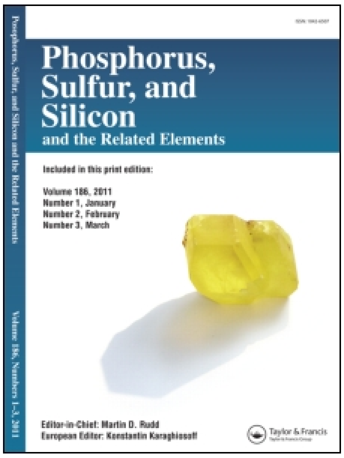

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METAL AND ORGANOMETAL COMPLEXES OF PHOSPHORUS OXY AND THIO ACIDS. PART VII. O,O'-DIALKYL(ALKYLENE) DITHIOPHOSPHATES OF BORON

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METAL AND ORGANOMETAL COMPLEXES OF PHOSPHORUS OXY AND THIO ACIDS. PART VII. O,O'-DIALKYL(ALKYLENE) DITHIOPHOSPHATES OF BORON

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2-(O,O'-Dialkyl and alkylene dithiophosphato)-1,3,2-dioxaborinanes, $\overline{OGOB}SP(S)(OR)_2$ and $OGOBSP(S)OG'O$, $G = —(CH_2)_3—, —(CH_2)_2CHMe—, —CH_2CMe_2CH_2—$; R = Et, Pr^n, Pr^i; $G' = —CHMeCHMe—, —CMe_2CMe_2—, —CMe_2CH_2CHMe—, —CH_2CMe_2CH_2—$ have been prepared as monomeric, volatile and readily hydrolyzable liquids. These have been characterized by molecular weight, IR and multinuclear (^1H, ^{11}B, ^{13}C and ^{31}P) NMR spectral data which are consistent with three coordinate boron and monodentate dithiophosphate groups. These derivatives react with organotin oxides with ready transfer of dithiophosphato moieties from boron to tin.

Key words: Boron-sulphur compounds, 2(dialkyl and alkylene dithiophosphato)-1,3,2-dioxaborinanes.

INTRODUCTION

There is considerable interest in boron-sulphur bonded compounds due to their high reactivity and possible use as synthetic intermediates for other classes of boron derivatives as well as organosulfur compounds.[1,2] The addition reactions of thioborates to unsaturated compounds (e.g., alkenes,[3] alkynes,[4] ketones,[5] aldehydes[6] and nitriles,[7] etc.) have been used to a considerable extent for the latter purpose. The work on thioborates has been confined mainly to B—S—C bonded complexes with few known examples of those containing B—S—M (M = hetero element) bonds.[8] The present paper describes the synthesis and characterization of O,O-dialkyl and alkylene dithiophosphates of boron, a new class of boron-sulphur derivatives containing a B—S—P linkage.

O,O-Dialkyl (and alkylene) dithiophosphoric acids constitute an important series of 1,1-dithio acids, the anions of which usually form 4-membered chelate rings with a large number of metals (both non-transition as well as transition) and metalloids.[9,10] The unidentate attachment of these dithio ligands is rare and has been reported only with triorganosilicon[11,12] and -tin moieties.[13,14] A survey of literature surprisingly reveals that no boron derivative of these acids has been described as yet.

RESULTS AND DISCUSSION

In spite of being strongly acidic (with pKa values of 2.65–2.67),[15] O,O-dialkyl and alkylene dithiophosphoric acids do not appear to react with boron-oxygen bonded compounds like boric acid, trialkyl borates and 2-alkoxy-1,3,2-dioxaborolanes and

TABLE I

Synthetic data and boiling points for O,O-dialkyl(alkylene) dithiophosphates of boron

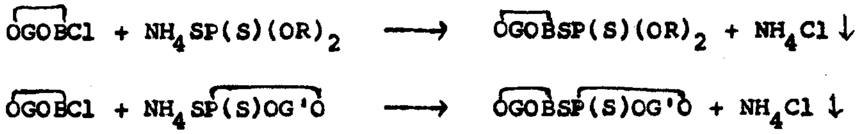
Compd. No.	Reactants (g) (mmole)		Product (g)	b.p. (°C/mm Hg)	Yield of dist. product	Analyses Found (Calcd)	
	Chloro-borinane	Ammonium dialkyl (alkylene) dithiophosphate				Boron	Sulphur
1	1.47 (12.22)	2.48 (12.22)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)P}(\text{OC}_2\text{H}_5)_2$ 1.58	50/0.5	48	4.00 (4.00)	23.14 (23.74)
2	1.69 (14.04)	3.24 (14.03)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)P}(\text{OC}_3\text{H}_7^{n})_2$ 1.98	55/0.5	47	3.58 (3.63)	21.01 (21.50)
3	1.52 (12.63)	2.92 (12.64)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)P}(\text{OC}_3\text{H}_7^{i})_2$ 1.95	42/0.9	52	3.56 (3.63)	21.02 (21.50)
4	1.19 (9.89)	1.99 (9.90)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)}\overline{\text{POCH}(\text{CH}_3)(\text{CH}_3)\text{CHO}}$ 1.30	90/0.4	49	4.05 (4.03)	23.54 (23.92)
5	1.58 (13.13)	3.01 (13.14)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)}\overline{\text{POC}(\text{CH}_3)_2(\text{CH}_3)_2\text{CO}}$ 1.66	100/1.0	43	3.54 (3.65)	21.14 (21.65)
6	1.05 (8.73)	1.99 (8.69)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)}\overline{\text{POC}(\text{CH}_3)_2\text{CH}_2(\text{CH}_3)\text{CHO}}$ 1.36	78/0.7	53	3.58 (3.65)	20.97 (21.65)
7	1.12 (9.32)	2.00 (9.30)	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{S(S)}\overline{\text{POCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}}$ 1.34	80/0.2	51	3.78 (3.83)	21.74 (22.73)
8	1.54 (11.47)	2.65 (11.47)	$\overline{\text{OCH}_2\text{CH}_2(\text{CH}_3)\text{CHOB}}\text{S(S)P}(\text{OC}_3\text{H}_7^{n})_2$ 1.86	45/0.3	52	3.38 (3.46)	20.82 (20.54)

Contd......

TABLE I (*continued*)

9	1.60 (11.91)	2.75 (11.90)	$\overparen{OCH_2CH_2(CH_3)CHO}BS(S)P(OC_3H_7^i)_2$ 1.84	40/0.4	50	3.32 (3.46)	20.33 (20.54)
10	1.42 (10.57)	2.12 (10.55)	$\overparen{OCH_2CH_2(CH_3)CHO}BS(S)P\overparen{OCH(CH_3)(CH_3)CHO}$ 1.42	50/0.3	48	3.65 (3.83)	22.10 (22.73)
11	1.20 (8.93)	2.05 (8.95)	$\overparen{OCH_2CH_2(CH_3)CHO}BS(S)P\overparen{OC(CH_3)_2CH_2(CH_3)CHO}$ 1.36	58/0.4	49	3.23 (3.48)	20.09 (20.67)
12	1.69 (12.58)	2.70 (12.56)	$\overparen{OCH_2CH_2(CH_3)CHO}BS(S)P\overparen{OCH_2C(CH_3)_2CH_2O}$ 1.73	60/0.3	47	3.48 (3.65)	21.00 (21.65)
13	1.42 (9.57)	1.94 (9.56)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P(OC_2H_5)_2$ 1.51	68/0.5	53	3.55 (3.67)	20.92 (21.50)
14	2.23 (15.04)	3.47 (15.02)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P(OC_3H_7^n)_2$ 2.41	56/0.5	49	3.26 (3.31)	19.06 (19.66)
15	2.03 (13.69)	3.16 (13.68)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P(OC_3H_7^i)_2$ 2.21	45/0.5	50	3.21 (3.31)	18.37 (19.66)
16	1.48 (9.98)	2.01 (10.00)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P\overparen{OCH(CH_3)(CH_3)CHO}$ 1.42	145/0.35	48	3.58 (3.65)	21.43 (21.65)
17	1.14 (7.69)	1.76 (7.69)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P\overparen{OC(CH_3)_2(CH_3)_2CO}$ 1.28	92/0.5	51	2.24 (3.33)	19.06 (19.78)
18	2.00 (13.49)	3.09 (13.49)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P\overparen{OC(CH_3)_2CH_2(CH_3)CHO}$ 2.21	120/0.5	91	3.25 (3.33)	19.11 (19.78)
19	1.52 (10.25)	2.20 (10.23)	$\overparen{OCH_2C(CH_3)_2CH_2O}BS(S)P\overparen{OCH_2C(CH_3)_2CH_2O}$ 1.49	120/0.3	47	3.43 (3.48)	20.12 (20.67)

-borinanes. This is due to the well established higher affinity of boron for oxygen than for sulphur.[1,2] The ammonium salts of these acids, however, react readily with 2-chloro-1,3,2-dioxaborinanes in refluxing benzene to yield the corresponding 2-(dialkyl and alkylene dithiophosphato)-1,3,2-dioxaborinanes:



$$\overline{OGOB}Cl + NH_4SP(S)(OR)_2 \longrightarrow \overline{OGOB}SP(S)(OR)_2 + NH_4Cl\downarrow$$

$$\overline{OGOB}Cl + NH_4S\overline{P(S)OG'O} \longrightarrow \overline{OGOB}S\overline{P(S)OG'O} + NH_4Cl\downarrow$$

$G = -(CH_2)_3-$, $R = Et$ (compound 1), Pr^n(2) , Pr^i(3) ,
$G' = -CHMe.CHMe-$(4) , $-CMe_2.CMe_2-$ (5) ,
$-CMe_2.CH_2.CHMe-$(6) , $-CH_2.CMe_2.CH_2-$ (7) ,

$G = -CH_2CH_2CHMe-$, $R = Pr^n$ (8) , Pr^i (9) ,
$G' = -CHMe.CHMe-$(10) , $-CMe_2.CH_2.CHMe-$(11) ,
$-CH_2.CMe_2.CH_2-$ (12).

$G = -CH_2CMe_2CH_2-$, $R = Et$ (13) , Pr^n (14) , Pr^i (15) ,
$G' = -CHMe.CHMe-$(16) , $-CMe_2.CMe_2-$ (17) ,
$-CMe_2.CH_2.CHMe-$(18) , $-CH_2.CMe_2.CH_2-$ (19).

All these derivatives are volatile, viscous liquids, miscible with common organic solvents and susceptible to atmospheric moisture.

IR SPECTRA

The IR spectra of these compounds have been recorded in the range of 4000–200 cm^{-1} as neat liquids (Table II).

The band positions for υ (P)—O—C and υ (B)—O—C in the range of 1155–1030 cm^{-1} in these derivatives are in accordance with those reported for parent acids[15,16] and chloroborinanes.[17] No significant shift has been observed in the band at 790–663 cm^{-1} assigned to υ P=S which is indicative of a free thiophosphoryl group. The bands in the regions 678–655 cm^{-1} and 692–590 cm^{-1} may be ascribed to υ P—S vibrations in dialkyl and alkylene dithiophosphato derivatives, respectively. The medium intensity band in the region 932–856 cm^{-1} is probably due to υ B—S.[17]

TABLE II

Some relevant IR spectral data for O,O-dialkyl(alkylene) dithiophosphates of boron (in cm^{-1})

Compd. No.	ν B-O	ν (P)-O-C & ν (B)-O-C	ν P=S	ν P-S	ν B-S
1	1330,s	1140,sbr	790,m 766,m	662,s	860,m
2	1340,s	1052,s	768,s	668,s	865,s
3	1330,s	1113,s	758,s	655,s	894,s
4	1310,s	1039,s	780,s 755,s	692,m	890,m
5	-	1137,s	705,s 662,s	602,s	857,s
6	-	1070,s	790,s 765,s	668,m	885,w
7	-	1137,sbr	780,s 764,s	667,s	932,s
8	-	1052,s	743,m	664,s	880,w
9	1325,s	1115,s	760,s	655,s	891,s
10	1325,s	1055,s	700,s	605,s	885,s
11	1320,s	1144,sbr	668,s 663,s	592,s	882,s
12	1330,s	1126,s	663,s	605,m 592m	890w,

Contd..

TABLE II (*continued*)

13	1340,s	1140,s	675,m	678,s	902,s
14	-	1142,s	746,w	670,s	915,w
15	1330,s	1112,s	765,s	658,s	894,s
16	-	1044,s	683,s	590,s	872,s
17	1340,s	1129,s	695,s 663,m	605,s	860,m
18	1340,s	1140,sbr	628,s	602,s	891,m
19	1340,s	1150,s	725,s	690,m 670,w	856,w

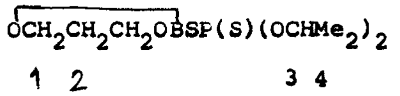
^1H NMR SPECTRA

The ^1H NMR spectra of these compounds (Table III) do not give much information regarding the coordination state of boron (or the denticity of dithiophosphato moieties) mainly due to (a) the large distance between the protons and the B—S linkage, and (b) excessive overlapping of the signals of the dithiophosphate and borinane moieties (particularly in compounds 8–12). Thus, the spectra in general show close resemblance with those of the starting moieties and the chemical shifts, and peak areas are consistent with the structure.

In the derivatives 1–7, the borinane moiety gives a triplet at ~ 3.95 and a quartet at 2.11–1.57 ppm for the two types of methylene protons present whereas in derivatives 13–19, the borinane moiety shows two singlets at ~ 0.95 and ~ 3.56 ppm for the methyl and methylene protons respectively. The protons attached to α-carbon atoms (OCH_n) of the dithiophosphato moieties show coupling with the phosphorus atom with $^3J(^1H-^{31}P)$ values of ~ 12 Hz and these signals usually overlap with those of the corresponding OCH_n protons of the borinane moieties except in derivatives 3, 7, 15 and 19. The spectra of tetramethylethylene dithiophosphates (5 and 17) are expectedly the simplest ones (with only three signals in each) and show only one signal for all four methyls as in the parent acid.[15]

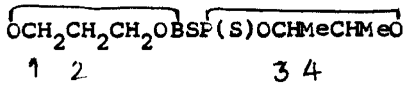
^{13}C NMR SPECTRA

The ^{13}C NMR spectra of two representative compounds 3 and 4 (one acyclic and the other cyclic dithiophosphate) recorded in CCl_4 show the following chemical shifts (in δ ppm):



$\underset{1}{O}\underset{2}{CH_2}CH_2CH_2OBSP(S)(O\underset{3}{C}H\underset{4}{Me_2})_2$

C^1, 62.02; C^2, 24.43,
C^3, 72.67; $^2J(^{13}C-^{31}P)=6.11$ Hz
C^4, 23.51



$\underset{1}{O}\underset{2}{CH_2}CH_2CH_2OBSP(S)O\underset{3}{C}H\underset{4}{Me}CHMeO$

C^1, 62.24; C^2, 20.69;
C^3, 78.98; $^2J(^{13}C-^{31}P)=4.88$ Hz
C^4, 17.44

The above chemical shifts are very close to those obtained for the parent compounds (2-chloro-1,3,2-dioxaborinane and dithiophosphoric acids) and indicate no substantial change in structural features.

^{31}P NMR SPECTRA

The ^{31}P NMR shifts obtained in CCl_4 (Table III) are in the range of 82.76–86.52 ppm for dialkyl dithiophosphates, 91.1–94.6 ppm for cyclic dithiophosphates con-

TABLE III

^1H, ^{11}B and ^{31}P chemical shifts for O,O-dialkyl(alkylene) dithiophosphates of boron in (δ ppm)

Compd. No.	^{11}B NMR (in CCl_4)	^{31}P NMR (in CCl_4)	^1H NMR (in $CDCl_3$)
1	19.36	85.82	1.41,t(6H,CH_3) J = 8.0 Hz 2.07-1.67,m (2H, CH_2) 4.46-3.40,m (8H, OCH_2)
2	19.87	86.43	0.99,t(6H, CH_3) J = 8.0 Hz; 2.05-1.21,m(6H, CH_2) 4.25-3.23,m(8H, OCH_2)
3	19.36	82.76	1.37,d(12H, CH_3) J = 6.0 Hz; 2.11-1.72,m(2H, CH_2) 3.95,t(4H, OCH_2) J = 5.6 Hz; 5.10-4.58,m(2H, OCH)
4	21.57	94.14	1.67-1.11,m(8H, CH_3 & CH_2) 4.17-3.70,m(6H, OCH_2 & OCH)
5	21.21	91.20	1.40,s(12H, CH_3) 2.11-1.57m(2H, CH_2) 3.95,t(4H,OCH_2)
6	18.17	73.31	-
7	18.34	76.72	0.88,s(6H, CH_3); 2.02-1.57,m(2H, CH_2) 3.49,t(4H, $BOCH_2$) J = 5.8 Hz 3.83,d(4H, $POCH_2$) J = 7.0 Hz

Contd..

TABLE III (*continued*)

8	19.53	86.52	-
9	19.70	82.85	-
10	19.10	94.57	-
11	19.36	73.31	-
12	19.36	-	-
13	19.28	86.08	0.97,s(6H, $C(CH_3)_2$); 1.28,t(6H, CH_2-CH_3) 3.56,s(4H, $BOCH_2$); 3.94-3.46,dq(4H, $POCH_2$)
14	19.85	86.43	-
15	19.24	82.85	0.92,s(6H, $C(CH_3)_2$); 1.34,d(6H, $CH(CH_3)_2$)J = 6.1Hz 3.56,s(4H, $BOCH_2$) ; 5.02-4.89,q(2H, OCH)
16	18.71	94.62	-
17	19.06	91.16	0.99,s(6H, $C(CH_3)_2$ 1.44,s(12H, $POC(CH_3)_2$) 3.61,s(4H, OCH_2)
18	19.32	73.39	-
19	19.98	76.63	0.95,s(6H, $C(CH_3)_2$) 1.04,s(6H, $POCH_2C(CH_3)_2$) 3.63,s(4H, $BOCH_2$) 3.86,d(4H, $POCH_2$) J = 7.2Hz

taining 5-membered dioxaphospholane ring and 73.3–76.7 ppm for cyclic dithiophosphates containing 6-membered dioxaphosphorinane ring. Thus, the shift increases in the order: 6-membered ring < open chain < 5-membered ring, and are indicative of the effect of the bond angles around phosphorus.[18] The positions of ^{31}P signals show no appreciable change as compared to the corresponding free acids, thus suggesting the monodentate nature of the dithiophosphato moieties in these complexes.[19]

^{11}B NMR SPECTRA

The most useful information regarding the structure of these dithiophosphato derivatives of boron is obtained from their ^{11}B NMR spectra. The observed chemical shifts of all these compounds are in the narrow range of 19 ± 1 ppm (Table III) which is consistent with the presence of three coordinate boron.[20] The following interesting observations may, however, be noted:

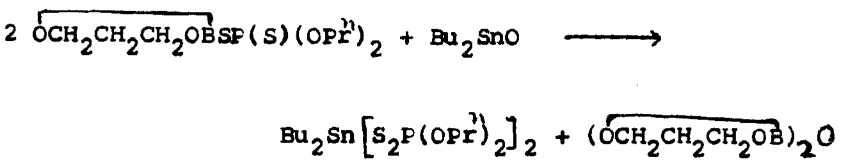
(1) These chemical shifts are slightly upfield in comparison to the corresponding 2-chloro-1,3,2-dioxaborinanes which is understandable in view of the higher electronegativity of chlorine. However, the observed values are in the same range as those for 2-alkoxy-1,3,2-dioxaborinanes or oxybis(1,3,2-dioxaborinanes).[20] This indicates that the extent of shielding of tricoordinate boron due to the back-bonding from three oxygens is almost same as that from two oxygens and one sulphur which is rather surprising. However, it may be pointed out that the reported chemical shifts of $(o\text{-}C_6H_4O_2B)_2S$ and $(o\text{-}C_6H_4O_2)BOEt$ are 22.1 and 23.0 ppm[21,22] indicating a similar pattern as our observations.

(2) The ^{11}B signals in some 2-(dialkyl dithiophosphato)-1,3,2-dioxaborinanes are sharp and narrow (particularly in open chain dithiophosphato derivatives) whereas in others, these are broad. The reason for this is not clear.

(3) In none of these derivatives, was ^{11}B—S—^{31}P coupling observed in the ^{11}B or ^{31}P NMR spectra.

On the basis of the above spectroscopic data it may be concluded that 2-(dialkyl and alkylene dithiophosphato)-1,3,2-dioxaborinanes possess tricoordinate boron and are additional examples of complexes containing the rare unidentate dithiophosphato moieties. Thus, structurally these compounds are similar to the 2-alkanethiolato-1,3,2-dioxaborolanes described earlier.[23]

The dithiophosphate group attached to boron may be readily transferred to tin as demonstrated by the reaction of 2-(dipropyl dithiophosphato)-1,3,2-dioxaborinane with dibutyltin oxide in a 2:1 molar ratio to yield the corresponding dibutyltin bis(dithiophosphate):



$$2\ \overline{\mathrm{OCH_2CH_2CH_2OB}}\mathrm{SP(S)(OPr^n)_2} + \mathrm{Bu_2SnO} \longrightarrow \mathrm{Bu_2Sn[S_2P(OPr^n)_2]_2} + (\overline{\mathrm{OCH_2CH_2CH_2OB}})_2\mathrm{O}$$

The products were not separated. However, the mixture showed a ^{119}Sn chemical shift of -184.7 ppm and ^{31}P shift of 94 ppm. These values are the same as observed for an authentic sample of dibutyltin bis(di-n-propyl dithiophosphate).[24]

EXPERIMENTAL

Moisture was carefully excluded throughout experimental manipulations. Dialkyl[25] and alkylene[15] dithiophosphoric acids and their ammonium salts were prepared by the methods reported earlier. 2-Chloro-1,3,2-dioxaborinanes have been prepared by the reactions of phosphorus pentachloride with different pyroborates.[26]

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer as neat liquids. Multinuclear NMR spectra of these complexes were recorded on JEOL FX 90Q spectrometer in $CDCl_3$(^1H) and in CCl_4(^{11}B, ^{13}C and ^{31}P) using TMS as an internal reference in case of ^1H and ^{13}C, $Et_2O.BF_3$ in case of ^{11}B and H_3PO_4 (85%) in case of ^{31}P.

Synthesis of 2-dialkyl (and alkylene) dithiophosphato-1,3,2-dioxaborinanes. These were prepared by the reactions of ammonium dialkyl (and alkylene) dithiophosphates with 2-chloro-1,3,2-dioxaborinanes in a 1:1 molar ratio in refluxing benzene.

Since the same method was used for the synthesis of all these derivatives, the preparation of one representative compound is described in detail and the results of the remaining experiments have been summarized in Table I.

To a solution of $OCH_2CH_2CH_2OBCl$ (1.47 g, 12.2 mmole) in benzene was added $(C_2H_5O)_2P(S)SNH_4$ (2.48g, 12.2 mmole) and the mixture was refluxed for ~ 3 hr. The precipitated NH_4Cl (0.63 g, calcd. 0.65 g) was filtered off under a blanket of dry nitrogen. The solvent was removed from the filtrate under reduced pressure and the resulting crude product was distilled to give 2-(diethyldithiophosphato)-1,3,2-dioxaborinane as a colourless liquid, b.p. 50°/0.5 mm (1.58 g, 48%).

Reaction of 2-(di-n-propyldithiophosphato)-1,3,2-dioxaborinane with Bu_2SnO in 2:1 molar ratio. Dibutyltin oxide (0.61 g, 2.45 mmole) was added to a solution of $\overline{OCH_2CH_2CH_2OB}$ $S(S)P(OC_3H_7^n)_2$ (1.47 g, 4.93 mmole) in 40 ml benzene. The contents were refluxed till complete dissolution of Bu_2SnO (~ 4 hr). The product formed was studied by ^{31}P and ^{119}Sn NMR spectroscopy in benzene solution without removing the solvent.

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