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Boron Derivatives of Dithiophosphoric Acids

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ABSTRACT: *The reactions of tetraphosphorus decasulfide* **1** *with trialkyl borates* **2a,b** *and O-isobutyl diphenylborate* **2c** *were studied. On the basis of these studies, a novel method of synthesizing S-boron derivatives of dithiophosphoric acids was developed. The use of low frequency ultrasonic irradiation (22 kHz, power 130 W) leads to a reduction in reaction temperature and time required for completion of the reactions studied.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:102–106, 2000

INTRODUCTION

There is considerable interest in compounds containing the P(S)SB structural fragment [1–7] due to their potential biological activity and similarly in other boron derivatives of pentavalent phosphorus [6], because of their high reactivity [1,4,6] and their use as synthetic intermediates in the preparation of other new classes of organothiophosphorus compounds [4,6]. Boron dithiophosphates containing the P(S)SB linkage have recently been studied. 2-(*O,O′*-Dialkyl and alkylene dithiophosphato)-1,3,2-dioxaborinanes have been prepared by the reactions of the corresponding dithiophosphoric acids or their ammonium salts with 2-chloro-1,3,2-dioxaborinanes or with trimethylaminoboranes [1,2]. *O*-Ethyl-*S,S′*-bis(*o*-carborane-9-yl)dithiophosphate, -trithiophosphate, and -diphenyldithiophosphinate have also been obtained by addition of elemental sulfur to the corresponding (*o*-carborane-9-yl)thiophosphite, -dithiophosphite, and -diphenyldithiophosphinite, respectively [3–7]. In this article, an alternative and efficient method is presented for the synthesis of S-boron derivatives of dithiophosphoric acids directly from phosphorus sulfide (P_4S_{10}).

RESULTS AND DISCUSSION

It should be noted that tetraphosphorus decasulfide (P_4S_{10}) is known to react with trialkyl borates in equimolar ratio under severe conditions (170–190°C, with exothermic temperature enhancement 250–270°C) with the formation of trialkyl tetrathiophosphates [8,9]. We have assumed that these tetrathiophosphates [8,9] are secondary products and may be formed via the destruction of some initial products containing labile B-S and B-O bonds at high temperatures. It is of interest to study the structures of these initial products in the reactions of P_4S_{10} with borates. Moreover, we have previously found that tetraphosphorus decasulfide reacts with alkoxides and alkylmercaptides of triorganylsilanes, -germanes, -stannanes, and -dialkylarsenites to form *S*-silyl, germyl, stannyl, and arsenic(III) esters, respectively, of dithiophosphoric and tetrathiophosphoric acids [10–13]. The formation of products of similar structure could be expected by the use of boron derivatives containing the B-O bond. In fact, the reactions of phosphorus sulfide **1** with trialkyl borates **2a,b** and *O*-isobutyl diphenylborate **2c** have been found to bring about the formation of S-(*O,O′*-diisobutyl)boron and *S*-diphenylboron *O,O′*-diisobutyldi-

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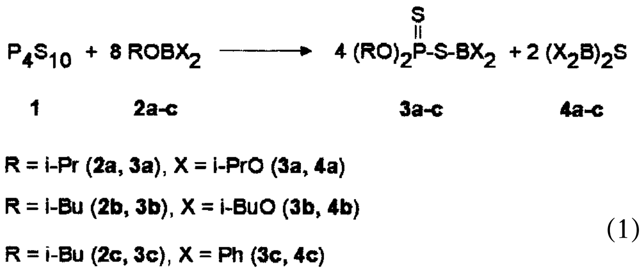
thiophosphates **3b** and **3c**, respectively (Reaction 1, Tables 1–5).



$$P_4S_{10} + 8\,ROBX_2 \longrightarrow 4\,(RO)_2\overset{S}{\overset{\|}{P}}\text{-S-}BX_2 + 2\,(X_2B)_2S$$

1 **2a-c** **3a-c** **4a-c**

R = i-Pr (**2a**, **3a**), X = i-PrO (**3a**, **4a**)

R = i-Bu (**2b**, **3b**), X = i-BuO (**3b**, **4b**)

R = i-Bu (**2c**, **3c**), X = Ph (**3c**, **4c**)

(1)

However, we have unexpectedly encountered difficulties owing to the low reactivity of the B-O bonds of borates. The reaction of phosphorus sulfide **1** with triisobutyl borate **2b** and *O*-isobutyl diphenylborate **2c** proceeds only at 150°C (2–3 hours). Reaction of **1** with triisobutyl borate **2b** proceeds with no solvent. Reaction of **1** with *O*-isobutyl diphenylborate **2c** was carried out in *p*-xylene suspension.

In order to increase the reactivity of tetraphosphorus decasulfide and to decrease the reaction temperature and time, we have used low-frequency ultrasonic irradiation (22 kHz, power 130 W) to promote Reaction 1. Ultrasonic irradiation has previously been shown to be an effective means of promoting the reactions of tetraphosphorus decasulfide and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with organic compounds [14]. Thus, we have now managed to involve triisopropyl borate **2a** in a reaction with **1** with ultrasound irradiation at 100–110°C for 0.5 hour in toluene suspension (Tables 1–5). In addition, ultrasonic irradiation produce substantial reaction rate enhancement in the reaction of **1** with triisobutyl borate **2b** (50–70°C, 20 minutes) compared with 3 hours (150°C) for nonultrasonic irradiation conditions. However, the yield of product **3b** remains about the same (48%) (with use of ultrasonic irradiation) compared to a 46% yield of **3b** in the absence of ultrasonic irradiation.

It should be noted that, in the case of trialkyl borates **2a**,**b**, only one alkoxy group of **2** takes part in the reaction with **1**. Reaction 1 was accompanied by the formation of diboronsulfides **4**, which were given off from the reaction mixtures. Bis(diphenylboron)sulfide **4c** was obtained as a crystalline solid. Products **3a–c** were formed as liquids. Product **3a** was purified by means of a falling-film distillation. Boron dithiophosphate **3b** was isolated by both com-

TABLE 1 Experimental Data and Yields of the Products Obtained

Initial Compounds Quantity, g (mmol)		*Reaction Conditions Temp. (°C) /Time (h)*	*Product Yield, g(%)*
1 3.0 (6.8)	/**2a** 10.2 (54.2)	100–110/0.5 10 ml PhMe USI[c]	**3a** 1.2 (52)[b]
1 2.9 (6.5)	/**2b** 12.0 (52.2)	150/3	**3b** 4.8 (46)[b]
1 2.9 (6.5)	/**2b** 12.0 (52.2)	50–70/20 min USI[c]	**3b** 5.0 (48)[b]
1 2.3 (5.2)	/**2c** 9.9 (41.6)	150/2 10 mL p-$C_6H_4Me_2$	**3c** 1.0 (12)[a] **4c** 1.5 (39)[a]

[a] Yield of crude product.
[b] Yield of isolated product.
[c] Ultrasound irradiation.

TABLE 2 Physical, Analytical, and ^{31}P NMR Data of the Products Obtained

Prod.	*Bp, °C (mm g)*	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found/Calc. %*		
				B	*P*	^{31}*P NMR, δ* (C_6H_6)
3a	125 (0.03)	1.4885	$C_{12}H_{28}BO_4PS_2$	3.54	9.15	81.1
			(342.0)	3.16	9.06	
3b	115–117 (0.04)[b]	1.4545	$C_{16}H_{36}BO_4PS_2$	2.66	7.63	85.0
			(398.1)	2.72	7.78	
3c		1.5321	$C_{20}H_{28}BO_2PS_2$	2.54	7.27	86.9
			(406.0)	2.66	7.63	
4c[d]	217[c]		$C_{24}H_{20}BS$	5.88		
			(361.8)	5.98		

[a] Temperature of thermal element of a falling-film distillation apparatus.
[b] b.p. (ordinary vacuum distillation). Product **3b** was also isolated by use of a falling-film distillation at 135–140°C (0.02 mm Hg).
[c] m.p.
[d] Analytical data, found, %: C 79.83; H 5.87. Calculated, %: C 79.60; H 5.58.

TABLE 3 IR Data of the Products Obtained

Prod.	*ν, CM^{-1}*
3a	2986, 2940, 2882 ν (CH_3 as, s; CH); 1388, 1340 δ (Me_2C gem s); 1010 ν (P-OC); 982 ν (B-O); 898 ν (B-S); 756; 655 ν (P=S); 550, 520 ν (P-S).
3b	2965, 2945, 2913, 2880 ν (CH_3 as, s; CH_2 as, s; CH); 1358, 1345, 1335 δ (Me_2C gem s); 1042 ν (P-OC); 1010 ν (B-O); 880 ν (B-S); 725; 675 ν (P=S); 575, 555, 533 ν (P-S).
3c	3063 ν (=C-H, Ar); 2970, 2940, 2900, 2880 ν (CH_3 as, s; CH_2 as, s; CH); 1605, 1473 ν (C=C, Ar); 1390, 1360 δ (Me_2C gem s); 1010 ν (P-OC); 980 ν (B-O); 860 ν (B-S); 665 ν (P=S); 538 ν (P-S).
4c^a	3083, 3060, 3050, 3030 ν (=C-H, Ar); 1605, 1500, 1406 ν (C=C, Ar); 807 ν (B-S); 712 ν [=C_{Ar}-(B)]; 583.

[a] In vaseline oil.

TABLE 4 ^{1}H NMR Data of the Products Obtained

Prod.	*δ, J[Hz]*
3a	1.07 (d, 12H, $\underline{CH}_3CHOB$, 12H, $\underline{CH}_3CHOP$, $^3J_{HH}$ 6.0); 4.28 (m, 2H, $CH_3\underline{CH}OB$, $^3J_{HH}$ 6.0); 4.68 (m, 2H, $CH_3\underline{CH}OP$, $^3J_{HH}$ 6.0, $^3J_{PH}$ 13.0).
3b	0.92 (d, 12H, $\underline{CH}_3CHCH_2OB$, $^3J_{HH}$ 6.0); 1.02 (d, 12H, $\underline{CH}_3CHCH_2OP$, $^3J_{HH}$ 6.0); 1.48–2.18 (m, 2H, $CH_3\underline{CH}CH_2OB$; 2H, $CH_3\underline{CH}CH_2OP$); 3.48 (d, 4H, $CH_3CH\underline{CH_2}OB$, $^3J_{HH}$ 6.0); 3.83 (d. d, 4H, $CH_3CH\underline{CH_2}OP$, $^3J_{HH}$ 6.0, $^3J_{PH}$ 8.0).
3c	0.70 (d, 12H, $\underline{CH}_3CHCH_2OP$, $^3J_{HH}$ 6.0); 1.07–1.82 (m, 2H, $CH_3\underline{CH}CH_2OP$); 3.40–3.93 (m, 4H, $CH_3CH\underline{CH_2}OP$, $^3J_{HH}$ 6.0); 6.70–7.35 (m, 10H, $C_6\underline{H}_5$).
4c	7.14–7.35 (m, 20H, $C_6\underline{H}_5$).

TABLE 5 Mass Spectral Data of the Products Obtained

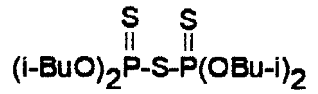
Prod.	*i-C_4H_{10}, m/e (I_{rel}, %)*
3a^a	198 [M + H − B(OPr-i)$_2$]$^+$ (10); 130 [M + H − S_2P(OPr-i)$_2$]$^+$ (100).
3b^a	243 [M + 2H − B(OBu-i)$_2$]$^+$ (10).
3b^b	398 [M]$^{+\cdot}$ (10).
3c^a	334 [M + H − i-BuO]$^+$ (40).
3c^b	287 [M − i-BuO − Ph]$^{+\cdot}$ (10).
4a^b	215 [M − OPr-i − O[$^{+\cdot}$ (32); 172]M − OPr-i − OPr-i]$^{+\cdot}$ (18).
4b^a	201 [M + H − 2 Bu-i]$^+$ (17).
4b^b	330 [M − O]$^{+\cdot}$ (10); 257 [M − O − OBu-i]$^{+\cdot}$ (100); 216 [M − OBu-i − Bu-i]$^{+\cdot}$ (10).
4c^a	287 [M + 2 H − Ph]$^+$ (10).
4c^b	208 [M − 2 Ph]$^{+\cdot}$ (10); 165 [M − Ph_2BS]$^{+\cdot}$ (20).

[a] Chemical ionization, 100 eV.
[b] Electron impact, 70 eV

mon vacuum distillation and by use of a falling-film distillation. However, we have not managed to isolate **3c** in its distilled form. Compound **3c** tends to decompose partially when falling-film distillations were used in attempted purification. Compound **3c** was characterized in its crude form (Tables 2–5) after removal of **4c**, but with starting **1** borate **2c** partially remaining unutilized in the reaction mixture (See Experimental section).

The ^{31}P NMR spectra of boron dithiophosphates **3a–c** (Table 2) show singlets in the range of δ = 81.1–86.9 in benzene solutions. These resonances appear in practically the same region as that for 2-(O,O′-dialkyldithiophosphato)-1,3,2-dioxaborinanes (δ = 82.76–86.43 in CCl_4 solution) [1]. As we can see, the ^{31}P NMR spectral signals of **3** reveal no significant change with respect to the corresponding free dithiophosphoric acids [15], similarly with 2-(O,O′-dialkyldithiophosphato)-1,3,2-dioxaborinanes [1]. The ^{1}H NMR spectra of **3a–c** (Table 4) show the characteristic resonances due to the presence of alkoxy groups attached to the phosphorus atom. Thus, the methyl protons of the two isopropoxy groups at the phosphorus atom of **3a** resonated in the range of δ = 1.07 as a doublet with $^3J_{HH}$ = 6.0. In the same range (δ = 1.37), there is a doublet of similar protons of the $\underline{CH}_3CHOP$ group of 2-(O,O′-diisopropyldithiophosphato)-1,3,2-dioxaborinane with the same spin-spin coupling constant ($^3J_{HH}$ = 6.0) [1]. The methyne protons of the isopropoxy group $(CH_3)_2\underline{CH}OP$ attached to the thiophosphoric group appear as a multiplet with the center at δ = 4.68 and show coupling with the phosphorus atom with $^3J_{PH}$ = 13.0 ($^3J_{HH}$ = 6.0). A doublet of doublets found in the ^{1}H NMR spectrum of **3b** at δ = 3.83 ($^3J_{HH}$ = 6.0, $^3J_{PH}$ = 8.0) has been assigned to the methylene protons of the isobutoxy group $(CH_3)_2CH\underline{CH_2}OP$. Bands of medium intensity found in the range of ν 898–860 cm^{-1} in the IR spectra of **3** (Table 3) may be attributed to the B-S valence vibrations (cf. ν B-S 932–856 cm^{-1} [1,16]). Bands in the region ν 1042–1010 and 1010–980 cm^{-1} are assigned to the P-OC and the B-O valence vibrations, respectively. Valence vibrations of the P=S bond was observed in the region ν 675–655 cm^{-1} for **3a–c**.

The electron-impact mass spectrum of **3b** exhibits the mass peak *m/e* 398 that may be attributed to its molecular ion [M]$^+$ (Table 5). In addition, there are mass peaks *m/e* 198 [M + H − B(OPr-i)$_2$]$^+$ and 243 [M + 2 H − B(OBu-i)$_2$]$^+$ in the mass spectra of **3a** and **3b**, respectively. Some secondary products were observed by examination of mass spectra of distillation fractions of **3**, however, in minor quantities. Thus, we have also observed a mass peak *m/e* 450 in the electron impact mass spectra of heavy volatile distillation fractions of **3b** that may be assigned to the molecular ion $[M]^+$ (8%) of bis(O,O′-diisobutylthiophosphoryl)sulfide **A** (calculated molecular mass M of **A** is 450). This secondary product **A** may be formed via the rupture of the S-P and S-B bonds of **3b**. It should be noted that **A** was observed only under conditions of recording of mass spectra.



$(i\text{-}BuO)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{S}{\overset{\|}{P}}(OBu\text{-}i)_2$

A

The ^1H NMR spectrum of **4c** reveals a multiplet at $\delta = 7.14$–7.35 due to the phenyl protons. The mass spectra of **4c** reveal mass peaks *m/e* 287 $[M + 2\,H - Ph]^+$ and 208 $[M - 2\,Ph]^+$. The presence of diboronsulfides **4a** and **4b** in the more volatile distillation fractions was confirmed by use of ^1H NMR and mass spectra. Thus, the electron-impact mass spectra of volatile liquids, collected in a liquid nitrogen cooled trap of the crude reaction mixture of phosphorus sulfide **1** with borate **2a**, show the mass peaks *m/e* 215 and 172 due to the ions $[M - i\text{-}PrO - O]^+$ (32%) and $[M - 2\,i\text{-}PrO]^+$ (18%), respectively, of diboronsulfide **4a** (calculated molecular mass M of **4a** is 290). In the case of **4b**, we have observed the mass peaks *m/e* 210 $[M + H - 2\,i\text{-}Bu]^+$ (100%) (calculated molecular mass M of **4b** is 346).

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with Bruker CXP-100 (36.6 MHz) and Bruker MSL 400 (162 MHz) instruments in C_6H_6 solutions with 85% H_3PO_4 as an external reference. The ^1H NMR spectra were taken on a Varian T-60 (60 MHz) spectrometer in C_6D_6 or CCl_4 with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained with Bruker IFS 113v and UR-20 infrared spectrophotometers. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on a M 80 B Hitachi chromatomass spectrometer.

S-Diisobutoxyboron O,O′-diisobutyldithiophosphate **3b** *in the absence of ultrasonic irradiation.* The mixture of **1** (2.9 g, 6.5 mmol) and **2b** (12.0 g, 52.2 mmol) was stirred at 150°C for 3 hours. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.08 mm Hg) at 50°C for 2 hours. Product **3b** (4.8 g, 46%) was isolated by common vacuum distillation (b.p. 115–117°C (0.04 mm Hg) (see Tables 1–5).

b *in the presence of ultrasonic irradiation.* The suspension of **1** [2.9 g (6.5 mmol)] and **2b** [12.0 g (52.2 mmol)] in 5 mL anhydrous toluene in a glass vessel was irradiated with ultrasound generated by an UZDN-A device (22 kHz, 130 W, direct immersion sonic horn) for 20 minutes at 50–70°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 50°C for 2 hours. Product **3b** (5.0 g, 48%) was isolated from the residue by means of a falling-film distillation at 135–140°C (0.02 mm Hg) (see Tables 1–5).

Compound **3a** was obtained similarly (by the use of ultrasonic irradiation, see Tables 1–5).

S-Diphenylboron O,O′-diisobutyldithiophosphate **3c.** A suspension of **1** [2.3 g (5.2 mmol)] and **2c** [9.9 g (41.6 mmol)] in 10 mL anhydrous *p*-xylene was stirred at 150°C for 2 hours. The mixture was filtered. The filtrate was evaporated under vacuum (0.1 and 0.08 mm Hg) for 2 hours. The crystalline precipitate of **4c** (1.5 g, 39%) that formed was filtered off, washed with anhydrous Et_2O, and dried under vacuum (0.08 mm Hg) (see Tables 1–5). The filtrate was evaporated at reduced pressure (0.08 mm Hg) at 60°C for 2 hours to give 1.0 g (12%) of crude **3c** (see Tables 1–5).

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