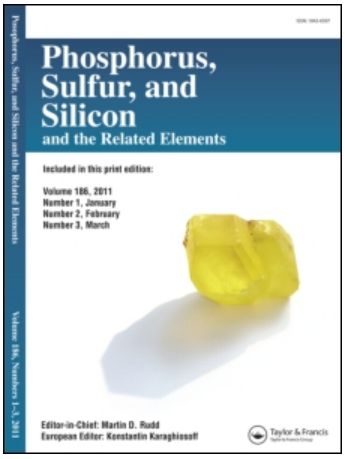

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Syntheses and Spectroscopic Studies of O,O'-Dialkyl(Alkylene)Dithiophosphates of Trimethylaminoboranes

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SYNTHESES AND SPECTROSCOPIC STUDIES OF O,O′-DIALKYL(ALKYLENE)DITHIOPHOSPHATES OF TRIMETHYLAMINOBORANES

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O,O′-Dialkyl (or alkylene) dithiophosphates of trimethylaminoborane of the types $B[S_2P(OR)_2]_3.NMe_3$ and $B[S_2\overline{POGO}]_3.NMe_3$ (where R = Me, Et, Pr^i, Bu^i, Ph; G = $-CMe_2CMe_2-$ and $-CH_2CMe_2CH_2-$) have been synthesized as monomeric, white crystalline solids, soluble in common organic solvents and are characterized by elemental analyses, molecular weight measurements, IR and multinuclear (^1H, ^{11}B and ^{31}P) NMR spectral studies which are consistent with four coordinated boron and the monodentate behaviour of the dithiophosphate moiety.

Key words: Trimethylaminoborane; O,O′-dialkyl- and alkylene dithiophosphates.

INTRODUCTION

There is considerable interest in boron-sulfur bonded compounds due to their high reactivity and possible use as synthetic intermediates.[1,2] O,O′-Dialkyl (or alkylene) dithiophosphoric acids constitute an important series of ligands which show an interesting versatility in their bonding modes [unidentate, bidentate (chelating/bridging), ionic] towards different metals.[3–6]

Hawthorne[7,8] and others[9,10] had studied the reactions of trimethylaminoborane with high boiling mercaptans which yield trialkylthioboranes. A survey of literature surprisingly reveals that no trialkylaminoborane derivatives of these dithiophosphoric acids have been described as yet. The present paper describes the synthesis and characterization of O,O′-dialkyl (or alkylene) dithiophosphates of trimethylaminoborane which is a new class of boron sulfur derivatives containing a B—S—P linkage.

RESULTS AND DISCUSSION

Tris O,O′-dialkyl (or alkylene) dithiophosphates of trimethylaminoborane have been synthesized by mixing and refluxing trimethylaminoborane with O,O′-dialkyl (or alkylene) dithiophosphoric acids in 1:3 molar ratio in dry benzene. The reaction goes to completion after complete dissolution of Me_3NBH_3 within 5 hrs.

$$Me_3NBH_3 + HS_2P(OR)_2 \rightarrow B[S_2P(OR)_2]_3.NMe_3 + 3H_2 \uparrow$$

[R = Me, Et, Pr^i, Bu^i & Ph]

$$Me_3NBH_3 + HS_2\overline{POGO} \rightarrow B[S_2\overline{POGO}]_3.NMe_3 + 3H_2 \uparrow$$

[G = $-CMe_2CMe_2-$ & $-CH_2CMe_2CH_2-$]

TABLE I

Reactions of trimethylaminoborane with O,O'-dialkyl (alkylene) dithiophosphates in 1:3 molar ratio

Compound No.	Reactants: Me_3NBH_3, g (mmole)	Reactants: $HS_2P(OR)_2/HS_2\overline{POGO}$ R=/G= g (mmole)	Product, g; %	Analyses % found (cald.) B	S	C	H	N	Molecular weight found (calcd.)
		Me	$B[S_2P(OMe)_2]_3.NMe_3$	2.00	35.16	20.51	5.17	2.32	526.27
I	1.06 (14.52)	6.88 (43.54)	5.48 73.6	(2.00)	(35.53)	(19.97)	(5.3)	(2.59)	(541.43)
		Et	$B[S_2P(OEt)_2]_3.NMe_3$	1.72	30.18	29.19	6.12	2.07	—
II	0.81 (11.09)	6.20 (33.33)	5.18 74.7	(1.73)	(30.75)	(28.80)	(6.28)	(2.24)	
		Pr^i	$B[S_2P(OPr^i)_2]_3.NMe_3$	1.41	27.55	35.43	7.06	1.82	—
III	0.59 (8.12)	5.15 (24.11)	4.05 71.2	(1.52)	(27.11)	(35.54)	(7.24)	(1.97)	
		Bu^i	$B[S_2P(OBu^i)_2]_3.NMe_3$	1.35	23.92	40.26	7.52	1.58	—
IV	1.34 (18.35)	13.14 (54.33)	11.16 76.7	(1.36)	(24.23)	(40.85)	(8.00)	(1.76)	
		Ph	$B[S_2P(OPh)_2]_3.NMe_3$	1.17	20.76	50.92	4.27	1.41	851.58
V	0.44 (6.02)	5.11 (18.12)	4.43 80.5	(1.18)	(21.05)	(51.20)	(4.30)	(1.53)	(913.86)
		$—CMe_2CMe_2—$	$B[S_2\overline{POCMe_2CMe_2O}]_3.NMe_3$	1.51	26.91	35.11	6.32	1.89	688.15
VI	0.27 (3.69)	2.34 (11.02)	2.11 81.1	(1.54)	(27.34)	(35.84)	(6.45)	(2.00)	(703.71)
		$—CH_2CMe_2CH_2—$	$B[S_2\overline{POCH_2CMe_2CH_2O}]_3.NMe_3$	1.63	28.78	32.54	5.67	2.07	—
VII	0.36 (4.93)	2.97 (15.0)	2.47 75.7	(1.63)	(29.08)	(32.68)	(5.94)	(2.12)	

These derivatives are white colored crystalline solids, soluble in common organic solvents, melt with decomposition at 90–103°C and are monomeric in chloroform.

IR Spectra

I.R. spectra of these derivatives (Table II) show the strong intensity absorption bands in the region of 1120–1015 cm^{-1} and 930–890 cm^{-1}, which are assigned to ν(P)—O—C and νP—O—(C) linkage, respectively. The appearance of a new medium intensity absorption band at 910–860 cm^{-1} is assigned to νB—S linkage.[5] The absorption band due to νP═S is observed in the region 695–670 cm^{-1}. No significant shift has been observed in the thiophosphoryl absorption band (P═S) in comparison to the parent dithio acids. This is indicative of free thiophosphoryl group. The absorption band due to νS—H in the region 2600–2450 cm^{-1} in the parent dithiophosphoric acids disappears which suggests the deprotonation of the ligands.

^{1}H NMR Spectra

^{1}H NMR spectra of these derivatives (Table III) show the characteristic resonances due to alkoxy and glycoxy protons. A sharp singlet in the range of 3.0–3.5 ppm; characteristic for —SH proton in the parent dialkyl (or alkylene) dithiophosphoric acids,[11,12] is found to be absent in the spectra of the newly synthesized derivatives. A singlet is observed in the region 2.62–2.86 ppm, which is due to the N-methyl protons.

^{11}B NMR Spectra

The ^{11}B NMR spectra of these derivatives (Table III) show a sharp singlet in the range of 10.53–20.55 ppm and provide convincing evidence for the purity of these derivatives as well as for the tetracoordinated nature of boron atom. In comparison to the ^{11}B chemical shift value for Me_3NBH_3 (5.09 ppm), the chemical shift observed in these derivatives shows a downfield shift of ~15–25 ppm and suggests that the boron atom is much more shielded in these derivatives than that of Me_3NBH_3.

^{31}P NMR Spectra

^{31}P NMR spectra show only one resonance signal in the region 99.07–109.34 ppm. The signal is shifted downfield in comparison to that of open chain (or cyclic)

TABLE II

I.R. spectral data of the newly synthesized derivatives

Compound No.	ν(P)—O—C	νP—O—(C)	Ring vibrations	νP═S	νP—S	νB—S
I	1010s	905vs	—	670vs	555m	870m
II	1015s	880vs	—	680vs	565m	890m
III	1030s	895vs	—	680vs	570m	860m
IV	1030s	895vs	—	695vs	570m	910m
V	1055vs	910vs	—	690vs	580m	890s
VI	1060vs	925s	970s	695s	630m	895s
VII	1120vs	930s	980s	695s	610m	890m

vs = very strong; s = strong; m = medium.

TABLE III

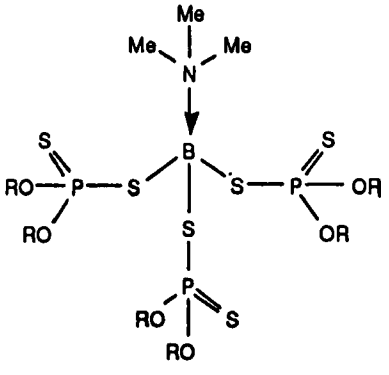
NMR (^1H, ^{11}B & ^{31}P) spectral data of newly synthesized derivatives

Compound No.	NMR chemical shift, ppm		
	^1H	^{11}B	^{31}P
I	2.66, s, 9H(NMe_3); 3.45, d, 18H(OCH_3)	11.28	105.72
II	0.91, t, 18H(CH_3); 3.51, dd, 12H(OCH_2); 2.71, s, 9H(NMe_3)	13.16	103.86
III	0.88, d, 36H(CH_3); 2.79, s, 9H(NMe_3); 3.79–4.14, m, 6H(OCH)	14.92	101.46
IV	0.94, d, 36H(CH_3) 1.69–2.10, m, 6H(CH) 2.86, s, 9H(NMe_3) 3.45, dd, 12H(OCH_2)	20.55	99.34
V	2.63, s, 9H(NMe_3); 6.86–7.25, m, 30H(OPh)	10.53	99.07
VI	1.21, s, 36H(CH_3) 2.71, s, 9H(NMe_3)	19.76	109.34
VII	1.39, s, 18H(CH_3); 2.87, s, 9H(NMe_3); 3.57, d, 12H(OCH_2), J = 14 Hz	16.23	100.26

s = singlet; d = doublet; dd = double doublet; t = triplet; m = multiplet.

dithiophosphoric acids.[11,12] This shift suggests the formation of a B—S—P linkage in this new class of boron-sulfur derivatives.

The complexes have been purified by repeated crystallization. To check the purity of the complexes chromatographic studies have been made which have supported the formation of single complex without any by-product. Due to the nonavailability of suitable crystals, the authentic structure of the complexes synthesized by us, could not be determined by X-ray crystallography. However, on the basis of above physico-chemical as well as spectroscopic studies the monodentate behaviour of dithiophosphate moiety and the four coordinated nature of boron atom have been suggested.



EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulations. Dialkyl[11] and alkylene dithiophosphoric acids[12] were prepared by the method reported earlier. Boron and sulfur were estimated by Thomas's method[13] and Messenger's method,[14] respectively. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer as KBr pellets. Multinuclear NMR spectra of these derivatives were recorded on a JEOL FX 90Q spectrophotometer in $CDCl_3$ (^1H) and C_6H_6 (^{11}B & ^{31}P) using TMS (for ^1H), $Et_2O.BF_3$ (for ^{11}B) and H_3PO_4 85% (for ^{31}P) as external references.

Reaction of Trimethylaminoborane with O,O'-Diisopropyl Dithiophosphoric acid in 1:3 Molar Ratio. Trimethylaminoborane (0.59 g, 8.12 mmole) and diisopropyl dithiophosphoric acid (5.15 g; 24.11 mmole) were dissolved in 40 ml benzene. This mixture was refluxed for ~5 hrs with constant stirring. After complete dissolution of the reactants and removal of solvent under reduced pressure, a white colored crystalline solid was obtained. It was washed 3–4 times with benzene for purification.

Yield (4.05 g, 71%). Analysis calcd. for $C_{21}H_{51}O_6P_3S_6NB$: B, 1.52; S, 27.11, found: B, 1.41, S, 27.55%.

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One of the authors (A. Chaturvedi) dedicates this article to Late Dr. G. Srivastava, Professor, Chemistry Department, Rajasthan University, Jaipur.

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