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Facile Methods of the Synthesis of S-Trialkylstannyl Esters of Dithio- and Tetrathiophosphoric Acids

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ABSTRACT

S-Trialkylstannyl dialkyldithiophosphates **3** *and tetrathiophosphates* **6** *were easily obtained in the reaction of tetraphosphorus decasulfide* **1** *with trialkylalkoxystannanes* **2** *or alkylthiostannanes* **5** *under mild conditions. Tetraphosphorus decasulfide* **1** *and hexaalkyl distannylsulfides* **4** *produce tris(trialkylstannyl) tetrathiophosphates* **9**.

INTRODUCTION

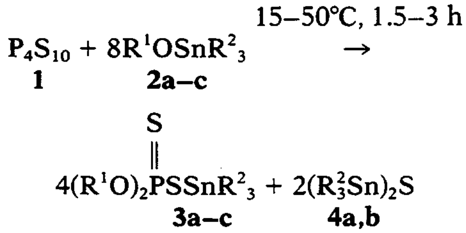
Organophosphorus compounds of tin possess properties of practical use. Triorganotin dialkyldithio- and tetrathiophosphates (**3** and **6**, respectively) are used as bactericides, insecticides, fungicides, miticides, and additives for lubricants [1–3]. Compounds **3** were obtained by the reaction of dialkyldithiophosphoric acids with organotin halides. Reactions of dialkyldithiophosphoric acids with organotin oxides or its hydroxides or protodemetallation of tetraalkyltin also result in **3**. Compounds **3** have also been obtained from metal or ammonium dialkyl dithiophosphates and triorganotin chlorides [1,2].

These techniques, however, are multistep procedures, as the initial dithiophosphoric acids had to be synthesized by treatment of organic hydroxy compounds with **1** [4]. The shortcomings of these syntheses also involve the use of solvents, heating of the reaction mixture (100°C), and formation of by-products [1,2].

The reactions of **1** with trimethylsilyldialkylamines and bis(trimethylsilyl)sulfide are reported to yield S-trimethylsilyl N,N-bis(dialkylamido)-dithiophosphates and tris(trimethylsilyl) tetrathiophosphates, respectively [5]. We have tried to extend these reactions of **1** to the use of organotin derivatives. In this article, facile and efficient methods are presented for the synthesis of **3** directly from **1**.

RESULTS AND DISCUSSION

We assumed that the reactions of trialkylstannylated alcohols with **1** lead to compounds **3**. In fact, **1** reacts with trialkyl alkoxystannanes **2a–c** to give S-trialkylstannyl 0,0-dialkyldithiophosphates **3a–c** and hexaalkyl distannylsulfides **4a,b**.



$$\underset{\mathbf{1}}{P_4S_{10}} + \underset{\mathbf{2a{-}c}}{8R^1OSnR^2_3} \xrightarrow{15\text{–}50^\circ C,\ 1.5\text{–}3\ h} \underset{\mathbf{3a{-}c}}{4(R^1O)_2\overset{S}{\overset{\|}{P}}SSnR^2_3} + \underset{\mathbf{4a,b}}{2(R^2_3Sn)_2S}$$

R^1 = Et, R^2 = Me (**a**)
R^1 = Me, R^2 = Bu (**b**)
R^1 = Et, R^2 = Bu (**c**)

This method is characterized by a minimum of steps, simple operation, mild conditions, high yields

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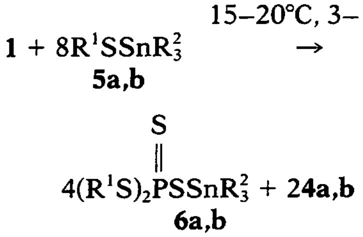
of products, no need for solvents, and formation of no by-products.

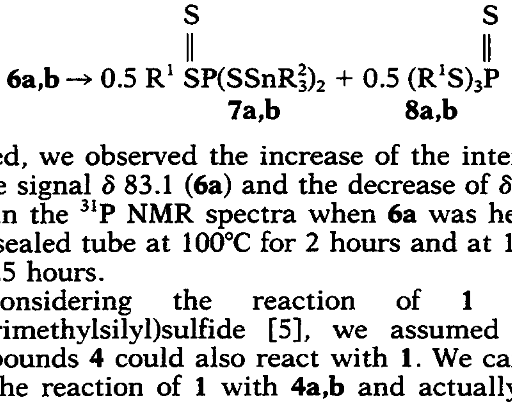
We have tried to extend this method to other reagents, in which reactive protons can be substituted by trialkylstannyl groups. Thus, we hoped to obtain triorganotin dialkyltetrathiophosphates **6** by the reaction of **1** with trialkylstannylated thiols. Indeed, we have found that the reactions of **1** with trialkyl alkylthiostannanes **5a,b** under mild conditions lead to dialkyl(trialkylstannyl)tetrathiophosphates **6a,b** and **4a,b**.



$$\mathbf{1} + 8\underset{\mathbf{5a,b}}{R^1SSnR^2_3} \xrightarrow{15\text{–}20°\mathrm{C},\ 3\text{–}10\ \mathrm{h}} 4\underset{\mathbf{6a,b}}{(R^1S)_2\overset{\overset{\displaystyle S}{\|}}{P}SSnR^2_3} + 2\mathbf{4a,b}$$

$R^1 = Et$, $R^2 = Bu$ (**a**)
$R^1 = i - Bu$, $R^2 = Bu$ (**b**)

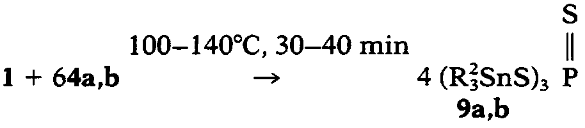
Compound **6a** was identified by its IR, ^1H NMR, and ^{31}P NMR spectra, as well as by mass spectral studies and elemental analyses of the crude product (see the Experimental section). However, we have not managed to isolate compounds **6** in pure form, as they decomposed even when a falling-film distillation apparatus was used. Triethyl tetrathiophosphate (δ 91.7) was isolated from the reaction mixture in pure form by distillation. Unlike these results, compounds **3** were not decomposed during distillation. We assumed that **6** decompose to form alkylbis(trialkylstannyl)tetrathiophosphates **7** and trialkyl tetrathiophosphates **8**.



$$\mathbf{6a,b} \rightarrow 0.5\ \underset{\mathbf{7a,b}}{R^1\,S\overset{\overset{\displaystyle S}{\|}}{P}(SSnR^2_3)_2} + 0.5\ \underset{\mathbf{8a,b}}{(R^1S)_3\overset{\overset{\displaystyle S}{\|}}{P}}$$

Indeed, we observed the increase of the intensity of the signal δ 83.1 (**6a**) and the decrease of δ 87.2 (**7a**) in the ^{31}P NMR spectra when **6a** was heated in a sealed tube at 100°C for 2 hours and at 160°C for 1.5 hours.

Considering the reaction of **1** with bis(trimethylsilyl)sulfide [5], we assumed that compounds **4** could also react with **1**. We carried out the reaction of **1** with **4a,b** and actually obtained tris(trialkylstannyl)tetrathiophosphates **9a,b**.



$$\mathbf{1} + 6\mathbf{4a,b} \xrightarrow{100\text{–}140°\mathrm{C},\ 30\text{–}40\ \mathrm{min}} 4\ \underset{\mathbf{9a,b}}{(R^2_3SnS)_3\overset{\overset{\displaystyle S}{\|}}{P}}$$

$R^2 = Me$ (**a**), Bu (**b**)

It is remarkable that the reactivity of organotin compounds toward **1** decreases in the series: **5a** (reaction conditions: 15°C, 3 hours), **2c** (50°C, 1.5 hours), and **4b** (140°C, 0.5 hour). As to the mechanisms for the formation of compounds **3**, **6** and **9**, it is suggested that all of these reactions of **1** most probably proceed via similar mechanisms. Perhaps these mechanisms are similar to those suggested by Roesky and Remmers for the reaction of **1** with trimethylsilyldimethylamine in which a nucleophilic nitrogen atom attacks a phosphorus atom [5].

EXPERIMENTAL

General Data

The initial trialkyl alkoxy- and alkylthiostannanes and hexaalkyl distannylsulfides were prepared according to the literature [6–9]. The ^{31}P NMR spectra were recorded with a Bruker WM 250 (101.3 MHz) in CH_3CN, a Bruker MSL-400 (162 MHz) in CCl_4, or a nonserial NMR KGU-4 (10.2 MHz) spectrometer relative to external H_3PO_4 (85%). The ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with C_6H_6 or Me_4Si as an internal reference or on a Bruker WM 250 (250 MHz) spectrometer in CD_3CN. The IR spectra were obtained in a KBr pellet with an UR-20 infrared spectrophotometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer.

S-Trimethylstannyl O,O-Diethyldithiophosphate **3a**; *Typical Procedure*

Compound **1** [8.6 g (19.4 mmol)] was added portionwise at 15°C to a stirred 32.6 g (156.1 mmol) of **2a**, and stirring was continued for 2 hours at 15°C. The mixture was evaporated at reduced pressure (0.03 mm Hg) at 40°C for 1 hour. Product **3a** (22.0 g, 82%) was isolated from the residue by means of a falling-film distillation apparatus at the temperature of the thermal element 90–105°C (0.04 mm Hg), d_4^{20} 1.4838, n_D^{20} 1.5461. ^{31}P NMR (neat, 10.2 MHz): δ 95. ^1H NMR and IR spectra were identical with those found in the literature [1,2]. (Ref. [1] bp 112–115°C (0.2 mm Hg); Ref. [2] n_D^{30} 1.5210). Distannylsulfide **4a** was distilled from light refluxed fractions; the yield: 5.0 g (36%); bp 54–55°C (0.05 mm Hg), n_D^{20} 1.5597. MS (CI) *m/e* 360 (M^+ + 1); Ref. [8] bp 50°C (0.05 mm Hg), n_D^{20} 1.5600.

S-Tri-n-butylstannyl O,O-Dimethyldithiophosphate **3b**

Similarly to the preparation of **3a**, 41.7 g (129.9 mmol) of **2b** and 7.2 g (16.2 mmol) of **1** (reaction conditions: 15°C, 3 hours) yielded 21.7 g (75%) of **3b** at the temperature of the thermal element of a falling-film distillation apparatus 140–150°C (0.02 mm Hg), a_4^{20} 1.2301, n_D^{20} 1.5246. ^{31}P NMR (neat, 10.2

MHz): δ 101. ^{1}H NMR (CCl$_4$, 60 MHz) δ 0.80–1.72 (m, 27H, C_4H_9Sn), 3.73 (d, 6H, H_3COP, $^3J_{PH}$ 15.0). IR ν_{max} 1150 [(P)–O–C], 1030 [P–O–(C)], ρ 809 (Sn–C), 666 (P=S), ν_{as} (PS$_2$), ν_{as} 533 (Sn–C), 500 cm^{-1} (P–S), ν_s (PS$_2$). MS (CI) *m/e* 449 (M$^+$ + 1). Anal. found: C, 37.00; H, 7.50; P, 6.69; S, 14.56; Sn, 26.64. $C_{14}H_{33}O_2PS_2Sn$ requires C, 37.59; H, 7.46; P, 6.93; S, 14.30; Sn, 26.25%. Distannylsulfide **4b**, 5.6 g (28%) [bp 186°C (0.02 mm Hg), n_D^{20} 1.5193, MS (CI) *m/e* 613 (M$^+$ + 1)], was also obtained.

S-Tri-n-butylstannyl O,O-Diethyldithiophosphate 3c

Similarly to the preparation of **3a** 70.5 g (211.0 mmol) of **2c** and 11.7 g (26.4 mmol) of **1** (reaction conditions: 50°C, 1.5 hours) yielded 42.4 g (85%) of **3c**, bp 150–153°C (0.03 mm Hg), d_4^{20} 1.1758, n_D^{20} 1.5142. ^{31}P NMR (neat, 10.2 MHz): δ 96. ^{1}H NMR and IR spectra are identical with those in the literature [1,2] (Ref. [2] bp 135–138°C (0.01 mm Hg), n_D^{30} 1.5266). Distannylsulfide **4b**, 21.3 g (66%), was also obtained.

Diethyl (Tri-n-butylstannyl)tetrathiophosphate 6a

Compound **1** [2.5 g (5.6 mmol)] was added portionwise at 15°C to a stirred 15.8 g (45.0 mmol) of **5a**, under an Ar atmosphere and stirring was continued for 3 hours at 15°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.02 mm Hg) at 150°C for 3 hours and gave 9.5 g (83%) of crude **6a**, d_4^{20} 1.1874, n_D^{20} 1.5548. ^{31}P NMR (CCl$_4$, 162 MHz) δ 87.2. ^{1}H NMR (CCl$_4$, 60 MHz) δ 0.90 (t, 6H, H_3CCS, $^3J_{HH}$ 7.5), 1.05–1.58 (m, 6H, $H_2CH_2CH_2C$), 1.35 (t, 3H, H_3CCCC, $^3J_{HH}$ 7.5), 2.90 (dq, 4H, H_2CSP, $^3J_{HH}$ 7.5, $^3J_{PH}$ 16.0). IR (neat); ν_{max} 680 (P=S), ν_{as} (PS$_2$), 540 ν_{as} (Sn–C), 525 (P–S), ν_s (PS$_2$). MS (CI) *m/e* 508 (M$^+$ + 1). Anal. found: C, 38.23; H, 7.35; P, 6.51; S, 24.95; Sn, 23.10. $C_{16}H_{37}PS_4Sn$ requires C, 37.88; H, 7.37; P, 6.11; S, 25.23; Sn, 23.41%. The distillations of the residue gave 2.0 g (71%) of **8a**, bp 114–118°C (0.02 mm Hg). ^{31}P NMR (neat, 10.2 MHz) δ 92. MS (CI) *m/e* 247 (M$^+$ + 1) (Ref. [10] bp 124–125°C (1.5 mm Hg), ^{31}P NMR δ 91.7).

Reaction of Tetraphosphorus Decasulfide 1 *with Tri-n-butyl i-Butylthiostannane* 5b

Compound **1** [2.8 g (6.3 mmol)] was added portionwise at 20°C to a stirred 19.1 g (50.4 mmol) of **5b** under an Ar atmosphere and stirring was continued for 10 hours at 20°C. The signals with δ 92.5, 88.8, and 83.7 were observed in the ^{31}P NMR spectra and corresponded to tri-*i*-butyl tetrathiophosphate **8b**, di-*i*-butyl (tri-n-butylstannyl)tetrathiophosphate **6b** and *i*-butyl bis(tri-n-butylstannyl)tetrathiophosphate **7b**, respectively. MS (CI) *m/e* 565 (M$^+$ + 1) corresponded to **6b**.

Tris(trimethylstannyl) Tetrathiophosphate 9a

Compound **1** [3.2 g (7.2 mmol)] was added portionwise at 100°C over a period of 45 minutes to a stirred solution of 15.6 g (43.4 mmol) of **4a** in 25 mL anhydrous toluene. The mixture was cooled to room temperature. The white precipitate that had formed was collected by filtration, washed with anhydrous benzene, and dried at reduced pressure (0.02 mm Hg) at 40°C for 1 hour. Yield of **9a** was 12.9 g (83%), mp 104–105°C. ^{31}P NMR (CH$_3$CN, 101.3 MHz) δ 79.2. ^{1}H NMR (CD$_3$CN, 250 MHz) δ 0.72 (s, 2d, 27H, H_3CSn, $^2J_{^{117}Sn-CH_3}$ 58.8, $^2J_{^{119}Sn-CH_3}$ 59.2. IR (vaseline oil): ν_{max} 790 ρ (Sn–C), 651 (P=S), ν_{as} (PS$_2$), 544 ν_{as} (Sn–C), 506 (P–S), ν_s (PS$_2$). Anal. found: C, 17.06; H, 4.25; P, 4.60; S, 19.69; Sn, 54.45. $C_9H_{27}PS_4Sn_3$ requires C, 16.61; H, 4.19; P, 4.76; S, 19.67; Sn, 54.77.

Tris(tri-n-butylstannyl) Tetrathiophosphate 9b

A mixture of 10.4 g (17.0 mmol) of **4b** and 1.26 g (2.8 mmol) of **1** was stirred for 0.5 hours at 140°C. The mixture was evaporated at reduced pressure (1 and 0.04 mm Hg) for 1 hour at 60°C. Light refluxed impurities were removed by means of a falling-film distillation apparatus at the temperature of the thermal element 190–200°C (0.02 mm Hg). The residue was **9b**. Yield of **9b** was 5.1 g (44%), d_4^{20} 1.3229, n_D^{20} 1.5768. ^{31}P NMR (CCl$_4$, 162 MHz) δ 78.2. ^{1}H NMR (CCl$_4$, 60 MHz) δ 0.72–2.13 (m, 81H, C_4H_9Sn). IR (neat): ν_{max} 650 (P=S), ν_{as} (PS$_2$), 530 ν_{as} (Sn–C), (P–S), ν_s (PS$_2$). MS (EI) *m/e* 707 [(Bu$_3$Sn)$_2$PS]$^+$. Anal. found: C, 41.71; H, 7.97; P, 3.09; S, 12.60; Sn, 34.41. $C_{36}H_{81}PS_4Sn_3$ requires C, 41.99; H, 7.95; P, 3.01; S, 12.43; Sn, 34.61. Distannylsulfide **4b**, 1.5 g (14%), was recovered.

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