0,0-Diisobutyl Phosphorodithioate, **8** *(R =* i-*Bu).* To a solution of 7.4 g (0.1 mol) of isobutyl alcohol in 100 ml of anhydrous tetrahydrofuran, maintained under an argon atmosphere, was added 6 g (0.025 mol) of phosphorus pentasulfide, and the mixture was stirred for two hours at room temperature. The excess phosphorus pentasulfide was removed by filtration through a silica gel pad (100–200 mesh), and the filtrate was concentrated to give a yellow oil. Anhydrous hexane (10 ml) was added to the yellow oil, and 1.2 g (0.05 mol) of sodium hydride was added to the hexane solution. The resulting white precipitate was collected by filtration and washed with 100 ml of hexane. The yield of sodium 0,0-diisobutyl phosphorodithioate was 18.5 g (0.05 mol, 100%), m.p. 55°C. The NMR spectrum (in D_2O solution) was identical with that of the sample of **8** (R = *i*-Bu) mentioned previously.

Reaction of **1** *(R =* i-*Bu) with Sodium 1-propanethiolate.* To a solution of 6.3 ml (0.069 mol) of *n*-propyl mercaptan in 100 ml of dry hexane, maintained under an argon atmosphere, was added 3.0 g (0.07 mol) of sodium hydride. The mixture was stirred for one hour at room temperature. A solution of 10.0 g (0.0108 mol) of antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu) in 50 ml. of hexane was added to the sodium 1-propanethiolate solution, and the mixture was refluxed for two hours. A white precipitate which had formed was collected and washed with 50 ml of hexane. The hexane filtrate was washed with 100 ml of 1 *N* NaOH solution and then with 100 ml of water. The hexane solution was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was distilled at 50–55°C (0.1 torr.) and gave 2.2 g (0.0063 mol, 58%) of antimony *tris*-(1-propanethiolate), **4**. The NMR (in $CDCl_3$ solution) and ir (in $CHCl_3$ solution) spectra were identical with those of the antimony *tris*-(1-propanethiolate), **4**, prepared previously.

The white solid product was stirred in 50 ml of tetrahydrofuran, and an insoluble precipitate (sodium 1-propanethiolate) was removed by filtration. The filtrate was concentrated to about 10 ml, and 20 ml of hexane was added to the residue to give a white precipitate. The yield of sodium 0,0-diisobutyl phosphorodithioate, **8** (R = *i*-Bu), was 4.2 g (0.0178 mol, 55%), m.p. 55°C. The NMR (D_2O) spectrum was identical with that of the sample of **8** (R = *i*-Bu) mentioned previously.

Reaction of Antimony tris-*(0,0-Diisobutyl Phosphorodithioate)*, **1** *(R =* i-*Bu with Phenyllithium.* To 15 ml (0.015 mol) of a 1 *M* solution of phenyllithium (commercially available) in benzene-ether, maintained under an argon atmosphere, was added 2.75 g (0.003 mol) of antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu). The solution was stirred at room temperature overnight. "Wet ether" (100 ml) was added to the reaction mixture, which was then washed with 100 ml of water. The ether solution was dried over anhydrous magnesium sulfate and concentrated to dryness. Triphenylstibine could be obtained by column chromatography of the residue, (silica gel as the absorbent, hexane as eluent). The yield was 0.75 g (0.0021 mol, 60%). The mp of the triphenylstibine was 51-52°C, also in admixture with an authentic sample (commercially available). The NMR (in $CDCl_3$ solution) and ir (in $CHCl_3$ solution) spectre of the two samples of triphenylstibine were identical.

Reaction of **1** *(R =* i-*Bu) with Pyrrolylsodium.* To a solution of 6.4 g (0.098 mol) of pyrrole in 100 ml of dry tetrahydrofuran, maintained under an argon atmosphere, was added 2.3 g (0.1 mol) of sodium hydride, and the mixture was stirred for 1 hour. To this dark green pyrrolylsodium solution was added 2.2 g (0.0023 mol) of antimony *tris*-(0,0-diisobutyl phosphorodithioate), **1** (R = *i*-Bu), and the mixture was stirred for two hours at room temperature. A precipitate which had formed was removed by filtration, and the filtrate was concentrated to dryness. A light brown residue which remained was washed with hexane a few times and extracted with 10 ml. of tetrahydrofuran. The final product was obtained by adding hexane to the tetrahydrofuran solution. There was obtained 1.64 g (0.0062 mol, 89%) of sodium 0,0-diisobutyl phosphorodithioate, **8** (R = *i*-Bu), mp. 55°C. The NMR spectrum (D_2O) was identical with that of the sample of **8** (R = *i*-Bu) mentioned previously.

Similar results were obtained when **1** (R = Et or R = *i*-Pr) was used in place of **1** (R = *i*-Bu). Sodium 0,0-diisopropyl phosphorodithioate, **8** (R = *i*-Pr) was obtained in 91% yield, mp. 189°C, NMR (D_2O) δ 1.12 (d, 12, J = 7), 4.91 (m, 2). Sodium 0,0-diethyl phosphorodithioate, **8** (R = Et), was obtained in 70% yield, mp. 182-183°C, (crystallized from tetrahydrofuran-Skelly F solution), NMR (D_2O) δ 1.13 (t, 6, J = 11.3), 3.85 (d of q, 4, $J_{H\text{-}H} = 11.3$, $J_{P\text{-}H} = 15.7$).

Anal. Calcd. for $C_4H_{10}O_2PS_2Na$: C, 23.07; H, 4.84; P, 14.88; S, 30.79. Found: C, 23.49; H, 5.03; P, 14.34; S, 30.79.

Reaction of **8** (R = Et) with dichloroantimony 0,0-diethylphosphorodithioate, **2**, gave antimony *tris*-(0,0-diethyl phosphorodithioate), **1** (R = Et), mp. 56°C., also in admixture with an authentic sample of the compound. NMR ($CDCl_3$) and ir (KBr) spectra of the two samples were identical.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. Also, this work was supported in part by a Faculty Research Grant provided by the Graduate School, University of Massachusetts.

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