J. Iranian Chem. Res.
5 (4) (**2012**) 223-229
ISSN 2008-1030

Synthesis and characterization of some antifungal O-alkyl (O-aryl) trithiophosphato derivatives of 1,3,2-dioxaborinanes

Mukesh Chand Gupta, Kiran Sankhala, Alok Chaturvedi *

Synthetic and Surface Science Laboratory, Dept. of Chemistry, Govt. College, Ajmer (Raj.), India
* *E-mail: alok_chat.ajm@rediffmail.com*

Received 06 January 2012
Received in revised form 06 September 2012
Accepted 08 September 2012

Complexes of the type $\overline{(OCH_2C(CH_3)_2CH_2O}B)_2S_2P(S)OR$ (where $R=Me,Et,Pr^i,Bu^i,Ph,CH_2Ph$) have been synthesized by the reactions of 2-chloro-1,3,2-dioxaborinanes and potassium salt of O-alkyl (O-aryl) trithiophosphates in 2:1 molar ratio in refluxing benzene. The product are formed as white or light yellow coloured monomeric solid, soluble in common organic solvents and exhibit high sensitivity towards atmospheric moisture. These complexes have been characterized by elemental analysis (C,H,S,B), molecular weight measurement, IR and NMR (^1H,^{11}B,^{31}P) spectral studies. On the basis of above studies it is postulated that boron is in three coordinated state. The newly synthesized complexes show effectiveness against powdery mildew disease at a fixed interval of days.

Keywords: 2-chloro-1,3,2-dioxaborinanes; O-alkyl(O-aryl)trithiophosphates (1H,11B,31P)spectral studies; Antifungal activity

1. INTRODUCTION

The development of organoboron chemistry during the last two decades indicates that synthesis and applications of organoboranes and borates in organic synthesis continue to be persued actively and represents a fruitful area [1,2].

The reactivity of boron as an electrophilic centre in a variety of 1,3-dioxa-2-borins has been studied[3]. It has been reported that 1,3,2-dioxaborolanes and borinanes behave in the same way as trialkoxyboranes[4-7]. On the other hand 2-alkoxy-1,3,2-banzodioxaborolanes,–borols, -borinanes and -borines are very reactive and tend to form four coordinated derivatives with a variety of bidentate oximes and β-diketonates[8-9].

Potassium salt of O-alkyl trithiophosphates $[(RO)P(S)(SK)_2]$ show the tendency of isomerization and there exist an equilibrium between >P=S and >P=O which can show interesting chemical bonding modes in metal and organometal derivatives[10-11]. Boron compounds have been extensively studied as soluble additives in lubricating oils, as solid lubricants and as surface coatings [12-15]. Oil soluble organoboron compounds are promising friction modifiers, corrosion inhibitors, antioxidants and effective antiwear additives [16-21].

In continuation to our earlier investigations[22,23] trithiophosphato derivatives of tin, it was considered worthwhile to synthesis O-alkyl trithiphosphato derivative of 1,3,2-dioxaborinane and show their effectiveness against powdery mildew disease at a fixed interval of days.

2. EXPERIMENTAL

2.1. Reagents and Solution

Moisture was carefully excluded throughout the experimental manipulations. Dipotassium salt of O-alkyltrithiophosphate were prepared by the method reported earlier. All the solvents and reagents used during present investigation were of reagent grade and even made anhydrous by standard methods. 2-Isopropoxy-4H-1,3,2-benzodioxaborin was prepared by the method reported earlier in the literature[24] Boron and sulfur were estimated by Thomas's method[25] and Messenger's method[25], respectively.

2.2. Apparatus

A Knauer – vapour pressure osmometer in chloroform was used for molecular weight determination. FT-IR spectra were recorded on Shimadzu 8201 PC spectrophotometer in the range 4000-400cm^{-1} using CsI cells.

^{1}H and ^{11}B NMR spectra were recorded in $CDCl_3$ and ^{31}P NMR spectra were recorded in benzene. NMR spectra were recorded on Bruker DRX 300 spectrophotometer using TMS (for ^{1}H) $Et_2O.BF_3$ (for ^{11}B) and H_3PO_4 85% (for ^{31}P) as external references.

2.3. Synthesis of 2-(O-methyltrithiophosphato) bis- (1,3,2-dioxaborinanes*)*

A mixture of 2-chloro-1,3,2-dioxaborinanes (0.9125g; 6.16mmol) and potassium-O-methyl trithiophosphate (0.7307g; 3.09mmol) in dry and distilled benzene (~40ml) was refluxed for 4 hours. Potassium chloride was precipitated. It was removed by filteration on removing the solvent under reduced pressure. A white or light yellow crystalline solid was obtained which was washed 3-4 times with n-hexane and recrystallized it by method of recrystalization [Table -1].

Yield (0.9617g; 81.1%).

Analysis found % $[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OMe$ C=34.08, B=5.42, H=5.72, S=24.82

calcd. $[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OMe$ C=37.37, B=5.74, H=5.98, S=25.06

Rest derivatives were synthesized by similar method.

Table 1. Synthetic and analytical data of 2-[O-alkyl (O-aryl) trithiophosphato]bis[1,3,2 dioxaborinanes].

S.No.	Reactants g(mmol)		Product		Analyses (%) Found (Calcd.)			
			----g	-----%	**C**	**B**	**H**	**S**
1	$OCH_2C(CH_3)_2CH_2OBCl$	K_2S_3POMe	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OMe$		34.08	5.42	5.72	24.82
	0.9125(6.16)	0.7307(3.09)	0.9617	81.1	(37.37)	(5.74)	(5.98)	(25.06)
2	$OCH_2C(CH_3)_2CH_2OBCl$	K_2S_3POEt	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OEt$		36.02	5.29	6.14	23.84
	0.8825(5.96)	0.7450(2.98)	0.9739	82.1	(36.18)	(5.52)	(6.28)	(24.12)
3	$OCH_2C(CH_3)_2CH_2OBCl$	$K_2S_3OPr^i$	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPr^i$		37.53	4.20	6.18	20.10
	0.8823(5.96)	0.8882(2.98)	1.2337	80.4	(37.86)	(4.94)	(6.55)	(21.57)
4	$OCH_2C(CH_3)_2CH_2OBCl$	$K_2S_3POBu^i$	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OBu^i$		39.40	5.02	6.68	23.00
	0.8823(5.96)	0.7586(2.87)	0.9625	81.4	(39.43)	(5.35)	(6.80)	(23.35)
5	$OCH_2C(CH_3)_2CH_2OBCl$	K_2S_3POPh	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPh$		42.87	4.82	5.38	21.34
	0.8823(5.96)	0.7555(2.71)	0.9225	79.8	(43.04)	(5.17)	(5.60)	(22.58)
6	$OCH_2C(CH_3)_2CH_2OBCl$	$K_2S_3POCH_2Ph$	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OCH_2Ph$		44.12	4.54	5.42	20.58
	0.8618(5.82)	0.9048(2.90)	1.2092	85.1	(44.34)	(4.78)	(5.65)	(25.86)

3. RESULTS AND DISCUSSION

Dipotassium salt of O-alkyl (O-aryl) trithiophosphates have been synthesized by dropwise addition of mixture of triethylamine and appropriate alcohol to a suspension of phosphorus pentasulphide in benzene. A solution of KOH in methanol was them added to a separated upper layer of the above solution.

$$P_2S_5 + 3ROH + 3Et_3N \longrightarrow ROPS_3K_2$$

$(R=Me,Et,Pr^i,Bu^i,Ph,CH_2Ph)$

Reaction of dipotassium salt of O-alkyl (O-aryl) trithiophosphate with 2-chloro-1,3,2-dioxaborinanes in 1:2 molar ratio have been carried out in refluxing dry and distilled benzene.

$$OCH_2C(CH_3)_2CH_2OBCl + K_2S_2P(S)\ OR \xrightarrow{\text{dry } C_6H_6} [OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OR+2KCl$$

$(R=Me,Et,Pr^i,Bu^i,Ph, CH_2Ph)$

The products, from the above reactions are obtained as white or light yellow crystalline solids after filtering off the precipitate potassium chloride and removing the solvent in vacuum. The newly formed compounds have been purified by washing them 3-4 times with n-hexane and recrystallized them. These complexes are soluble in common organic solvents like benzene, toluene, chloroform and are readily hydrolysed by atmospheric moisture.

3.1. IR spectra

Assignment of some important IR spectral frequencies of 2-[O-alkyl(O-aryl) trithiophosphato] bis-[1,3,2-dioxaborinanes] are listed in Table-2. A medium intensity band is observed in the region 1328-1307 cm^{-1} which is assigned to νB-O vibrations. The bands due to ν(P)-O-C and νP-O-(C) vibrations are present in the region 1028-1010cm^{-1} and 825-812 cm^{-1}, respectively. The absorption band for ν(P=S) is found in the region 700-682 cm^{-1}. The absorption bands in the region 552-545 cm^{-1} may be attributed to ν(P-S) vibrations. The appearance of a new medium intensity absorption band in the region 899-890 cm^{-1} is assigned to νB-S band suggesting the chelation of trithio ligands with boron atom.

Table 2. IR spectral data of 2-[O-alkyl(O-aryl) trithiophosphato] bis-[1,3,2-dioxaborinanes]

S.No.	Compound	ν(B-O)	ν(P)-O-C	νP O-(C)	ν(B-S)	ν(P=S)	ν(P-S)
1	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OMe$	1307s	1010s	820s	893m	700s	545s
2	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OEt$	1309s	1012s	816s	899m	698s	546s
3	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OPr^i$	1310s	1016s	812ms	895m	682s	548s
4	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OBu^i$	1315m	1020s	818m	898s	690s	552s
5	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OPh$	1324m	1028s	825m	890m	695m	550m
6	$[\overline{OCH_2C(CH_3)_2CH_2OB}]_2S_2P(S)OCH_2Ph$	1328m	1026s	821m	894m	698m	552m

3.2. ^1H NMR spectra

^1H NMR spectra of these derivatives have been recorded in $CDCl_3$ and spectral data are listed in Table-3.

In the NMR spectrum of $(\overline{OCH_2C(CH_3)_2CH_2OB})_2\ S_2P(S)OCH_3$, two singlets are observed at δ1.10 and δ3.80ppm for CH_3 and OCH_2 protons of glycolate moiety, respectively. A doublet is observed at δ3.64ppm for OCH_3 protons of ligand moiety.

3.3. ^{11}B NMR spectra

^{11}B NMR spectra of the newly synthesized compounds have been recorded in $CDCl_3$, It shows a sharp singlet at δ18.42 to δ19.16ppm and provide a convincing evidence for the chelation of boron to sulphur as well as purity of these derivatives and suggests three coordinated nature of boron atom [Table - 4].

3.4. ^{31}P NMR spectra

^{31}P NMR spectra of these derivatives have been scanned in $CHCl_3$ and the spectral data are summarized in [Table-4].

The ^{31}P NMR spectra of 2-[O-alkyl (O-aryl) trithiophato] bis-[1,3,2-dioxaborinanes) show only one resonance signal for each complex in the region δ82.45-94.38ppm. The chemical shift values are shifted to downfield (δ11-22ppm) as compared to parent trithiophosphates (^{31}P=δ71.21-72.55ppm).

Table 3. ^{1}H NMR spectral data of 2-[O-Alkyl(O-aryl) trithiophosphato]bis[1,3,2-dioxaborinanes]

S.No.	Compound	Chemical Shift (δppm)
1	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OMe$	1.10s, 12H(CH_3); 3.80s, 8H(OCH_2); 3.64d, 3H(OCH_3).
2	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OEt$	1.12,s,12H(CH_3),0.96,t,3H(CH_3), 3.47,s,8H(OCH_2), 2.47,q,2H(CH_2)
3	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPr^i$	0.80d,6H(CH_3); 1.12s,12H(CH_3); 3.74s,8H(OCH_2);4.72-4.88m, 1H(OCH)
4	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OBu^i$	0.85d,6H(CH_3);1.10s,12H(CH_3);2.10m,1H(CH);3.64s,8H(CH_3); 3.72-3.86,m(OCH_2).
5	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPh$	1.10s,12H(CH_3); 3.80s, 8H(CH_3);6.90-7.30m, 5H(C_6H_5)
6	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OCH_2Ph$	1.05,s,12H(CH_3);3.86s8H(OCH_2);3.46,s,2H(OCH_2)7.32-7.85,m,54(C_6H_5)

Table 4. ^{31}P NMR spectral data of 2-[O-alkyl(O-aryl) trithiophosphato] bis-[1,3,2-dioxaborinanes]**.**

S.No.	Compound	Chemical Shift (δppm)	
		^{11}B NMR	^{31}P NMR
1	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OMe$	19.16	94.38
2	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OEt$	19.06	90.56
3	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPr^i$	19.12	82.45
4	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OBu^i$	18.82	86.14
5	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OPh$	18.42	86.14
6	$[OCH_2C(CH_3)_2CH_2OB]_2S_2P(S)OCH_2Ph$	18.68	88.24

3.5 Antifungal studies

It is observed that when O-alkyltrithiophosphates derivates of 1,3,2-dioxaborinanes are applied in the form of dilute solution to various concentrations, they show their effectiveness against powdery mildew disease at a fixed interval of days.

Antifungal activity of newly synthesized complexes has been carried out with the powdery mildew of roses. Percent disease intensity (PDI) was recorded by modifying the coyier rating scale[26] and it (PDI) was calculate using following formula:

$$\text{PDI} = \frac{\text{Sum of all rating x 100}}{\text{Total number of observations x Maximum class rating}}$$

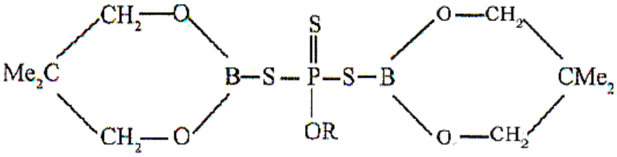
All these compounds indicates their potency against *Sphaerotheca pannosa var. rosae* at different concentrations (Table – 5). The rose plants were severely infected by powdery mildew disease, when the first foiler spray was carried out. Remarkable results were observed after seventh day of first spray. The intensity of powdery mildew disease decreases. Second spray was done after seventh day of first spray. After 15 day and after 21st day of first spray observation were again made. The 21st day resulted in a very small change in PDI values in comparison to previous spray.

Table 5. Effect of newly synthesized complexes on powdery mildew disease of roses caused by *Sphaeotheca pannosa* pathogens on different concentrations

	Percent Disease Intensity (PDI)				
Conc.(%)	During I Spray	After 7th Day During II spray	After 15 Days	After 21 Day During III spray	After 28 Days
0.5000	100	86	72	53	29
0.2500	100	80	71	51	24
0.1250	100	66	56	43	19
0.0625	100	61	54	45	18
0.0312	100	58	46	37	14
0.0156	100	53	43	37	13
0.0078	100	44	38	27	12

4. CONCLUSION

On the basis of above IR and NMR (^{1}H, ^{11}B, ^{31}P) studies following structure may be proposed for the newly synthesized complexes.



(R=Me,Et,Pr^i,Bu^i,Ph,CH$_2$Ph)

Boron is in tricoordinated state. Derivatives show antifungal activity against powdery mildew disease.

ACKNOWLEDGMENT

Authors Mukesh Chand Gupta and Kiran Sankhala (S.R.F) are thankful to C.S.I.R. New Delhi for financial assistance and also thankful to S.A.I.F. (C.D.R.I.), Lucknow for spectral analysis.

REFERENCES

[1] O.P.Singh, A.Chaturvedi, D.B. Saxena, R.K. Mehrotra, G.Srivastava, Monatshafte fur Chemie, 125 (1994) 607-613.
[2] A. Chaturvedi, P.N. Nagar, G.Srivastava, Phosphorus Sulfur and Silicon, 90 (1994) 229-233.
[3] G.E.Mc Achran, S.G. Shore, Inorg. Chem, 5 (1966) 2044-2049.
[4] S.K.Mehrotra, G. Srivastava, R.C. Mehrotra, Synth. React Inorg. Met. Org-Chem, 4 (1974) 27-36.
[5] P.N.Bhardwaj, G. Srivastava, J. Indian Chem. Soc. 59 (1982) 300-307.
[6] P.N. Nagar, G. Srivastava, R.C. Mehrotra, Synth. React. Inorg. Met-Org. Chem., 12 (1982) 749-759.
[7] O.P. Singh, R.K. Mehrotra, G. Srivastava, Synth. React. Inorg. Met Org. Chem., 21 (1991) 717-728.
[8] A.S. Kothiwal, A. Singh, A.K. Rai, R.C. Mehrotra, Ind. J. Chem. 24 (1985) 828-834.
[9] Y.P. Singh, P. Rupani, A. Singh, A.K. Rai, R.D. Rogers, J.L. Atwood, Inorg. Chem., 25 (1985) 3076-3081.
[10] A. Chaturvedi, C.S. Sharma, P.N. Nagar, Phosphorus sulfur and Silicon, 178 (2003) 1923-1929.
[11] L. Chordia, A. Chaturvedi, Phosphorus, Sulfur and Silicon, 182 (2007) 2821-2831.
[12] Y. Kimuva, T. Wakabayashi, K. Okada, T. Wada, H. Nishikawa, Wear, 232 (1999) 199-206.
[13] M. Lovell, C.F. Higgs, P. Deshmukh, A.J. Mobleymat, Pro. Teeh, 177 (2006) 87-90.
[14] C.C. Klepper, J.M. Williams, J.J.J. Truhan, J. Qu, L. Riestev, R.C. Hazelton, J.J. Moshchella, P.J. Blau, J.P. Anderson, O.O. Popooia, M.D. Keitz, Thin Solid films, 516 (2008) 3070-3080.
[15] J.H.Wu, B.S.Phillips, W.Jiang, J.H.Sanders, J.S. Zabinsk, A.P. Malshe, Wear 261 (2006) 592-599.
[16] B.A. Baldwin, Wear, 45 (1977) 345-353.
[17] Z.S. Hu, Y. Yie, L.G. Wang, G.X. Chen, J.X. Dong, Tribol. Lett. 8 (2000) 45-50.
[18] W. Liu, Z. Jin, Q. Xue, Lubricat. Sci.7 (1994) 49-60.
[19] J.M. Herdan, Lubricat Sci. 2 (2000) 265-276.
[20] W. Liu, Q. Xue, X. Zhang, H. Wang, C. Huang, Tribol. Trans. 48 (1992) 475-479.
[21] G. Shen, Z. Zheng, Y. Wan, X. Xu, L. Cao, Q. Yue, T. Sun, A. Liu, Wear, 246 (2000) 55-58.
[22] L. Chordia, A. Chaturvedi, Main group Met. Chem. 31 (2008) 319-329.
[23] L. Chordia, A. Chaturvedi, J. Chin. Chem. Soc. 56 (2009) 636-641.
[24] P.N. Bhardwaj, G. Srivastava, Bull. Chem. Soc. Japan 51 (1978) 524-531.
[25] A.I. Vogel. A Textbook of Qualitative Inorganic Analysis ELBS, IV Edition 1973.
[26] A.K.Sobti, A.K. Mathur, B.S. Siradhana, India Phytopathology 45 (1992) 200-208.