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Reactions of Dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with Trialkylsilyl and Stannyl Derivatives

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ABSTRACT

The reactions of homologues of Davy's reagent **1** *and Lawesson's reagent* **9** *with trimethylalkylthiosilanes* **2**, *trimethylsilyl enol ether* **4**, *trimethyl(diethylamino)silane* **7**, *trialkylalkoxystannanes* **14**, *and trialkylalkylthiostannane* **15** *were studied. On the basis of these studies, novel advantageous methods of synthesizing S-trialkylsilyl and stannyl esters of tetrathio-, trithio-, and amidotrithiophosphoric acids* **3, 5, 6**, *and 4-methoxyphenyldithio- and trithiophosphonic acids* **10–13** *were developed*

INTRODUCTION

Organophosphorus compounds of silicon and tin possess properties of practical use [1–3]. S-Trimethylsilyl dithiophosphates are important intermediates for synthesizing useful organothiophosphorus compounds [1]. S-Triorganotin dithio- and tetrathiophosphates are used as pesticides and as additives for lubricants [2,3]. Organosilyl and stannylthiophosphorus compounds were obtained by the reactions of 2,4-bis substituted 2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with heptamethyldisilazane [4], trimethylsilylazide [5], trimethylchlorosilane [6], trimethyl(dimethylamino) silane [7,8], bis(trimethylsilyl)sulfide [7], bis(trimethylsilyl)acetamide [9], and bis(trimethylstannyl)sulfide [10].

However, the chemical behavior of the homologues of Davy's reagent and Lawesson's reagent remained unknown in reactions with alkoxy- and alkylthiosilanes, silylamines, alkoxy- and alkylthiosilanes, silylamines, and alkoxy- and alkylthiostannanes. In this article, facile and efficient methods are presented for the synthesis of S-trialkylsilyl and stannyl esters of tetrathio-, trithio-, and amidotrithiophosphoric acids and of 4-methoxyphenyldithio- and trithiophosphonic acids.

RESULTS AND DISCUSSION

We have previously found that tetraphosphorus decasulfide reacts with trimethylalkoxysilanes, trimethylsilyl enol ethers, trimethylsilylated thiols, bis(trimethylsiloxy)alkylenes and phenylene [11,12], and trialkylalkoxystannanes and trialkylalkylthiostannanes [13–15] to form S-trialkylsilyl and stannyl esters of dithio- and tetrathiophosphoric acids. As we expected, the corresponding reaction of 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes **1a,b** with trimethylalkylthiosilanes **2a,b** has been found to bring about the formation of the same dialkyl(trimethylsilyl)-tetrathiophosphates **3a,b** under mild conditions (20–50°C, 9–12 hours) which we had previously obtained in the reaction of tetraphosphorus decasulfide with **2a,b** [11,12] (Equation 1).

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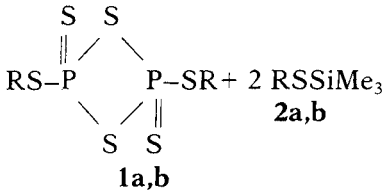
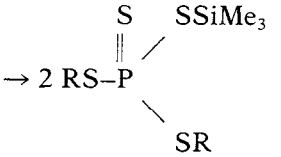


1a,b **2a,b**

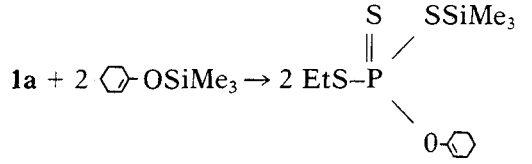


(1)

3a,b

R = Et (**a**)
R = *i* – Bu (**b**)

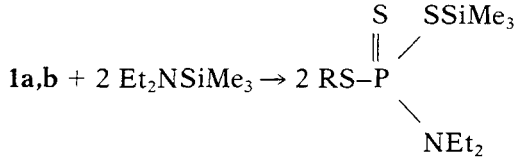
We have tried to find the range of application of this preparative method. For this purpose, we varied the silyl and stannyl derivatives on the one hand and the 1,3,2,4-dithiadiphosphetane-2,4-disulfides on the other hand. The trimethylsilyl enol ethers and silylamines are also involved in the reaction of homologues of Davy's reagent. Thus, we have shown that the reaction of **1a** with trimethylsilyl cyclohexenylol ether **4** under mild conditions (20°C, 8 hours) gives S-ethyl-O-cyclohexenyl-S-trimethylsilyl trithiophosphosphate **5** (Equation 2).



(2)

4 **5**

Silylamines have proven to be less reactive toward **1**. Thus, the mixed S-trimethylsilyl esters of S-alkyl-N,N′-diethylamido trithiophosphates **6a,b** were formed in the reaction of **1a,b** with trimethyl(diethylamido)silane **7** when heated for 9–10 hours at 50–80°C (Equation 3).



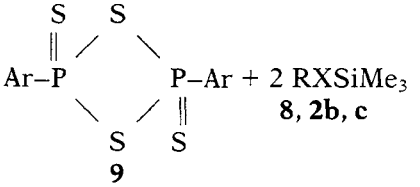
(3)

7 **6a, b**

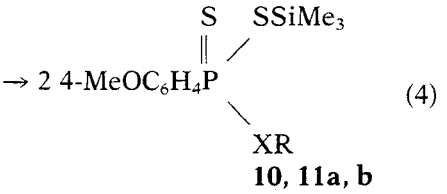
Et (**a**)
i – Bu (**b**)

The ^{31}P NMR spectra of **6a** and **6b** reveal resonances at δ 83.3 (CCl_4) and 84.1 (C_6H_6), respectively. However, Roesky and Remmers reported δ for S-trimethylsilyl N,N′-bis-(diethylamido)thiophosphate [7]. The fragment P–Si is expected to appear in the same region of ^{31}P NMR spectra as $\overset{S}{\underset{N}{>}}P(S)S–Si$ of the compounds. We assume that the value of δ 95.7 [7] is incorrect. Therefore, we reinvestigated the reaction of thiophosphorus decasulfide with silylamines according to the literature reaction conditions (CH_2Cl_2, 50°C, 1 hour). We found that this reaction proceeds with the formation of S-trimethylsilyl N,N′-bis(diethylamido)dithiophosphate, and, as we expected, its ^{31}P NMR spectrum reveals the signal at δ 83.6 (CH_2Cl_2). This fact supports the structures of amidotriothiophosphates **6a,b**.

This fragmentation behavior of the 1,3,2,4-dithiadiphosphetane ring may be extended to other 1,3,2,4-dithiadiphosphetane-2,4-disulfides, *e.g.*, the well-known Lawesson's reagent. Thus, we have shown that trimethylmethoxysilane **8** and trimethylalkylthiosilanes **2b,c** open the 1,3,2,4-dithiadiphosphetane ring of Lawesson's reagent **9** with the formation of S-trimethylsilyl esters of 4-methoxyphenyl dithio- and trithiophosphonic acids **10** and **11a,b** by treatment at 20–50°C for 2–11 hours (Equation 4).



9 **8, 2b, c**



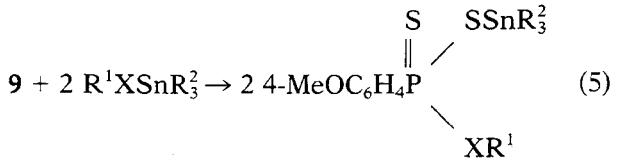
(4)

10, 11a, b

Ar = 4-$MeOC_6H_4$
R = Me, X = 0 (**8**, **10**)
R = *i*-Bu, X = S (**2b**, **11a**)
R = Pr, X = S (**2c**, **11b**)

It is noteworthy that the reactivity of alkylthiosilanes **2b,c** toward **9** (reaction conditions: 20°C, 6–11 hours) is higher than that of alkoxysilane **8** (50°C, 2 hours).

The formation of products of similar structure could be expected in the reaction of Lawesson's reagent with stannyl derivatives. In fact, the facile methods of synthesizing S-trialkylstannyl esters of 4-methoxyphenyl dithio- and trithiophosphonic acids **12a–c** and **13** were developed on the basis of the reactions of Lawesson's reagent **9** with trialkylstannylated alcohols **14a–c** and thiol **15** (Equation 5).



(5)

14a–c, 15 **12a–c, 13**

R^1 = Me, R^2 = Me, X = 0 (**14a, 12a**)
R^1 = Me, R^2 = Bu, X = 0 (**14b, 12b**)
R^1 = Et, R^2 = Bu, X = 0 (**14c, 12c**)
R^1 = *i*-Bu, R^2 = Bu, X = S (**15, 13**)

It is remarkable that the reaction of alkoxystannanes **14** with **9** (reaction conditions: 15°C, 1 hour) proceeds more easily than that of alkylthiostannane **15** (100–130°C, 22 hours).

Although there is no information in the literature on the mechanism of the reaction of 1,3,2,4-dithiadiphosphetane-2,4-disulfides with silyl and stannyl derivatives, the reactions of compounds **1** and **9** with the silyl and stannyl derivatives **2**, **4**, **7**, **8**, **14**, and **15** are of interest from the point of view of preparative organophosphorus chemistry.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with Bruker MSL 400 (162 MHz) and Bruker WM 250 (101.3 MHz) instruments in CCl_4, C_6H_6, and CH_2Cl_2. The ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with CH_2Cl_2 or Me_4Si as an internal reference or on a Bruker WM 250 (250 MHz) spectrometer in C_6D_6. The IR spectra were obtained in a KBr pellet with a UR-20 infrared spectrophotometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer. All distillations were performed with a thin layer distillation apparatus, and the temperature given was read from the thermoelement.

Diethyl(trimethylsilyl)tetrathiophosphate **3a**; *Typical Procedure*

Compound **1a** [10.4 g (33.5 mmol)] was added portionwise with stirring at 15°C to 9 g (67.1 mmol) of **2a**, and stirring was continued for 9 hours at 50°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.02 mm Hg) at 50°C for 2 hours and gave 11.2 g (57%) of crude **3a**. Product **3a** (6.5 g, 33%) was isolated from the residue at 100°C (0.02 mm Hg), d_4^{20} 1.1060, n_D^{20} 1.5888. ^{31}P NMR (C_6H_6, 162 MHz): δ 82.7. ^1H NMR (CCl_4, 60 MHz) δ 0.54 (s, 9H, $\underline{CH_3}Si$), 1.35 (t, 6H, $^3J_{H-H}$ 7.5, $\underline{CH_3}CH_2$), 2.92 (2q, 4H, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 17, $CH_3\underline{CH_2}SP$). IR (neat): γ_{max} 2964, 2928, 2895, 2870 (CH_3 as, s; CH_2 as, s), 1252 δ [CH_3(Si) s], 846 ρ [CH_3(Si)], 680 γ (P=S), γ_{as} (PS_2), 546, 516 γ (P–S, S–Si). MS (CI) *m/e* 291 ($M^+ + 1$). Anal. found: C, 28.43; H, 6.35; P, 10.71; S, 43.87; Si, 9.56. $C_7H_{19}PS_4Si$ requires C, 28.96; H, 6.62; P, 10.68; S, 44.09; Si, 9.65% [Ref. [11] bp 90–100°C (0.02 mm Hg) (a thin layer distillation), n_D^{20} 1.5885. ^{31}P NMR (neat, 10.2 MHz); δ 83].

Di-i-butyl(trimethylsilyl)tetrathiophosphate **3b**

Similarly to the preparation of **3a**, 20 g (54.4 mmol) of **1b** and 17.6 g (108.6 mmol) of **2b** (reaction conditions: 20°C, 12 hours) yielded 12.8 g (34%) of **3b** at 125–135°C (0.02 mm Hg), d_4^{20} 1.0377, n_D^{20} 1.5638. ^{31}P NMR (C_6H_6, 162 MHz): δ 83.1. ^1H NMR (CCl_4, 60 MHz): δ 0.52 (s, 9H, $\underline{CH_3}Si$), 1 (d, 12H, $^3J_{H-H}$ 6, $\underline{CH_3}CHCH_2$), 1.77–2.22 (m, 2H, $CH_3\underline{CH}CH_2$), 2.76 (2d, 4H, $^3J_{H-H}$ 6, $^3J_{P-H}$ 15, CH_3 $CH\underline{CH_2}$). IR (neat): γ_{max} 2960, 2930, 2900, 2874 (CH_3 as, s; CH_2 as, s), 1384, 1370 δ [$(CH_3)_2C$ gem s], 1252 δ [CH_3(Si) s], 851 ρ [CH_3(Si)], 684 γ (P = S), 550, 525 γ (P–S, S–Si). Anal. found: C, 38.26; H, 7.74; P, 8.88; S, 36.75; Si, 8.26. $C_{11}H_{27}PS_4Si$ requires C, 38.14; H, 7.88; P, 8.95; S, 36.95; S, 36.95; Si, 8.08% [Ref. [11] bp 120–130°C (0.02 mm Hg) (a thin layer distillation), n_D^{20} 1.5635. ^{31}P NMR (neat, 10.2 MHz): δ 83].

S-Ethyl-O-cyclohexenyl-S-trimethylsilyl Trithiophosphate **5**

Similarly to the preparation of **3a**, 5.2 g (16.8 mmol) of **1a** and 5.7 g (33.5 mmol) of **4** (reaction conditions: 20°C, 8 hours) yielded 8.9 g (82%) of **5** at 120°C (0.02 mm Hg), d_4^{20} 1.0946, n_D^{20} 1.5222. ^{31}P NMR (C_6H_6, 162 MHz): δ 60.8. ^1H NMR (C_6D_6, 250 MHz) δ 0.24 (s, 9H, $\underline{CH_3}Si$), 0.62 (t, 3H, $^3J_{H-H}$ 6, $\underline{CH_3}CH_2S$), 0.71–1.76 (m, 8H, $\underline{CH_2}$ cycle), 2 (2q, 2H, $^3J_{H-H}$ 6, $^3J_{P-H}$ 6, $CH_3\underline{CH_2}SP$), 4.92–5.66 (m, 1H, $\underline{HC}$=COP). IR (neat): γ_{max} 2970, 2940, 2865, 2840 (CH_3 as, s; CH_2 as, s; CH_3(Si) s), 1630 γ (C = C), 1450 δ (CH_3 as), 1340 δ (CH_3 s), 1260 δ [CH_3(Si) s], 1025 γ (PO–C), 855 ρ [CH_3(Si)], 741 γ (P=S). Anal. found: C, 40.38; H, 7.51; P, 9.54; S, 29.58; Si, 8.60. $C_{11}H_{23}OPS_3Si$ requires C, 40.48; H, 7.12; P, 9.50; S, 29.41; Si, 8.58%.

S-Ethyl-S'-trimethylsilyl-N,N'-bis(diethyl)amido Trithiophosphate **6a**

Similarly to the preparation of **3a**, 22.2 g (71.6 mmol) of **1a** and 20.8 g (143.3 mmol) of **7** (reaction condition: 50°C, 9 hours) yielded 21.3 g (49%) of **6a** at 100°C (0.02 mm Hg), d_4^{20} 1.0639, n_D^{20} 1.5478. ^{31}P NMR (CCl_4, 162 MHz): δ 83.3. ^1H NMR (CCl_4, 60 MHz) δ 0.53 (s, 9H, $\underline{CH_3}Si$), 1.17 (t, 6H, $^3J_{H-H}$ 7, $\underline{CH_3}CH_2N$), 1.40 (t, 3H, $^3J_{H-H}$ 7.5, $\underline{CH_3}CH_2S$), 2.95 (2q, 2H, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 15, $CH_3\underline{CH_2}SP$), 3.36 (2q, 4H, $^3J_{H-H}$ 7, $^3J_{P-H}$ 14, $CH_3\underline{CH_2}NP$). IR (neat): γ_{max} 2980, 2935, 2880, 2815 (CH_3 as, s; CH_2 as, s; CH_3(Si) s), 1455 δ (CH_3 as), 1385 δ (CH_3 s), 1260 δ [CH_3(Si) s], 1025 γ (C–N–C as), 855 ρ [CH_3(Si)], 665 γ (P = S, PS_2 as), 560, 555, 515 γ (PS_2 s, S–Si, P–SC). Anal. found: C, 35.69; H, 8.25; N, 5.10, P, 10.59; S, 32.10; Si, 9.44. $C_9H_{24}NPS_3Si$ requires C, 35.87; H, 8.05; N, 4.65; P, 10.29; S, 31.85; Si, 9.29%.

S-i-Butyl-S'-trimethylsilyl-N,N'-bis(diethyl)amido Trithiophosphate **6b**

Similarly to the preparation of **3a**, 15.8 g (42.9 mmol) of **1b** and 12.5 g (86.1 mmol) of **7** (reaction conditions: 80°C, 10 hours) yielded 4.4 g (16%) of **6b** at 120°C (0.02 mm Hg), d_4^{20} 1.0133, n_D^{20} 1.5483. ^{31}P NMR (C_6H_6, 162 MHz): 84.1. ^1H NMR (CCl_4, 60 MHz): δ 0.56 (s, 9H, $\underline{CH_3}Si$), 1.06 (d, 6H, $^3J_{H-H}$ 7,

$\underline{CH_3}CHCH_2S$), 1.17 (t, 6H, $^3J_{H-H}$ 7, $\underline{CH_3}CH_2N$), 2.82 (2d, 2H, $^3J_{H-H}$ 7, $^3J_{P-H}$ 15, $CHCH_2SP$), 3.42 (2q, 4H, $^3J_{H-H}$ 7, $^3J_{P-H}$ 14, CH_3CH_2NP). IR (neat): γ_{max} 2965, 2940, 2900, 2875 (CH_3 as, s; CH_2 as, s; CH_3(Si) s), 1465 δ (CH_3 as), 1383, 1370 [$(CH_3)_2C$ gem s], 1255 [CH_3(Si) s], 1025 γ (C–N–C as), 855 ρ [CH_3(Si)], 685 γ (P = S, PS_2 as), 565, 525 γ (PS_2 s, S–Si, P–SC). Anal. found: C, 41.10; H, 5.93; P, 10.10; S, 30.16; Si, 9.57. $C_{11}H_{18}NPS_3Si$ requires C, 41.37; H, 5.70; P, 9.71; S, 30.06; Si, 8.77.

O-Methyl-S-trimethylsilyl 4-Methoxyphenyldithiophosphonate **10**

Similarly to the preparation of **3a**, 28.3 g (70 mmol) of **9** and 14.6 g (140.1 mmol) of **8** (reaction conditions: 10 mL of toluene, 50°C, 2 hours) yielded 10.8 g (26%) of **10** at 150°C (0.02 mm Hg), d_4^{20} 1.2824, n_D^{20} 1.6208. ^{31}P NMR (C_6H_6, 101.3 MHz): δ 87.6. ^{1}H NMR (CCl_4, 250 MHz): δ 0.11 (s, 9H, $\underline{CH_3}Si$), 3.85 (s, 3H, $\underline{CH_3}OC_6H_4$), 3.86 (d, 3H, $^3J_{P-H}$ 16, $\underline{CH_3}OP$), 6.94 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 5, 2, 6 – $\underline{H_2}C_6H_2$), 7.87 (2d, 2H, 3, 5 – $H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3072, 3010 (=C–H, Ar), 2970, 2948, 2910, 2842 γ (CH_3 as, s; CH_2 as, s; CH_3(Si) s), 1595, 1500, 1465 γ (C=C, Ar), 1260 δ [CH_3(Si) s], 1035 γ (PO–C), 848 ρ [CH_3(Si)], 688 γ (P = S), 540, 520 γ (P–S, S–Si). MS (EI) *m/e* (I_{rel}) 291 $[M - Me]^+$ (10), 202 $[M - MeO - Me_3Si]^+$ (100); (CI) *m/e* (I_{rel}) 234 $[M + H - Me_3Si]^+$ (10). Anal. found: C, 43.24; H, 6.08; P, 9.88; S, 20.64; Si, 9.01. $C_{11}H_{19}O_2PS_2Si$ requires C, 43.13; H, 6.27; P, 10.12; S, 20.89; Si, 9.14.

i-Butyl(trimethylsilyl) 4-Methoxyphenyltrithiophosphonate **11a**

Similarly to the preparation of **3a**, 34.3 g (84.9 mmol) of **9** and 27.5 g (169.6 mmol) of **2b** (reaction conditions: 20°C, 11 hours) yielded 46.7 g (76%) of **11a** at 175–180°C (0.02 mm Hg), d_4^{20} 1.1202, n_D^{20} 1.5979. ^{31}P NMR (neat, 10.2 MHz): δ 71. ^{1}H NMR (CCl_4, 60 MHz): δ 0.48 (s, 9H, $\underline{CH_3}Si$), 1.03 (d, 6H, $^3J_{H-H}$ 7, $\underline{CH_3}CHCH_2$), 1.57–2.93 (m, 3H, $CH_3\underline{CH}CH_2$, $CH_3CH\underline{CH_2}$), 3.87 (s, 3H, $\underline{CH_3}OC_6H_4$), 6.86 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4, 2,6–$\underline{H_2}C_6H_2$), 7.96 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 15, 3, 5–$H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3070, 3010 (=C–H, Ar), 2965, 2935, 2210, 2840 γ [CH_3 as, s; CH_2 as, s; CH_3(Si) s], 1595, 1500, 1465 γ (C=C, Ar), 1387, 1370 δ [$(CH_3)_2C$ gem s], 1260 δ [CH_3(Si) s], 851 ρ [CH_3(Si)], 690 γ (P = S), 540, 510 γ (S–Si, P–S, PS_2 s). Anal. found: C, 46.32; H, 6.60; P, 8.98; S, 26.72; Si, 7.25. $C_{14}H_{25}OPS_3Si$ requires C, 46.14; H, 6.93; P, 8.51; S, 26.34; Si, 7.68%.

n-Propyl(trimethylsilyl) 4-Methoxyphenyltrithiophosphonate **11b**

Similarly to the preparation of **3a**, 33.1 g (81.9 mmol) of **9** and 24.3 g (163.7 mmol) of **2c** (reaction conditions: 20°C, 6 hours) yielded 37.4 g (65%) of **11b** at 150–160°C (0.05 mm Hg), d_4^{20} 1.1347, n_D^{20} 1.6058. ^{31}P NMR (neat, 10.2 MHz): δ 69. ^{1}H NMR (CCl_4, 60 MHz): δ 0.54 (s, 9H, $\underline{CH_3}Si$), 1.06 (t, 3H, $^3J_{H-H}$ 7, $\underline{CH_3}CH_2CH_2$), 1.43–1.90 (m, 2H, $CH_2\underline{CH_2}CH_2$), 2.67–3.13 (m, 2H, $CH_3CH_2\underline{CH_2}SP$), 3.88 (s, 3H, $\underline{CH_3}OC_6H_4$), 6.88 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4.5, 2, 6 – $\underline{H_2}C_6H_2$), 7.95 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 15, 3, 5 – $H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3080, 3010 (=C–H, Ar), 2970, 2938, 2915, 2880, 2845 γ [CH_3 as, s; CH_2 as, s; CH_3(Si) s], 1594, 1500, 1465 γ (C=C, Ar), 1260 δ [CH_3(Si) s], 851 ρ [CH_3 (Si)], 690 γ (P=S), 540, 510 γ (PS_2 s, S–Si, P–S). Anal. found: C, 44.76; H, 6.41; P, 8.54; S, 26.94; Si, 7.69. $C_{13}H_{23}OPS_3Si$ requires C, 44.56; H, 6.64; P, 8.85; S, 27.39; Si, 7.99%.

O-Methyl-S-trimethylstannyl 4-Methoxyphenyldithiophosphonate **12a**

Similarly to the preparation of **3a**, 9.3 g (23 mmol) of **9** and 9 g (46.2 mmol) of **14a** (reaction conditions: 30 mL of benzene, 15°C, 1 hour) yielded 12.8 g (70%) of **12a** at 160–175°C (0.02 mm Hg), d_4^{20} 1.2376, n_D^{20} 1.6178. ^{31}P NMR (neat, 10.2 MHz): δ 98. ^{1}H NMR (CCl_4, 60 MHz): δ 0.67 (s, 9H, $\underline{CH_3}Sn$; d, $^2J_{117Sn-CH_3}$ 56; d, $^2J_{119Sn-CH_3}$ 59), 3.77 (d, 3H, $^3J_{P-H}$ 16, $\underline{CH_3}OP$), 3.86 (s, 3H, $\underline{CH_3}O-C_6H_4$), 6.92 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4, 2,6-$\underline{H_2}C_6H_2$), 7.92 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 14.5, 3,5-$H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3070, 3010 (=C–H, Ar), 2950, 2920, 2845 γ (CH_3 as, s; CH_2 as, s), 1598, 1505, 1470 γ (C=C, Ar), 1035 γ [P–O–(C)], 788 ρ (Sn–C), 684 γ (P=S), 538, 514 γ (Sn–C, P–S). Anal. found: C, 32.93; H, 5.17; P, 8.36; S, 15.76; Sn, 30.03. $C_{11}H_{19}O_2PS_2Sn$ requires C, 33.27; H, 4.84; P, 7.81; S, 16.11; Sn, 29.91%.

O-Methyl-S-tri-n-butylstannyl 4-Methoxyphenyldithiophosphonate **12b**

Similarly to the preparation of **3a**, 31.8 g (78.7 mmol) of **9** and 50.5 g (157.3 mmol) of **14b** (reaction conditions: 15°C, 1 hour) yielded 62 g (74%) of **12b** at 170–190°C (0.02 mm Hg), d_4^{20} 1.2297, n_D^{20} 1.5233. ^{31}P NMR (neat, 10.2 MHz): δ 100. ^{1}H NMR (CCl_4, 60 MHz): δ 0.82–1.67 (m, 27H, C_4H_9Sn), 3.70 (d, 3H, $^3J_{P-H}$ 15, $\underline{CH_3}OP$), 3.77 (s, 3H, $\underline{CH_3}O-C_6H_4$), 6.85 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4, 2,6–$\underline{H_2}C_6H_2$), 7.85 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 15, 3, 5 – $H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3010 (=C–H, Ar), 2960, 2930, 2880, 2860 γ (CH_3 as, s; CH_2 as, s), 1598, 1500, 1465 γ (C=C, Ar), 1035 γ [PO–(C)], 788 ρ (Sn–C), 686 γ (P=S), 538, 527 γ (Sn–C, P–S). MC (CI) *m/e* (I_{rel}): 525 $[M + H]^+$ (92), 492 $[M + H - S]^+$ (100), 467 $[M + H - Bu]^+$ (50), 435 $[M + H - Bu - S]^+$ (25). Anal. found: C, 45.44; H, 7.02; P, 5.99; S, 11.96; Sn, 22.95. $C_{20}H_{37}O_2PS_2Sn$ requires C, 45.89; H, 7.15; P, 5.92; S, 12.22; Sn, 22.70%.

O-Ethyl-S-tri-n-butylstannyl 4-Methoxyphenyldithiophosphonate **12c**

Similarly to the preparation of **3a**, 10.3 g (25.5 mmol) of **9** and 17 g (50.9 mmol) of **14c** (reaction conditions: 15°C, 1 hour) yielded 22.1 g (81%) of **12c** at 170–180°C (0.02 mm Hg), d_4^{20} 1.2271, n_D^{20} 1.5608. ^{31}P NMR (neat, 10.2 MHz): δ 95. ^{1}H NMR (CCl_4, 60 MHz): δ 0.77–1.77 (m, 30H, $\underline{CH_3}CH_2O$ + C_4H_9Sn), 3.87 (s, 3H, $\underline{CH_3}OC_6H_4$), 4.10 (2q, 2H, $^3J_{H-H}$ 7, $^3J_{P-H}$ 9, $CH_3\underline{CH_2}OP$), 6.87 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4, 2, 6 – $\underline{H_2}C_6H_2$), 7.90 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 14.5, 3,5–$H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3070 (=C–H, Ar), 2966, 2930, 2880, 2860 γ (CH_3 as, s; CH_2 as, s), 1598, 1505, 1465 (C=C, Ar), 1035 γ [PO–(C)], 950 γ (OC–C), 788 ρ (Sn–C), 675 γ (P=S), 555, 535, 520 γ (Sn–C as, P–S). MS (CI) *m/e* (I_{rel}): 538 $[M + H]^+$ (13), 338 $[M + H - 3Bu - Et]^+$ (8); (EI) *m/e* (I_{rel}):480 $[M - Bu]^+ \cdot$ (100), 366 $[M - 3Bu]^+$ (30). Anal. found: C, 47.02; H, 7.30; P, 5.65; S, 11.68; Sn, 21.84. $C_{21}H_{39}O_2PS_2Sn$ requires C, 46.93; H, 7.33; P, 5.77; S, 11.91; Sn, 22.10%.

i-Butyl(tri-n-butylstannyl) 4-Methoxyphenyltrithiophosphonate **13**

Similarly to the preparation of **3a**, 13.5 g (33.4 mmol) of **9** and 25.3 g (66.8 mmol) of **15** (reaction conditions: 100–130°C, 22 hours) yielded 34.6 g (89%) of **13** at 150–160°C (0.008 mm Hg), d_4^{20} 1.1946, n_D^{20} 1.4905. ^{31}P NMR (C_6H_6, 101.3 MHz): δ 74.5. ^{1}H NMR (CCl_4, 60 MHz): 0.80–2.90 (m, 36H, *n*-C_4H_9 + *i*-C_4H_9), 3.77 (s, 3H, $\underline{CH_3}OC_6H_4$), 6.77 (2d, 2H, $^3J_{H-H}$ 9, $^4J_{P-H}$ 4, 2,5 – $\underline{H_2}C_6H_2$), 7.85 (2d, 2H, $^3J_{H-H}$ 9, $^3J_{P-H}$ 15, 3,5 – $H_2C_6\underline{H_2}$). IR (neat): γ_{max} 3070, 3040 γ (=C–H, Ar), 2965, 2930, 2870, 2860 γ (CH_3 as, s; CH_2 as, s), 1598, 1500, 1465 γ (C=C, Ar), 1382, 1365 δ [$(CH_3)_2C$ gem s], 695, 680 γ (P=S, PS_2 as), 543 γ (Sn–C as), 515 γ (P–S, PS_2 s). MS (CI) *m/e* (I_{rel}): 551 $[M + H - S]^+$ (30), 526 $[M + H - Bu]^+$ (10), 493 $[M + H - SBu]^+$ (70). Anal. found: C, 47.80; H, 7.87; P, 5.43; S, 16.43; Sn, 20.81. $C_{23}H_{43}OPS_3Sn$ requires C, 47.50; H, 7.48; P, 5.33; S, 16.51; Sn, 20.43%.

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