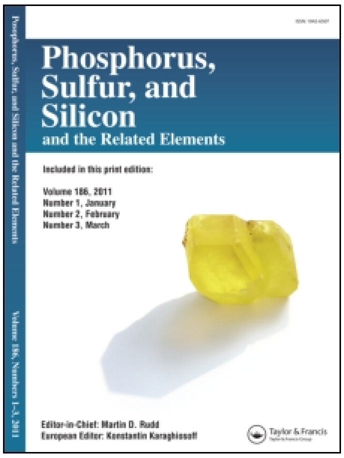

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H. P. S. Chauhan[a]; G. Srivastava[a]; R. C. Mehrotra[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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SYNTHESIS AND REACTIONS OF MIXED HALIDE DIALKYLDITHIOPHOSPHATE DERIVATIVES OF BISMUTH(III)

H. P. S. CHAUHAN, G. SRIVASTAVA and R. C. MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

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Mixed chloride dialkyldithiophosphates of bismuth(III), $[(RO)_2PS_2]_nBiCl_{3-n}$ ($n = 1, 2$; R = Et, Pr^n, Pr^i and Bu^i) have been synthesized for the first time by the reactions of bismuth trichloride with sodium diisopropyldithiophosphate or alternatively by co-disproportionation reactions of bismuth trichloride with bismuth *tris*(dialkyldithiophosphates) in different stoichiometric ratios in suitable organic solvents. Monohalobismuth *bis*(diisopropyldithiophosphates) have also been synthesized by the cleavage reactions of bismuth *tris*(dialkyldithiophosphates) with bromine or iodine in 2 : 1 molar ratio.

These new derivatives have been characterized by elemental analysis, molecular weight determinations (both cryoscopic and ebullioscopic) as well as spectroscopic (IR, ^1H NMR and ^{31}P NMR) studies. On the basis of these data chelated structures with bidentate dialkyldithiophosphate groups have been proposed for these monomeric derivatives. Hydrolysis reactions of some of these compounds have also been studied.

INTRODUCTION

Amongst the ligands involving both phosphorus and sulphur, dialkyldithiophosphates have been investigated extensively.[1] These ligands exhibit bidentate[1-3] as well as monodentate[4-6] behaviour and form stable complexes with transition[1-4] as well as nontransition[1,5,6] elements. In spite of an extensive literature on derivatives of bismuth with sulphur ligands,[1,7,8] the studies on corresponding dialkyldithiophosphate derivatives seem to be limited.[1,2] A few tris derivatives $[(RO)_2PS_2]_3Bi$[1,2,9-12] have been reported and studied by some of the spectroscopic techniques. The single crystal X-ray structure[2] of $[(Pr^iO)_2PS_2]_3Bi$ has also been determined. Besides the synthetic and structural aspects, photometric properties[13] and analytic applications[13-15] of a few bismuth dialkyldithiophosphates have also been reported.

The mixed halide dialkyldithiophosphate derivatives of bismuth are still unknown. In view of the exciting chemistry of mixed halide dialkyldithiophosphate derivatives of arsenic(III)[16] and antimony(III)[16] and mixed halide dialkyldithiocarbamates of bismuth(III)[17-19] it was considered worthwhile to synthesize a number of *tris* as well as mixed halide dialkyldithiophosphate derivatives of bismuth(III) and investigate their physicochemical properties.

RESULTS AND DISCUSSION

Bismuth *tris*(dialkyldithiophosphates) have been prepared by the reactions of bismuth trichloride (bismuth oxychloride dissolved in dilute hydrochloric acid) with dialkyldithiophosphoric acids or their sodium or ammonium salts in 1 : 3 molar ratio:

$$\mathrm{BiCl_3 + 3(RO)_2PSSH \rightarrow [(RO)_2PS_2]_3Bi + 3HCl}$$

$$(\mathrm{R = Et, Pr^n, Pr^i\ and\ Bu^i})$$

$$\mathrm{BiCl_3 + 3(RO)_2PSSM \rightarrow [(RO)_2PS_2]_3Bi + 3MCl}$$

(When $\mathrm{M = Na}$; $\mathrm{R = Et, Pr^i}$ and when $\mathrm{M = NH_4}$; $\mathrm{R = Ph}$)

All these exothermic reactions are quite facile and have been carried out in dilute hydrochloric acid and alcohol mixture. Bismuth *tris*(dialkyldithiophosphates) were immediately precipitated on adding the reactants.

Mixed chloride diisopropyldithiophosphates of bismuth have been synthesized by the reaction of bismuth trichloride with sodium diisopropyldithiophosphate in 1 : 2 and 1 : 1 molar ratio in acetonitrile

$$\mathrm{BiCl_3 + 2(Pr^iO)_2PSSNa \rightarrow [(Pr^iO)_2PS_2]_2BiCl + 2NaCl\downarrow}$$

$$\mathrm{BiCl_3 + (Pr^iO)_2PSSNa \rightarrow [(Pr^iO)_2PS_2]BiCl_2 + NaCl\downarrow}$$

In view of the insolubility of bismuth trichloride as well as sodium dialkyldithiophosphates in a number of suitable organic solvents (benzene, hexane, carbon tetrachloride, chloroform, ether etc.), most of the mixed chloride dialkyldithiophosphates of bismuth have been synthesized employing the co-disproportionation reactions between bismuth trichloride and bismuth *tris*(dialkyldithiophosphates) in different (1 : 2 and 2 : 1) molar ratios:

$$\mathrm{BiCl_3 + 2[(RO)_2PS_2]_3Bi \rightarrow 3[(RO)_2PS_2]_2BiCl}$$

$$\mathrm{2BiCl_3 + [(RO)_2PS_2]_3Bi \rightarrow 3[(RO)_2PS_2]BiCl_2}$$

All the above reactions are quite facile and may be carried out in benzene or acetonitrile simply by stirring the reactants for about one hour at room temperature; however, the reaction mixture was heated moderately, to ensure the completion of the reactions.

Monohalobismuth *bis*(diisopropyldithiophosphates) have been synthesized by the cleavage reactions of bismuth *tris*(diisopropyldithiophosphate) with halogens (bromine or iodine) in 2 : 1 molar ratio:

$$\mathrm{2[(Pr^iO)_2PS_2]_3Bi + X_2 \rightarrow 2[(Pr^iO)_2PS_2]_2BiX + [(Pr^iO)_2PS]_2}$$

These reactions are also quite facile and are completed at room temperature in benzene/carbon tetrachloride solution simply by stirring the reactants for about one hour. The *bis*(diisopropylthiophosphoryl) disulphide and monohalobismuth *bis*(diisopropyldithiophosphates) so formed have been separated by washing the mixture with light petroleum (b.p., 60–80°C); the latter being less soluble remains insoluble in small amounts of light petroleum.

Other bismuth *tris*(dialkyldithiophosphates), $\mathrm{[(RO)_2PS_2]_3Bi}$ ($\mathrm{R = Et, Pr^n}$ and $\mathrm{Bu^i}$) also appear to react with halogens in a similar manner (disappearance of colour of bromine and iodine takes place in all the cases), but the expected products, monohalobismuth *bis*(dialkyldithiophosphates) and *bis*(dialkylthiophosphoryl) disulphides could not be separated in any case. Attempts to prepare dihalobismuth diisopropyldithiophosphates, by the reaction of bismuth *tris*(diisopropyldithiophosphate) with halogens (bromine or iodine) in 1 : 1 molar ratio, were also made, but in these cases also the products could not be separated.

Most of these bismuth(III) dialkyldithiophosphates are yellow crystalline solids (Table I) with the exception of corresponding dinormalpropyldithiophosphate derivatives which are yellow viscous liquids and monoiodobismuth *bis*(diisopropyldithiophosphate) which is a brown red solid. These compounds are soluble in common organic solvents like benzene, hexane, carbon tetrachloride, chloroform, acetonitrile and alcohols. The *tris* derivatives are insoluble in water and can be crystallized from aqueous alcohols. Bismuth *tris*(dialkyldithiophosphates) are stable in aqueous as well as dilute hydrochloric acid media but in an excess of ammonia solution, these decompose to give insoluble bismuth oxide:

$$2[(RO)_2PS_2]_3Bi + 6NH_4OH \rightarrow Bi_2O_3 + 6(RO)_2PSSNH_4 + 3H_2O$$

The alcoholic solutions of mixed chloride dialkyldithiophosphates of bismuth on treatment with excess of water give bismuth oxide and bismuth *tris*(dialkyldithiophosphates):

$$6[(RO)_2PS_2]_2BiCl + 3H_2O \rightarrow 4[(RO)_2PS_2]_3Bi + Bi_2O_3 + 6HCl$$

$$3[(RO)_2PS_2]BiCl_2 + 3H_2O \rightarrow [(RO)_2PS_2]_3Bi + Bi_2O_3 + 6HCl$$

The mixed halide dialkyldithiophosphate derivatives can be crystallized from acetonitrile or carbon tetrachloride—light petroleum (b.p., 60–80°C) mixture.

All the *tris* as well as mixed halide dialkyldithiophosphate derivatives of bismuth are monomeric in freezing as well as in refluxing benzene. These compounds could not be volatilized even under reduced pressure and tend to decompose at ~ 120°C.

The dichlorobismuth dialkyldithiophosphates on standing for a few days, even in a stoppered flask, are changed from light yellow to orange red and become partially insoluble in solvents like benzene and alcohols in which they were initially soluble. The compound $[(Pr^iO)_2PS_2]_2BiI$ also decomposes on warming a benzene or chloroform solution and also on slight exposure to atmosphere; the decomposition products could not be characterized.

IR spectra of these new derivatives have been recorded in the range 4000–200 cm^{-1} and assignments of some important bands have been made on the basis of earlier reports.[1,3,5,10,20] The bands in the region 1030–950 cm^{-1} and 850–755 cm^{-1} are assigned to (P)—O—C and P—O—(C) stretching vibrations respectively.[20] A sharp band due to ν(P=S)[1,3,5] present in the region 690–640 cm^{-1} in the spectra of corresponding free dialkyldithiophosphoric acids or their sodium or ammonium salts, is shifted towards lower side by ~ 50 cm^{-1}; this shifting appears to be due to a strong bidentate chelation of ligands with bismuth. The bands of medium intensities present in the region 580–510 cm^{-1} have been assigned to (P—S) asymmetric and symmetric vibrations.[3,5] The bands of medium intensities in the region 400–200 cm^{-1} may be due to Bi—S[10] and Bi—X (X = Cl, Br or I) stretching vibrations.

The PMR spectra (Table II) show the proton resonances due to the corresponding alkyl protons of dialkyldithiophosphate moieties. The coupling of α protons of alkyl groups with phosphorus is observed; in a few cases coupling of β proton of alkyl groups with phosphorus is also observed.

TABLE I

Synthesis and physical properties of dialkyldithiophosphate derivatives of bismuth(III)

Sl. no.	Reactants (g)		Molar ratio	Medium of the reaction	Product (yield g; %)	Physical state	Melting point °C	Analysis %		Molecular weight found (Calcd.)
	A	B						Bismuth found (Calcd.)	Sulphur found (Calcd.)	
1	2	3	4	5	6	7	8	9	10	11
1	BiOCl 5.00	$(EtO)_2PSSNa$ 10.73	1 : 3	HCl and Alcohol	$[(EtO)_2PS_2]_3Bi$ (11.42; 78)	Yellow crystalline solid	55	26.98 (27.33)	25.42 (25.16)(25.16)	752 (764)
2	BiOCl 5.00	$(Pr^nO)_2PSSH$ 12.35	1 : 3	"	$[(Pr^nO)_2PS_2]_3Bi$ (15.28; 94)	Yellow crystalline low melting solid	—	24.44 (24.62)	23.37 (22.66)	825 (848)
3	Bi_2O_3 2.83	$(Pr^iO)_2PSSNa$ 8.61	1 : 6	"	$[(Pr^iO)_2PS_2]_3Bi$ (9.72; 94)	Yellow crystalline solid	68	24.24 (24.62)	22.93 (22.66)	862 (848)
4	Bi_2O_3 3.28	$(Pr^iO)_2PSSH$ 9.05	1 : 6	"	$[(Pr^iO)_2PS_2]_3Bi$ (10.14; 85)	Yellow crystalline solid	68	24.31 (24.62)	22.41 (22.66)	—
5	BiOCl 5.00	$(Bu^iO)_2PSSH$ 13.96	1 : 3	"	$[(Bu^iO)_2PS_2]_3Bi$ (15.69; 88)	Yellow crystalline solid	160	22.09 (22.40)	20.91 (20.62)	908 (932)
6	BiOCl 0.38	$(PhO)_2PSSNH_4$ 1.32	1 : 3	"	$[(PhO)_2PS_2]_3Bi$ (1.19; 77)	Yellow sticky solid	—	19.62 (19.85)	17.94 (18.27)	—
7	$BiCl_3$ 1.12	$(Pr^iO)_2PSSNa$ 1.68	1 : 2	Benzene Acetonitrile	$[(Pr^iO)_2PS_2]_2BiCl$ (2.05; 86)	Yellow crystalline solid	145	30.93 (31.15)	18.74 (19.11)	—
8	$BiCl_3$ 1.72	$(Pr^iO)_2PSSNa$ 1.28	1 : 1	"	$[(Pr^iO)_2PS_2]BiCl_2$ (2.03; 76)	Yellow crystalline solid	138	41.92 (42.38)	12.78 (13.00)	—
9	$BiCl_3$ 0.48	$[(EtO_2)PS_2]_3Bi$ 2.33	1 : 2	Benzene	$[(EtO)_2PS_2]_2BiCl$ (2.81; 100)	Yellow crystalline solid	85	33.31 (33.98)	21.06 (20.85)	603 (615)
10	$BiCl_3$ 1.20	$[(EtO)_2PS_2]_3Bi$ 1.46	2 : 1	"	$[(EtO)_2PS_2]BiCl_2$ (2.55; 96)	Yellow crystalline solid	82	45.24 (44.93)	14.04 (13.79)	—
11	$BiCl_3$ 0.29	$[(Pr^nO)_2PS_2]_3Bi$ 1.56	1 : 2	"	$[(Pr^nO)_2PS_2]_2BiCl$ (1.57; 85)	Yellow viscous liquid	—	31.87 (31.15)	18.84 (19.11)	692 (671)
12	$BiCl_3$ 0.80	$[(Pr^nO)_2PS_2]_3Bi$ 1.68	2 : 1	"	$[(Pr^nO)_2PS_2]BiCl_2$ (1.56; 83)	Yellow viscous liquid	—	42.98 (42.38)	12.65 (13.00)	504 (493)
13	$BiCl_3$ 0.42	$[(Pr^iO)_2PS_2]_3Bi$ 2.26	1 : 2	"	$[(Pr^iO)_2PS_2]_2BiCl$ (2.64; 99)	Yellow crystalline solid	145	30.44 (31.15)	18.87 (19.11)	654 (671)
14	$BiCl_3$ 0.89	$[(Pr^iO)_2PS_2]_3Bi$ 1.20	2 : 1	"	$[(Pr^iO)_2PS_2]BiCl_2$ (1.58; 76)	Yellow crystalline solid	138	43.14 (42.38)	12.77 (13.00)	473 (493)
15	$(BiCl_3$ 0.41	$[(Bu^iO)_2PS_2]_3Bi$ 2.43	1 : 2	"	$[(Bu^iO)_2PS_2]_2BiCl$ (2.83; 100)	Yellow crystalline solid	110	29.23 (28.74)	19.82 (17.64)	704 (727)
16	$BiCl_3$ 1.00	$[(Bu^iO)_2PS_2]_3Bi$ 1.48	2 : 1	Benzene	$[(Bu^iO)_2PS_2]BiCl_2$ (2.44; 98)	Yellow crystalline solid	90	40.80 (40.10)	11.75 (12.30)	507 (521)
17	$[(Pr^iO)_2PS_2]_3Bi$ 3.74	Br_2 0.35	2 : 1	Carbon tetrachloride	$[(Pr^iO)_2PS_2]_2BiBr$ (2.25; 71)	Yellow crystalline solid	135	29.50 (29.21)	18.24 (17.93)	732 (715)
18	$[(Pr^iO)_2PS_2]_3Bi$ 3.13	I_2 0.47	2 : 1	Benzene	$[(Pr^iO)_2PS_2]_2BiI$ (1.24; 44)	Red brown crystaline solid	130	29.03 (27.37)	15.99 (16.80)	—

TABLE II

^{1}H NMR spectral data for a few dialkyldithiophosphates of bismuth(III)

Sl. no.	Compound	Chemical shift (δ, ppm)
1	$[(\mathrm{EtO})_2\mathrm{PS}_2]_3\mathrm{Bi}$	1.38, dt, 18 H (CH_3); $J_{CH_3CH_2}$ = 7 cps, J_{POCCH_3} = 1 cps 4.23, dq, 12 H (CH_2O); $J_{CH_3CH_2}$ = 7 cps, J_{POCH_2} = 10 cps
2	$[(\mathrm{Pr}^n\mathrm{O})_2\mathrm{PS}_2]_3\mathrm{Bi}$	0.81–1.16, t, 18 H (CH_3) 1.45–2.01, m, 12 H (CH_2) 3.85–4.22, dt, 12 H (CH_2O)
3	$[(\mathrm{Pr}^i\mathrm{O})_2\mathrm{PS}_2]_3\mathrm{Bi}$	1.10–1.20, d, 36 H (CH_3) 4.30–4.95, m (7 peaks), 6 H (CHO)
4	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]_3\mathrm{Bi}$	0.80, d, 36 H (CH_3); J_{CH_3CH} = 6.5 cps 1.52–2.05, m, 6 H (CH) 3.73, dd, 12 H (CH_2O); J_{CHCH_2O} = 6.5 cps, J_{POCH_2} = 9 cps
5	$[(\mathrm{EtO})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	1.40, dt, 12 H (CH_3); $J_{CH_3CH_2}$ = 7 cps, J_{POCCH_3} = 1 cps 4.28, dq, 8 H (CH_2O); $J_{CH_3CH_2}$ = 7 cps, J_{POCH_2} = 10 cps
6	$[(\mathrm{Pr}^n\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	0.85–1.09, t, 12 H (CH_3) 1.47–2.03, m, 8 H(CH_2) 3.90–4.29, dt, 8 H (CH_2O)
7	$[(\mathrm{Pr}^i\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	1.43, d, 24 H (CH_3); J_{CH_3CH} = 6 cps 4.97, m (7 peaks), 4 H (CHO); J_{CH_3CH} = 6 cps
8	$[(\mathrm{Pr}^i\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiBr}$	1.44, d, 24 H (CH_3); J_{CH_3CH} = 6 cps 4.98, m (7 peaks), 4 H (CHO); J_{CH_3CH} = 6 cps
9	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	0.81, d, 24 H (CH_3); J_{CH_3CH} = 7 cps 1.52–2.06, m, 4 H (CH) 3.80, dd, 8 H (CH_2O); J_{CHCH_2O} = 6.5 cps, J_{POCH_2} = 9 cps
10	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]\mathrm{BiCl}_2$	1.01, d, 12 H (CH_3); J_{CH_3CH} = 6.5 cps 1.77–2.32, m, 2 H (CH) 4.14, dd, 4 H (CH_2O); J_{CHCH_2O} = 6.5 cps, J_{POCH_2} = 9 cps

d = doublet, dd = doubled doublet, dq = doubled quartet, dt = doubled triplet, m = multiplet and t = triplet.

TABLE III

^{31}P NMR spectral data for a few dialkyldithiophosphate derivatives of bismuth(III)

Sl. no.	Compound	Proton decoupled ^{31}P chemical shift (δ, ppm)
1	$[(\mathrm{EtO})_2\mathrm{PS}_2]_3\mathrm{Bi}$	95.5
2	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]_3\mathrm{Bi}$	96.7
3	$[(\mathrm{EtO})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	93.0
4	$[(\mathrm{Pr}^i\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	89.7
5	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]_2\mathrm{BiCl}$	94.2
6	$[(\mathrm{Bu}^i\mathrm{O})_2\mathrm{PS}_2]\mathrm{BiCl}_2$	87.9

^{31}P NMR spectral data (Table III) for only a few representative compounds could be recorded. In the proton decoupled spectra, only one ^{31}P chemical shift for each compound in the range 87–97 ppm is obtained which indicates the bidentate[21] behaviour of dialkyldithiophosphate ligands towards the bismuth in all these derivatives.

The above data indicate the bidentate nature of dialkyldithiophosphate groups in these newly synthesized, monomeric mixed halide dialkyldithiophosphate derivatives of bismuth. Considering the previously reported trigonally distorted octahedral structure[2] (by X-ray crystallographic data) of $[(Pr^iO)_2PS_2]_3Bi$ and proposed structure of corresponding mixed halide dialkyldithiophosphate derivatives of arsenic(III) and antimony(III),[16] the monohalobismuth *bis*(dialkyldithiophosphates) should contain a 5 coordinate bismuth atom and possess a distorted octahedral geometry with the stereochemically active lone pair occupying one of the positions. The corresponding dichlorobismuth dialkyldithiophosphates should contain a 4 coordinate bismuth atom and similarly possess a trigonal bipyramidal geometry. Efforts to obtain X-ray crystallographic data for a few of these interesting derivatives are in progress.

EXPERIMENTAL

Owing to the hydrolizable nature of bismuth halides, precautions were taken to exclude moisture during the course of all the experimental manipulations. Solvents [benzene, carbon tetrachloride, chloroform, light petroleum, acetonitrile and alcohols (ethanol, *n*-propanol, *i*-propanol and *i*-butanol)] were dried by standard methods before use. Dialkyldithiophosphoric acids[22-25] and their sodium[3] and ammonium[23] salts were prepared by methods reported earlier. Bismuth trichloride was prepared by passing chlorine gas through a boiling solution of BiOCl in conc. hydrochloric acid and simultaneously distilling the volatile solvents. The solid mass so obtained was sublimed under reduced pressure to yield bismuth trichloride as a white crystalline solid.

Sulphur was estimated gravimetrically as barium sulphate.[5] Bismuth was estimated[26] by titrating against standard EDTA solution using xylenol orange as indicator. Molecular weights were determined cryoscopically in freezing and evullioscopically in boiling benzene (for only a few derivatives). IR spectra were recorded as Nujol mulls using CsI cells on a Perkin-Elmer 557 spectrometer in the range 4000–200 cm^{-1}. ^1H and ^{31}P NMR spectra in CCl_4 and $CDCl_3$ solutions were recorded using tetramethylsilane and H_3PO_4 standards respectively.

General methods of synthesis of various dialkyldithiophosphate derivatives of bismuth

(1) *Reaction of bismuth trichloride with dialkyldithiophosphoric acids or their sodium or ammonium salts in 1 : 3 molar ratio.* On mixing bismuth trichloride (prepared *in situ* by dissolving BiOCl or Bi_2O_3 in dilute hydrochloric acid) and alcoholic solution of appropriate amount of dialkyldithiophosphoric acid (or the sodium or ammonium salt) an exothermic reaction took place with the precipitation of yellow crystalline solid. The precipitate was washed thoroughly with cold water and further purified by crystallization from aqueous alcohol or isopropanol.

In the case of corresponding normal propyl derivative which is low melting solid the reaction mixture was cooled by placing it in ice and the precipitate was washed with ice cold water.

(2) *Reaction between bismuth trichloride and sodium diisopropyldithiophosphate in 1 : 2 and 1 : 1 molar ratio.* To bismuth trichloride dissolved in acetonitrile/benzene mixture was added sodium diisopropyldithiophosphate in 1 : 2 or 1 : 1 molar ratio and the contents were heated for about one hour at 50–60°C. Precipitated sodium chloride was removed by filtration. On removing the solvent from the filtrate the desired mixed chloride diisopropyldithiophosphate was obtained, which was further purified by crystallization from acetonitrile solution.

(3) *Reaction between bismuth trichloride and bismuth tris(dialkyldithiophosphates) in 1 : 2 and 2 : 1 molar ratio.* Mixture of bismuth trichloride and bismuth *tris*(dialkyldithiophosphate) in 1 : 2 or 2 : 1 molar ratio in acetonitrile was heated at 50–60°C for one hour and the solvent was removed under reduced pressure giving the desired product.

(4) *Reaction of bismuth tris(diisopropyldithiophosphate) with bromine in 2 : 1 molar ratio.* Disappearance of the colour of bromine was observed on mixing the carbon tetrachloride solutions of bromine (0.35 g; 2.19 mmols) and bismuth *tris*(diisopropyldithiophosphate) (3.74 g; 4.41 mmole). Solvent was removed under reduced pressure and the yellow solid so obtained was washed three times with light petroleum (b.p., 60–80°C) (taking about 10 ml of the solvent each time). The residue monobromobismuth *bis*(diisopropyldithiophosphate) (2.25 g., 71%) was finally dried under reduced pressure. The compound was recrystallized from acetonitrile solution.

(5) *Reaction of bismuth tris(diisopropyldithiophosphate) with iodine in 2 : 1 molar ratio.* The benzene solutions of bismuth *tris*(diisopropyldithiophosphate) (3.13 g., 3.69 mmole) and iodine (0.47 g; 1.84 mmole) were mixed and stirred for half an hour. The solution was concentrated to about 20 ml by removing the solvent *in vacuo* and about 20 ml light petroleum (b.p., 60–80°C) was added. The mixture was left overnight when brown crystals were separated (yield 1.24 g., 44%).

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