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LETTERS TO THE EDITOR

Reactions of Trimethylsilyl Phosphites with Anhydrides of Phthalic and 2-Sulfobenzoic Acids

A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, and V. S. Petrosyan

Lomonosov Moscow State University, Vorob'yovy Gory, Moscow, 119991 Russia
e-mail: aprishchenko@yandex.ru

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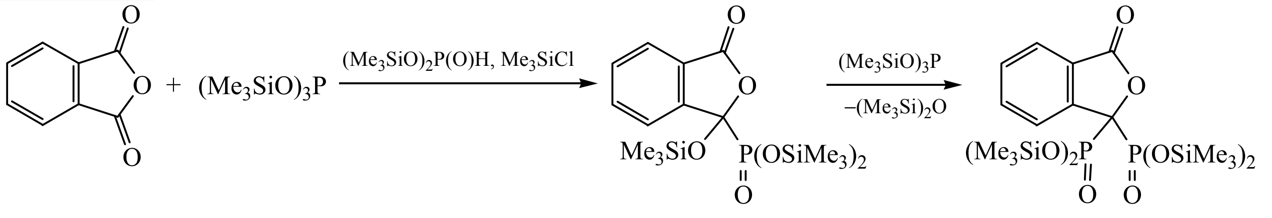
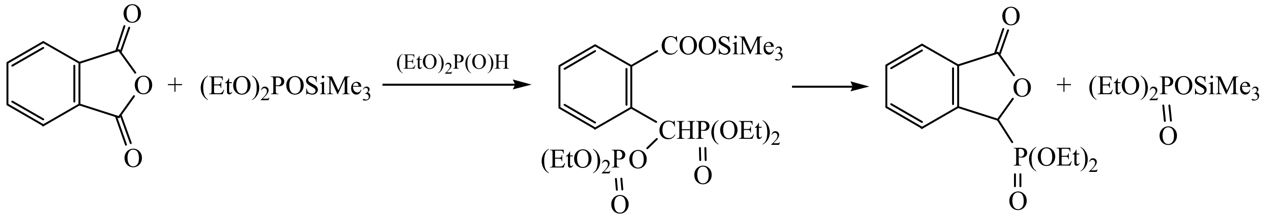
Anhydrides of phthalic and 2-sulfobenzoic acids readily react with various nucleophiles and are widely used in the organic and organometallic synthesis [1]. Previously, we have developed a number of convenient methods for the synthesis of the functionalized phosphorus amides of iso- and terephthalic acids [2]. In this work we studied the reactions of trimethylsilyl phosphites with phthalic and 2-sulfobenzoic anhydrides and showed that different results of these reactions were determined by different reactive precursors. Thus, an excess of tris(trimethylsilyl) phosphite reacts slowly with phthalic anhydride in methylene chloride in the presence of bis(trimethylsilyl) phosphite and trimethylchlorosilane already at 20°C. The reaction proceeds via an intermediate formation of phosphonate **I** detected by the NMR, and results in diphosphonate **II** in high yield (cf. [3]).



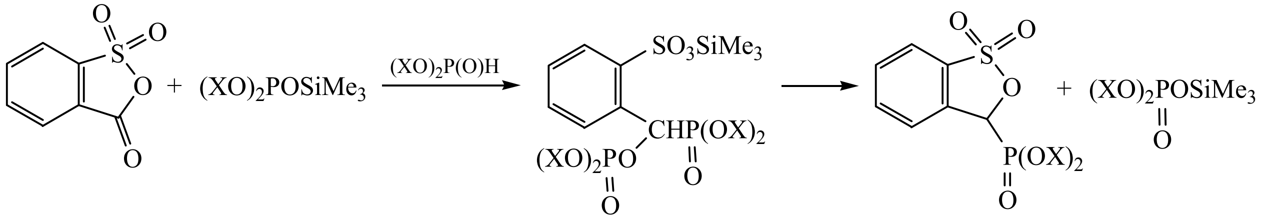
I **II**

Under similar conditions, the nucleophilic reaction of diethyl trimethylsilyl phosphite and diethyl phosphite with phthalic anhydride proceeds exothermally and results in the product of a phosphonate-phosphate rearrangement **III** in a high yield. On distilling compound **III**, a formation of some phosphonate **IV** and diethyl trimethylsilyl phosphate was registered by the NMR (cf. [4]).



III **IV**

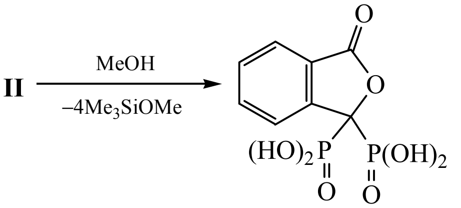
Under these conditions, 2-sulfobenzoic anhydride reacts with trimethylsilylphosphites to give only the phosphonate-phosphates **V** and **VII**, which are transformed into phosphonates **VI**, **VIII** and the corresponding trimethylsilyl phosphates at distillation.



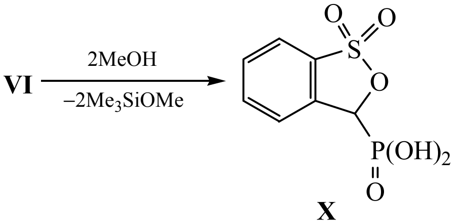
V, VII **VI, VIII**

X = Me_3Si (**V, VI**), Et (**VII, VIII**).

The reaction of diphosphonate **II** and phosphonate **VI** with an excess of methanol results in mono- and diphosphonic acids **IX**, **X**, which are white hygroscopic crystals.

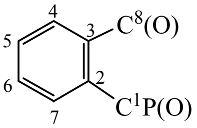


IX



X

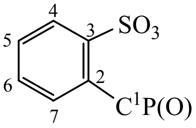
The resulting compounds **II**, **III**, **VI**, **VIII–X** containing phosphonate groups along with the cyclic moieties are of interest as potential ligands and biologically active substances. The NMR spectra of compounds **I–X** contain the characteristic signals of the **A–C** fragments whose parameters are listed below.



A

$P^2(O)OC^1HP^1(O)$

B



C

Tetra(trimethylsilyl) (3-oxo-1,3-dihydro-2-benzofuran-1,1-diyl)bisphosphonate (II). A mixture of 16.4 g of tris(trimethylsilyl) phosphite, 5.7 g of bis(trimethylsilyl) phosphite, 3.7 g of phthalic anhydride, and 2 ml of trimethylchlorosilane in 15 ml of methylene chloride was stirred for 1 h. Then the solvent was distilled off. In the NMR spectrum of the mixture the signals of the phosphonate **I** were observed. ^{1}H NMR spectrum, δ, ppm: 7.25–7.50 m (C_6H_4), –0.05 s (Me_3SiOC), –0.31 s and –0.38 s ($2Me_3SiOP$). ^{13}C NMR spectrum, δ_C, ppm: 101.86 d (C^1, $^1J_{PC}$ 227.5 Hz 126.32 (C^2), 145.98 d (C^3, $^3J_{PC}$ 9.5 Hz), 133.66 (C^4), 124.26 and 124.29 (C^5, C^6), 130.35 (C^7), 166.60 (C^8), 0.85 (Me_3SiOC), 0.54 and 0.14 ($2Me_3SiOP$). ^{31}P NMR spectrum: δ_P –6.45 ppm.

Then to the reaction mixture was added 2 ml of trimethylchlorosilane. The mixture was kept at 20°C for two weeks and then distilled to obtain 12.7 g of bisphosphonate **II**. Yield 87% yield, bp 172°C (1 mm Hg), mp 52°C. ^{1}H NMR spectrum, δ, ppm: 7.25–7.55 m (C_6H_4), –0.23 s and –0.09 s ($2Me_3Si$). ^{13}C NMR spectrum, δ_C,ppm: 83.14 t (C^1, $^1J_{PC}$ 162.5 Hz), 124.8–125.3 (C^2, C^5, C^6), 145.20 t (C^3, $^3J_{PC}$ 5.6 Hz), 133.63 (C^4), 129.40 (C^7), 169.04 (C^8), –0.23 and –0.09 ($2Me_3Si$). ^{31}P NMR spectrum: δ_P –8.91 ppm. Found, %: C 41.03; H 6.84. $C_{20}H_{40}O_8P_2Si_4$. Calculated, %: C 41.22; H 6.92.

Trimethylsilyl 2-{(diethoxyphosphoryl)[(diethoxyphosphoryl)oxy]methyl}benzoate (III). To a mixture of 3.7 g of phthalic anhydride and 15 ml of methylene chloride was added a solution of 12 g of diethyl trimethylsilyl phosphite and 3.8 g of diethyl phosphite in 20 ml of methylene chloride. After the completion of the exothermic reaction the solvent was distilled off, and the residue was distilled. Yield 11 g (89%), bp 187°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 6.79 d.d (C^1H, $^2J_{PH}$ 14.8, $^3J_{PH}$ 10.8 Hz), 6.9–7.6 m (C_6H_4), 3.4–3.7 m ($4CH_2OP$), 0.7–0.9 m ($4CH_3$), –0.04 s (Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 69.70 d.d (C^1, $^1J_{PC}$ 166.9, $^2J_{PC}$ 5.6 Hz), 129.41 d (C^2, $^2J_{PC}$ 5.6 Hz), 135.61 (C^3), 131.72 (C^4), 127.81 and 127.97 (C^5, C^6), 130.80 (C^7), 166.11 (C^8), 62.5–63.7 m ($4CH_2OP$), 15.5–16.1 m (4Me), –0.74 (Me_3Si). ^{31}P NMR spectrum, δ_P, ppm: 16.45 d (P^1, $^3J_{PP}$ 33.4 Hz), –1.49 d (P^2, $^3J_{PP}$ 33.4 Hz). Found, %: C 45.82; H 6.78. $C_{19}H_{34}O_9P_2Si$. Calculated, %: C 45.96; H 6.90.

The fraction boiling at 110–130°C (1 mm Hg) contains phosphonate **IV** [δ_H 5.44 ppm (d, C^1H, $^2J_{PH}$ 8.3 Hz); δ_C 75.10 ppm (d, C^1, $^1J_{PC}$ 163.4 Hz); δ_P 13.48 ppm] and diethyl trimethylsilyl phosphate (δ_P –9.32 ppm).

The phosphonates **VI** and **VIII** were obtained similarly.

Bis(trimethylsilyl) (1,1-dioxido-3*H*-2,1-benzoxathiol-3-yl)phosphonate (VI). Yield 52%, bp 142°C (1 mm Hg). ^1H NMR spectrum, δ, ppm: 5.53 d (C^1H, $^2J_{PH}$ 8.2 Hz), 7.3–7.5 m (C_6H_4), –0.01 br.s (Me_3Si). ^{13}C NMR spectrum, δ_C, ppm: 77.85 d (C^1, $^1J_{PC}$ 171.2 Hz), 130.91 d (C^2, $^2J_{PC}$ 5.3 Hz), 135.61 d (C^3, $^3J_{PC}$ 4 Hz), 133.56 (C^4), 127.30 and 125.04 (C^5, C^6), 130.34 (C^7), 0.23 (Me_3Si). ^{31}P NMR spectrum: δ_P –6.80 ppm. Found, %: C 39.43; H 5.72. $C_{13}H_{23}O_6PSSi_2$. Calculated, %: C 39.58; 5.88.

The fraction boiling at 90–110°C (1 mm Hg) contains tris(trimethylsilyl) phosphate (δ_P –26.01 ppm). Before the distillation the reaction mixture contained compound **V** [δ 6.15 ppm (d.d, C^1H, $^2J_{PH}$ 14.8, $^3J_{PH}$ 10 Hz); δ_C 69.90 ppm (d.d, C^1, $^1J_{PC}$ 179.5, $^3J_{PC}$ 6.6 Hz); δ_P –1.76 ppm (d, P^1, $^3J_{PP}$ 41.6 Hz) and –19.66 ppm (d, P^2, $^3J_{PP}$ 41.6 Hz)].

Diethyl (1,1-dioxido-3*H*-2,1-benzoxathiol-3-yl)phosphonate (VIII). Yield 47%, bp 133°C (1 mm Hg). ^1H NMR spectrum, δ, ppm: 5.79 d (C^1H, $^2J_{PH}$ 8.1 Hz), 7.4–7.9 m (C_6H_4), 3.7–3.9 m ($2CH_2O$), 1.1–1.3 m ($2CH_3$). ^{13}C NMR spectrum, δ_C, ppm: 77.15 d (C^1, $^1J_{PC}$ 165.3 Hz), 130.78 d (C^2, $^2J_{PC}$ 5.2 Hz), 132.30 d (C^3, $^3J_{PC}$ 4.3 Hz), 133.95 (C^4), 121.63 and 124.79 (C^5, C^6), 130.57 (C^7), 64.61 d and 64.30 d ($2CH_2OP$, $^2J_{PC}$ 7 Hz), 15.92 d (CH_3, $^3J_{PC}$ 5.9 Hz). ^{31}P NMR spectrum: δ_P 11.11 ppm. Found, %: C 42.94; H 4.87. $C_{11}H_{15}O_6PS$. Calculated, %: C 43.14; 4.94.

The fraction boiling at 80–100°C (1 mm Hg) contains diethyl trimethylsilyl phosphate (δ_P –9.46 ppm). Before the distillation of the reaction mixture it contains compound **VII** [δ_H 6.41 ppm (d.d, C^1H, $^2J_{PH}$ 12, $^3J_{PH}$ 11.2 Hz); δ_C 69.20 ppm (d.d, C^1, $^1J_{PC}$ 167.9, $^3J_{PC}$ 5.4 Hz); δ_P 15.73 ppm (d, P^1, $^3J_{PP}$ 29.8 Hz) and –2.42 ppm (d, P^2, $^3J_{PP}$ 29.8 Hz)].

(3-Oxo-1,3-dihydro-2-benzofuran-1,1-diyl)diphosphonic acid (IX). A mixture of 12.7 g of diphosphonate **II** and 50 ml of methanol was heated to boiling. The solvent was distilled off, and the residue was kept in a vacuum at 1 mm Hg for 1 h. Yield 97% (6.2 g), mp > 250°C. ^1H NMR spectrum, δ, ppm: 7.60–8.05 m (C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 84.25 t (C^1, $^1J_{PC}$ 149.3 Hz), 125.15 t (C^2, $^2J_{PC}$ 3.9 Hz), 145.71 (C^3), 134.07 (C^4), 124.78 and 125.03 (C^5, C^6), 129.41 (C^7), 170.83 (C^8). ^{31}P NMR spectrum: δ_P 9.17 ppm. Found, %: C 32.42; H 2.92. $C_8H_8O_8P_2$. Calculated, %: C 32.67; H 2.74.

(1,1-Dioxido-3*H*-2,1-benzoxathiol-3-yl)phosphonic acid (X). Yield 96%, mp 70°C. ^1H NMR spectrum, δ, ppm: 6.07 d (C^1H, $^2J_{PH}$ 8 Hz), 7.6–7.9 m (C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 78.90 d (C^1, $^1J_{PC}$ 162 Hz), 130.73 d (C^2, $^2J_{PC}$ 4.2 Hz), 133.69 d (C^3, $^3J_{PC}$ 4 Hz), 134.06 (C^4), 121.44 and 124.71 (C^5, C^6), 130.47 (C^7). ^{31}P NMR spectrum: δ_P 9.81 ppm. Found, %: C 33.37; H 2.74. $C_7H_7O_6PS$. Calculated, %: C 33.61; H 2.82.

The NMR spectra were obtained on a Bruker Avance 400 spectrometer relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 in D_2O (^{31}P) using $CDCl_3$ (**I–VIII**) and CD_3OD (**IX**, **X**) as the solvents.

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