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> LETTERS TO THE EDITOR

## 3,3-Bis(diethylphosphono)-1(3*H*)-isobenzofuranone and Its Properties

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The reaction of *o*-phthalyl chloride with sodium diethylphosphite was found to give 3,3-bis(diethylphosphono)-1(3*H*)-isobenzofuranones **I**. The reaction evidently proceeds through the formation of keto-phosphonate **A**, which reacts with the second molecule of sodium diethylphosphite in keeping with the mechanism of 1,1-diphosphorylation and results in isobenzofuranone **I** through intramolecular cyclization of intermediate **B**.

The structure of bisphosphonate I was confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR, mass- and IR spectral data, and also by chemical transformations. Thus, the <sup>13</sup>C NMR spectrum contains signal of the carbon atom bonded with two phosphorus atoms as a triplet at 83.26 ppm ( $J_{PC}$  155.9 Hz) proving the presence of 1,1-bis-phosphonate fragment.

Refluxing of 1(3H)-isobenzofuranone with potassium carbonate leads to the ring opening and the elimination of one phosphonate group to give acyclic 1-ketophosphonate II. At the same time refluxing of bisphosphonate I in the concentrated hydrochloric acid do not lead to ring opening, but affords bisphosphinic acid III in high yield, which was earlier obtained by another method [1].



3,3-Bis(diethylphosphono)-1(3H)-isobenzofuranone (I). To diethylphosphite sodium salt obtained from 1.0 g of sodium and 4.7 ml of diethylphosphite, in 40 ml of anhydrous diethyl ether was added 2.9 ml of o-phthaloyl dichloride over 10-15 min at stirring and cooling to -40°C. Then the reaction mixture was stirred for 1-2 h, raising the bath temperature gradually to ambient, after which the mixture was refluxed for 1-2 h. The precipitate was filtered off and washed with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was recrystallized from a mixture ethyl acetate-hexane in the ratio 1:2. Yield 3.2 g (40%). Bisphosphonate I can be also purified by sublimation in a vacuum at 0.1 mm Hg at  $100-120^{\circ}$ C, mp 90-91°C. IR spectrum, v, cm<sup>-1</sup> (CCl<sub>4</sub>): 2988.57 m (CH), 1781.74 s (C=O), 1262.43 s (P=O), 1022.40 s (P–O–C). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (J, Hz): 1.08 t (6H, CH<sub>3</sub>, J<sub>PH</sub> 7); 1.27 t (6H, CH<sub>3</sub>, J<sub>PH</sub> 7); 3.91 m (2H, OCH<sub>2</sub>-trans); 4.02 m (2H, OCH<sub>2</sub>*trans*); 4.26 m (4H, OCH<sub>2</sub>-*cis*); 7.55 d.d (1H, H<sup>5</sup>,  $J_{\rm HH}$ 6, J<sub>HH</sub> 8); 7.69 d.d (1H, H<sup>6</sup>, J<sub>HH</sub> 6, J<sub>HH</sub> 8); 7.88 d (2H,  $H^4+H^7$ ,  $J_{HH}$  6). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 16.09 (CH<sub>3</sub>); 16.32 (CH<sub>3</sub>); 64.82 (CH<sub>2</sub>); 65.14 (OCH<sub>2</sub>); 83.26 t (C<sup>1</sup>,  $J_{PC}$  155.9); 124.85 (C<sup>9</sup>,  $J_{PC}$  3); 124.95 (C<sup>7</sup>); 125.84 (C<sup>4</sup>); 130.04 (C<sup>5</sup>); 134.33 (C<sup>6</sup>); 143.73 (C<sup>8</sup>); 169.14 (C=O). <sup>31</sup>P NMR spectrum,  $\delta_P$ , ppm (CDCl<sub>3</sub>): +10.28. Mass-spectrum, m/e: 406. Found, %: C 47.30, H 5.85, P 14.92. C<sub>16</sub>H<sub>24</sub>O<sub>8</sub>P<sub>2</sub>. Calculated, %: C 47.30; H 5.95; P 15.25.

**2-(Diethylphosphorylcarbonyl)benzoic acid (II).** A mixture of 0.20 g of bisphosphonate I and 0.2 g of potassium carbonate in 2 ml of water was refluxed for 0.5 h to complete release of CO<sub>2</sub>. The solution was cooled with ice water and acidified with diluted sulfuric acid to pH 2-3. *o*-Phthalic acid was filtered off and the filtrate was extracted with ethyl acetate. The solution was concentrated under reduced pressure. The residue was recrystallized from hexane, mp 165°C. Yield 0.12 g (80%). <sup>1</sup>H NMR spectrum [(CD<sub>3</sub>)<sub>2</sub>CO],  $\delta$ , ppm (*J*, Hz): 1.21 t (6H, Me); 3.97 d.q (4H, OCH<sub>2</sub>, *J*<sub>PH</sub> 7, *J*<sub>HH</sub> 7); 6.64 s (1H, CO<sub>2</sub>H); 7.63 t (1H, H<sup>5</sup>, *J*<sub>HH</sub> 6); 7.69 d.d (1H, H<sup>7</sup>, *J*<sub>HH</sub> 6); 7.76 d (2H, H<sup>4</sup>, H<sup>7</sup>, *J*<sub>HH</sub> 6). <sup>31</sup>P NMR spectrum,  $\delta_P$ , ppm (CDCl<sub>3</sub>): +1.19.

**3-Oxo-1,1(3***H***)-isobenzofurandiphosphonic acid (III)**. A solution of 0.2 g of bisphosphonate II in 1 ml of concentrated hydrochloric acid was refluxed for 3–4 h to complete release of ethyl chloride, adding 1 ml of hydrochloric acid every hour. Then the solution was concentrated in a vacuum. The residue was recrystallized from ethyl acetate. Yield 0.12 g (82.9%), mp > 260°C. The <sup>1</sup>H and <sup>31</sup>P NMR spectra data and melting point correspond to published data [2]. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm (*J*, Hz): 7.57 d.d (1H, H<sup>5</sup>, *J*<sub>HH</sub> 7); 7.75 d.d (1H, H<sup>7</sup>, *J* 6); 7.80 d (2H, H<sup>4</sup>, H<sup>7</sup>, *J*<sub>HH</sub> 7). <sup>31</sup>P NMR spectrum,  $\delta_P$ , ppm (DMSO-*d*<sub>6</sub>): +8.02.

The NMR spectra were recorded on a Varian-300 instrument relative to internal TMS ( ${}^{1}$ H,  ${}^{13}$ C) and 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O ( ${}^{31}$ P).

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