ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 1, pp. 155–156. © Pleiades Publishing, Ltd., 2008. Original Russian Text © M.A. Pudovik, L.K. Kibardina, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 1, pp. 163–164.

> LETTERS TO THE EDITOR

## Synthesis of 1,3,4-Diazaphospholidine by the Reaction of Phenyl (Chloromethyl)phosphonoisocyanatidate with Diphenyl [Phenyl(phenylamino)methyl]phosphonate

M. A. Pudovik and L. K. Kibardina

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Akad. Arbuzova 8, Kazan, Tatarstan, 420088 Russia e-mail: pudovik@iopc.knc.ru

Received July 17, 2007

**DOI:** 10.1134/S1070363208010301

The chemistry of  $\alpha$ -aminoalkylphosphonates has progressed over the past decade. Thus, methods of their synthesis have been developed and improved [1], and the biologic activity of these compounds has been studied. Much effort has been directed to chemical modification of  $\alpha$ -aminophosphonates [2]. It is known that in the presence of triethylamine as catalyst these compounds can add to alkyl iso(thio)cyanates with formation of N,N-disubstituted (thio)ureas. The latter are stable compounds which undergo cyclization into 1,4,2-diazaphospholidines only under rigid conditions in the presence of 1,4-diazabicyclo[2,2,2]octane as catalyst [3]. Proceeding with the development of synthetic approaches to new heterophosphacyclanes with endocyclic P-C bonds on the basis of functional  $\alpha$ -substituted alkylphosphonates [4, 5], we explored the reactions of diphenyl  $\alpha$ -(phenylamino)benzylphosphonate I with aromatic and phosphorylated iso-(thio)cyanates. We found that phosphonate I reacts with phenyl isocyanate and phenyl isothiocyanate neither under heating nor in the presence of any catalysts (such as 1,4-diazabicyclo[2,2,2]octane and triethylamine), probably due to reduced basicity of the nitrogen atom in this compound. We succeeded in accomplishing this reaction with a more active phosphorylated isocyanate II. The reaction gave diazaphospholidine V and chloromethylphosphonate VI and occurred by the following scheme involving intermediate formation of urea III and its cyclization into phospholidine IV with phenol liberation. Subsequent phenolysis of heterocycle IV results in P-N bond rupture and formation of the final products.



According to the <sup>1</sup>H NMR spectra of the reaction mixture, phosphpholidine V consists of a mixture of two diastereomers in a 76:24 ratio. The composition and structure of product V were confirmed by means of high-resolution mass spectrometry.

**1,5-Diphenyl-4-phenoxy-1,3,4** $\lambda^5$ **-diazaphospholidin-2-one 4-oxide (V).** A mixture of 7.06 g of phosphonate I and 3.76 g of isocyanate II in 20 ml of anhydrous chloroform was heated at 70°C for 3 h. One day later, 3.2 g (44%) of compound V was separated, mp 201–203°C. IR spectrum (KBr), v, cm<sup>-1</sup>: 1197 (POPh), 1258 (P=O), 1589 (Ph), 1695 (C=O), 3100– 3230 (NH). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 5.11 d (1H, PCH, <sup>2</sup>*J*<sub>PH</sub> 19.5), 5.46 d (1H, PCH, <sup>2</sup>*J*<sub>PH</sub> 19.5), 7.40 m (15H, Ph). <sup>31</sup>P NMR spectrum,  $\delta_{\rm P}$ , ppm: 18.86. Mass spectrum, *m/z*: 364.2 [*M*]<sup>+</sup>. Found, %: C 65.47; H 4.61; N 7.28; P 8.18. C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>P. Calculated, %: C 65.93; H 4.67; N 7.69; P 8.51. Distillation of the filtrate gave 1.67 g (35%) of phosphonate **VI**, bp 90°C (0.02 mm Hg), <sup>31</sup>P NMR spectrum:  $\delta_{\rm P}$  39.20 ppm [6].

The IR spectrum was recorded on a UR-20 spectrometer in the range of 400–3600 cm<sup>-1</sup> in mineral oil. The <sup>1</sup>1H NMR spectrum was obtained on a Bruker WM-250 instrument at 250.132 MHz against internal TMS. The <sup>31</sup>P NMR spectra were recorded on a Bruker MSL-400 Fourier spectrometer at 100.62 MHz. The mass spectrum was registered on a Finnigan MAT TRACE MS instrument, ionizing energy 70 eV, ion source temperature 200°C.

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 06-03-32085).

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