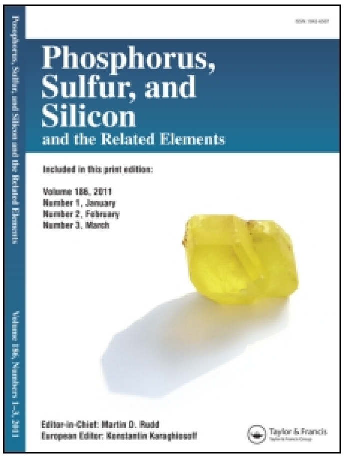

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SYNTHESIS AND CHARACTERIzATION OF TRIPHENYLANTIMONY (V) (O-ALKYL, O-CYCLOALKYL AND O-ARYLTRITHIOPHOSPHATES)

U. N. Tripathi[a]; Mohd. Safi Ahmad[a]
[a] School of Studies in Chemistry, Vikram University, Ujjain, India

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SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLANTIMONY (V) (O-ALKYL, O-CYCLOALKYL AND O-ARYLTRITHIOPHOSPHATES)

U. N. Tripathi and Mohd. Safi Ahmad
School of Studies in Chemistry, Vikram University, Ujjain, India

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Triphenylantimony (V) (O-alkyl,O-cycloalkyl and O-aryltrithiophosphates) of the type $Ph_3Sb[S_2(S)P(OR)]$ (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph and C.h. = cyclohexyl) have been synthesized for the first time by the reaction of triphenylantimony (V) dibromide with potassium trithiophosphates in 1:1 molar ratio in methanol. These new compounds have been characterized by elemental analysis, molecular weight determinations, and spectroscopic (IR, ^{13}C and ^{31}P NMR) studies. On the basis of these data trigonal bipyramidal geometry has been proposed for these compounds.

Keywords: Antimony; triphenylantimony (V); trithiophosphate

INTRODUCTION

The synthesis and spectral aspects of dialkyldithiophosphates and dithiophosphinates of arsenic, antimony, and bismuth and their organometallic moieties have recently been reviewed.[1] The interest in the chemistry of organoantimony derivatives of dithiophosphato ligands arises from their potential biological activity, i.e., antitumour properties.[2] The reaction of $[(RO)_2PS_2]NH_4$ with Ph_3SbBr_2 has resulted in an intramolecular redox process leading to the formation of Ph_3Sb and $[(RO)_2PS_2]_2$.[3] Attemts to prepare $Ph_3Sb(S_2CNR_2)_2$ have resulted in the formation of Ph_3Sb and $(S_2CNR_2)_2$.[4,5]

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Address correspondence to U. N. Tripathi, School of Studies in Chemistry, Vikram University, Ujjain (M.P.), 456010, India. E-mail: un_tripathi@yahoo.com

Potassium trithiophosphates exist in two isomeric forms:

$$[(RO)P(S)S_2]K_2 \rightleftharpoons [(RS)P(O)S_2]K_2$$

Organic trithiophosphate esters have been used as defoliants,[6] insecticides,[6,7] nematodicides,[7] and inhibitors[8] of steel corrosion. The perusal of literature revealed only scanty information about the metallic esters of trithiophosphoric acids[9,10] and in continuation of our research interest in ligands containing both phosphorus and sulphur, we thought it worthwhile to synthesize a number of compounds of the type $Ph_3Sb[S_2(S)P(OR)]$, which must probably be biocidal in nature.

In the present communication we report the synthesis and characterization of a number of triphenylantimony (V) trithiophosphates.

RESULTS AND DISCUSSION

Triphenylantimony (V) (O-alkyl,O-cycloalkyl and O-aryltrithiophosphates) have been prepared by the reaction of triphenylantimony (V) dibromide with potassium trithiophosphates in 1:1 molar ratio in methanol:

$$Ph_3SbBr_2 + [(RO)P(S)S_2]K_2 \rightarrow Ph_3Sb[S_2(S)P(OR)] + 2KBr \downarrow$$

$$(R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, Bu^i, Am^i, Ph, \text{and C.h.} = \text{cyclohexyl})$$

Triphenylantimony (V) trithiophosphates are colorless viscous liquids (Table I) soluble in common organic solvents like chloroform, carbon tetrachloride, acetone, etc. Molecular weight determinations in chloroform indicate the monomeric nature of these compounds. All these compounds are nonvolatile, even under reduced pressure.

All these compounds tend to decompose, even in a closed environment. Decomposition is marked by the change from colorless to yellow-orange and insolubility in solvents in which they were initially soluble, like acetone and carbon tetrachloride.

IR spectra of these new compounds have been measured in the range 4000–200 cm^{-1}, and assignments have been made by comparison with the IR spectra of potassium trithiophosphates.[11,12] The bands present in the regions 1057–1040 and 828–816 cm^{-1} have been assigned to ν[(P)—O—C] and ν[P—O—(C)] stretching modes, respectively. A strong band due to ν(P=S) is found in the region 691–681 cm^{-1}. The bands of medium intensity present in the region 503–493 cm^{-1} may be ascribed to ν(P—S) vibrations. The presence of a new band of medium intensity in the region 382–376 cm^{-1} in the spectra of triphenylantimony (V) trithiophosphates (as compared to the potassium trithiophosphates) may be due to ν(Sb—S) stretching vibrations. Ph groups of these

TABLE I Synthesis and Physical Properties of Triphenylantimony (V) Trithiophosphates

Sl. no.	Reactants		Molar ratio	Product yield (g:%)	Physical state	Analysis %				Molecular weight found (calcd.)
	Ph_3SbBr_2	$[(RO)P(S)S_2]K_2$				Hydrogen found (calcd.)	Carbon found (calcd.)	Sulphur found (calcd.)	Antimony found (calcd.)	
1	2	3	4	5	6	7	8	9	10	11
1	2.56	$[(MeO)P(S)S_2]K_2$ 1.18	1:1	$Ph_3Sb[S_2(S)P(OMe)]$ (0.77:89)	Colorless viscous liquid	3.39 (3.52)	44.27 (44.64)	18.61 (18.79)	23.63 (23.84)	515 (511)
2	2.56	$[(EtO)P(S)S_2]K_2$ 1.25	1:1	$Ph_3Sb[S_2(S)P(OEt)]$ (0.83:93)	”	3.68 (3.81)	45.39 (45.74)	18.14 (18.29)	23.25 (23.20)	535 (525)
3	2.56	$[(Pr^nO)P(S)S_2]K_2$ 1.32	1:1	$Ph_3Sb[S_2(S)P(OPr^n)]$ (0.83:90)	”	4.13 (4.08)	46.52 (46.77)	17.65 (17.82)	22.53 (22.60)	532 (539)
4	2.56	$[(Pr^iO)P(S)S_2]K_2$ 1.32	1:1	$Ph_3Sb[S_2(S)P(OPr^i)]$ (0.86:94)	”	— (4.08)	46.83 (46.77)	17.79 (17.82)	22.43 (22.60)	548 (539)
5	2.56	$[(Bu^nO)P(S)S_2]K_2$ 1.39	1:1	$Ph_3Sb[S_2(S)P(OBu^n)]$ (0.85:90)	”	— (4.34)	47.85 (47.76)	17.45 (17.37)	22.17 (22.03)	567 (553)
6	2.56	$[(Bu^sO)P(S)S_2]K_2$ 1.39	1:1	$Ph_3Sb[S_2(S)P(OBu^s)]$ (0.86:92)	”	4.36 (4.34)	47.81 (47.76)	17.21 (17.37)	22.21 (22.03)	557 (553)
7	2.56	$[(Bu^iO)P(S)S_2]K_2$ 1.39	1:1	$Ph_3Sb[S_2(S)P(OBu^i)]$ (0.83:88)	”	4.29 (4.34)	47.38 (47.76)	17.39 (17.37)	21.85 (22.03)	560 (553)
8	2.56	$[(Am^iO)P(S)S_2]K_2$ 1.46	1:1	$Ph_3Sb[S_2(S)P(OAm^i)]$ (0.89:93)	”	4.47 (4.59)	48.79 (48.70)	16.97 (16.94)	21.23 (21.48)	568 (567)
9	2.56	$[(C.h.O)P(S)S_2]K_2$ 1.52	1:1	$Ph_3Sb[S_2(S)P(OC.h.)]$ (0.93:95)	”	4.51 (4.49)	49.84 (49.76)	16.43 (16.59)	20.91 (21.04)	584 (579)
10	2.56	$[(PhO)P(S)S_2]K_2$ 1.49	1:1	$Ph_3Sb[S_2(S)P(OPh)]$ (0.88:91)	”	3.35 (3.49)	50.01 (50.28)	16.58 (16.76)	20.01 (21.26)	564 (573)

compounds show their characteristic out-of-plane bending vibrations in the region 716–724 cm^{-1} and C—H stretching vibrations at ~3052 cm^{-1}.

The ^{13}C NMR spectra (Table II) of these compounds show characteristic resonances due to the alkoxy, phenoxy, and phenyl groups. The ^{13}C resonances for the carbon atoms of Ph_3Sb group are as expected. The ^{13}C resonance for the carbon atom of P—O—C group appears as doublet due to coupling with the ^{31}P nuclei. As compared to potassium trithiophosphates, the α-carbon resonance of —OR group in these compounds is deshielded by (3.2–4.6 ppm), whereas the resonances due to β-carbon and γ-carbon atoms are shielded by (0.8–1.4 ppm) and (2.9–3.9 ppm), respectively.

In the proton decoupled ^{31}P NMR spectra (Table III), only one resonance for each compound in the range 96.59–97.99 ppm is obtained.

On the basis of above studies, the most plausible geometry for these compounds appears to be trigonal bipyramidal (Figure 1). The central antimony atom appears to acquire coordination number five. The trithiophosphate moieties in these compounds behave as bidentate ligand.

EXPERIMENTAL

Moisture was carefully excluded throughout experimental manipulations. Solvents (methanol, carbon tetrachloride, benzene, and acetone), alcohols (methanol, ethanol, n-propanol, i-propanol, n-butanol, s-butanol, i-butanol, and i-amyl alcohol), cyclohexanol, phenol, and triethyl amine were dried by standard methods.[13] Triphenylantimony (V) dibromide[14] and potassium salt of O-alkyl O-cycloalkyl and O-aryltrithiophosphoric acids[11,12] were prepared by previously reported methods.

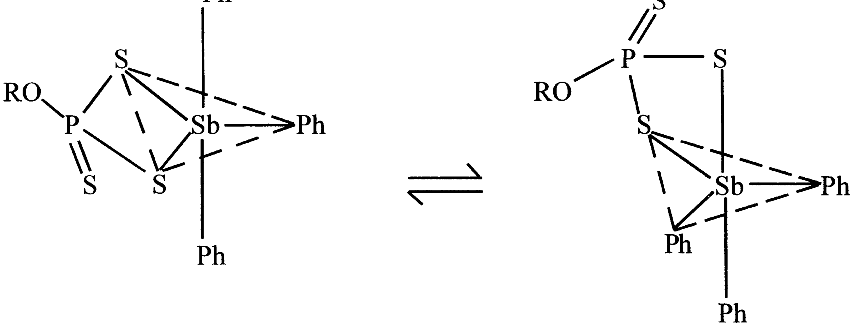


FIGURE 1 Structure of $Ph_3Sb[S_2(S)P(OR)]$.

TABLE II ^{13}C NMR Spectral Data for Triphenylantimony (V) Trithiophosphates

		Chemical shift (δ, ppm)	
Sl. no.	Compound	Ph_3Sb carbons	$S_2(S)P(OR)$ carbons
1	$Ph_3Sb[S_2(S)P(OMe)]$	138.4, C_1 136.2,$C_{2,6}$ 133.6,$C_{3,5}$ 128.6, C_4	59.96,d,C; $^2J_{P-C} = 15$ cps
2	$Ph_3Sb[S_2(S)P(OEt)]$	138.0, C_1 136.1, $C_{2,6}$ 133.9, $C_{3,5}$ 128.7, C_4	68.61,d,C_1; $^2J_{P-C} = 18$ cps 17.93, C_2
3	$Ph_3Sb[S_2(S)P(OPr^n)]$	138.2, C_1 135.7, $C_{2,6}$ 133.7, $C_{3,5}$ 128.7, C_4	74.26,d, C_1; $^2J_{P-C} = 21$ cps 24.56, C_2 9.58, C_3
4	$Ph_3Sb[S_2(S)P(OPr^i)]$	138.3, C_1 135.6, $C_{2,6}$ 133.8, $C_{3,5}$ 128.8, C_4	70.09,d, C_1; $^2J_{P-C} = 18$ cps 24.43, C_2
5	$Ph_3Sb[S_2(S)P(OBu^n)]$	138.2, C_1 136.0, $C_{2,6}$ 133.8, $C_{3,5}$ 128.7, C_4	72.21,d, C_1; $^2J_{P-C} = 15$ cps 33.16, C_2 17.27, C_3 14.7, C_4
6	$Ph_3Sb[S_2(S)P(OBu^s)]$	138.1, C_1 135.9, $C_{2,6}$ 133.7, $C_{3,5}$ 128.5, C_4	21.9, C_1 75.29,d, C_2; $^2J_{P-C} = 9$ cps 31.41, C_3 9.12, C_4
7	$Ph_3Sb[S_2(S)P(OBu^i)]$	138.4, C_1 135.8, $C_{2,6}$ 133.6, $C_{3,5}$ 128.9, C_4	75.07,d, C_1; $^2J_{P-C} = 12$ cps 29.7, C_2 17.44, C_3
8	$Ph_3Sb[S_2(S)P(OAm^i)]$	138.3, C_1 135.5, $C_{2,6}$ 133.8, $C_{3,5}$ 128.8, C_4	65.98,d, C_1; $^2J_{P-C} = 24$ cps 40.55, C_2 23.64, C_3 23.67, C_4
9	$Ph_3Sb[S_2(S)P(OC.h.)]$	138.0, C_1 135.8, $C_{2,6}$ 133.6, $C_{3,5}$ 128.5, C_4	77.82,d, C_1; $^2J_{P-C} = 342$ cps 32.8, $C_{2,6}$ 23.2, $C_{3,5}$ 24.7, C_4
10	$Ph_3Sb[S_2(S)P(OPh)]$	138.1, C_1 136.1, $C_{2,6}$ 133.9, $C_{3,5}$ 128.8, C_4	163.7,d, C_1; $^2J_{P-C} = 438$ cps 117.51, $C_{2,6}$ 129.5, $C_{3,5}$ 120.4, C_4

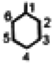
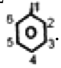
d, doublet; Et, $\overset{2}{C}H_3-\overset{1}{C}H_2-$; Pr^n, $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-$; Pr^i $(\overset{2}{C}H_3)_2-\overset{1}{C}H-$; Bu^n, $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-$; $Bu,^s$ $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H-\overset{1}{C}H_3$; Bu^i, $(\overset{3}{C}H_3)_2-\overset{2}{C}H-\overset{1}{C}H_2-$; Am^i, $(\overset{4}{C}H_3)_2-\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}H_2-$; C.h., ; Ph, .

TABLE III ^{31}P NMR Spectral Data for Triphenylantimony (V) Trithiophosphates

Sl. no.	Compound	Chemical shift (δ, ppm)
1	$Ph_3Sb[S_2(S)P(OMe)]$	97.38
2	$Ph_3Sb[S_2(S)P(OEt)]$	96.87
3	$Ph_3Sb[S_2(S)P(OPr^n)]$	96.98
4	$Ph_3Sb[S_2(S)P(OPr^i)]$	97.05
5	$Ph_3Sb[S_2(S)P(OBu^n)]$	96.59
6	$Ph_3Sb[S_2(S)P(OBu^s)]$	97.99
7	$Ph_3Sb[S_2(S)P(OBu^i)]$	96.91
8	$Ph_3Sb[S_2(S)P(OAm^i)]$	97.11
9	$Ph_3Sb[S_2(S)P(OC.h.)]$	96.87
10	$Ph_3Sb[S_2(S)P(OPh)]$	97.76

Sulphur was estimated gravimetrically as barium sulphate.[13] Antimony was estimated by decomposing the compound by H_2SO_4 and oxidizing Sb (III) to Sb (V) by heating with $KMnO_4$. The excess of $KMnO_4$ was decolorized by H_2O_2, and excess H_2O_2 was removed by evaporation. The remaining solid mass was dissolved in HCl, KI was added to it, and the liberated iodine was titrated against standard sodium thiosulphate solution using starch as an internal indicator.[15]

Molecular weights were determined on a Knauer vapor pressure osmometer. IR spectra were recorded as neat liquids using CsI cells on a Perkin-Elmer 577 spectrometer in the range 4000–200 cm^1. ^{13}C and ^{31}P NMR spectra in $CDCl_3$ were recorded on a Bruker DRX-300 spectrometer using tetra methyl silane and H_3PO_4 standards, respectively.

General Method of Synthesis of Ph_3 $Sb[S_2(S)P(OR)]$: Reaction of Triphenylantimony (V) Dibromide with Potassium Trithiophosphates in 1:1 Molar Ratio

Triphenylantimony (V) dibromide (5 mmole) was added to the methanolic solution of potassium trithiophosphates (5 mmole) and stirred for 4–5 h at room temperature. The solvent was stripped off in vacuo, and the resulting solid was extracted with carbon tetrachloride. The insolubles were removed by filtration. The volatiles were removed from filtrate to get colorless viscous liquid.

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