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LETTERS TO THE EDITOR

First Example of Phosphorylation of Macrocyclic Azomethine with Secondary Phosphine Oxides

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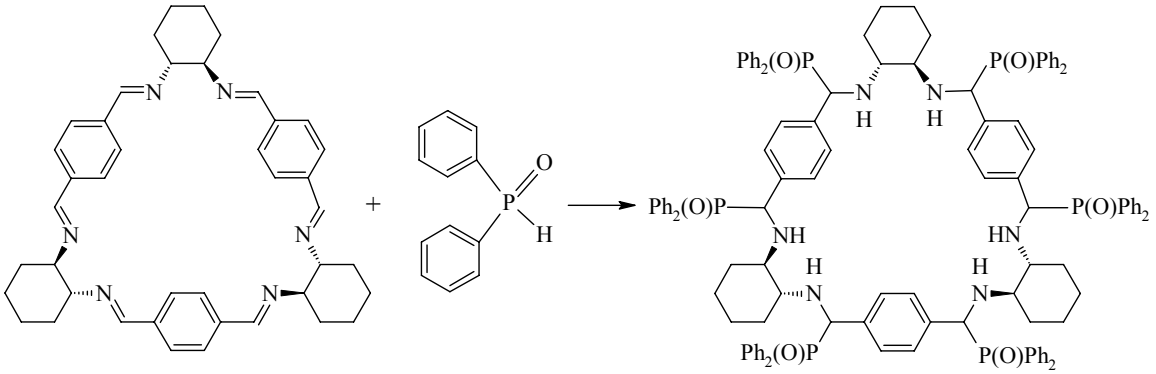
Macrocyclic azomethines are classical *host* molecules of supramolecular systems [1]. Broad prospects for their use in this capacity have resulted from the development of template-free methods of the synthesis of such compounds [2]. In the last decade, the compounds with different ring sizes, various number of the C=N bonds, structure of hydrocarbon moiety (aliphatic, cycloaliphatic, or aromatic) in the ring have been obtained.

One of the most important transformations in organophosphorus chemistry is Pudovik reaction consisting in the addition of hydrophosphoryl compounds to multiple bonds. The addition to the C=N bond leads to the formation of α-aminophosphoryl compounds possessing unique biologically active properties and complexing ability [3].

In this regard, it seemed appropriate to perform the phosphorylation of macrocyclic Schiff bases to produce new compounds, in which the nitrogen atom is a part of a heterocycle, and the phosphoryl group bonded to the adjacent carbon atom is exocyclic. Hitherto such compounds have not been synthesized and used as *hosts* for the creation of supramolecular systems. At the same time it is known that aminophosphoryl compounds containing only one P(O)–C–NH group show high efficiency and selectivity in the solvent extraction processes of metal ions and mineral acids, and also in the membrane transport of organic and mineral acidic substrates [3]. These properties are largely conditioned by the ability of aminophosphoryl group to form five-membered chelate structures. In macrocyclic aminophosphoryl compounds these properties may be significantly expanded and enhanced through a combination of the chelate and macrocyclic effects, which are known to increase significantly the thermodynamic stability of the *host-guest* complex.

In this work, we first carried out the phosphorylation of macrocyclic azomethine with secondary phosphine oxides by an example of hexaimine **I** obtained via [3+3]-cyclization of terephthalaldehyde and 1,2-diaminocyclohexane. Diphenylphosphine oxide **II** was used as a secondary phosphine oxide. The reaction



I **II** **III**

was performed under prolonged reflux of the reaction mixture at a ratio azomethine : dichloromethane : diphenylphosphine oxide = 1 : 6.

The reaction progress was monitored by decrease in the signal intensity of diphenylphosphine oxide in the ^{31}P NMR spectrum (δ_P 21.3 ppm, $^1J_{PH}$ 482 Hz). It should be noted that adding diphenylphisphine oxide to all C=N bonds requires prolonged heating; 95% conversion of the starting organophosphorus compound was achieved in 30 h.

The structure of the obtained α-aminophosphoryl macrocyclic product **III** containing six $P(O)Ph_2$ groups on the macrocycle rim was confirmed by IR, ^1H, ^{13}C, ^{31}P NMR spectroscopy and mass spectrometry. Thus, the IR spectrum contains strong absorption bands of NH (3428 cm^{-1}) and P=O groups (1190 cm^{-1}). In the ^{31}P NMR spectrum there are two signals of equal intensity at 31.1 and 31.6 ppm characteristic of the tertiary phosphine with two phenyl groups at the phosphorus atom and pointing to a different spatial arrangement of these groups with respect to the ring fragments. ^1H NMR spectrum contains broad signals owing to large molecular weight of **III**. The spectrum contains characteristic signal of the methine protons of P(O)CH groups at 4.6 ppm. The signals of methine protons of cyclohexane ring were observed in the range of 2.1–2.4 ppm that differs from their position in the spectrum of the starting hexaimine (δ 3.4 ppm). The protons of methylene groups resonate as multiplets in the range of 1.2–1.6 ppm. In the ^{13}C NMR spectrum there are the signals of the carbon atoms of P(O)CH (δ_C 58.7, 61.0 ppm), CH_2 (δ_C 24.4, 29.6, 33.1 ppm) and NHCH groups (δ_C 54.1, 56.9 ppm), of the benzene rings at 128.3–132.6 ppm and no signals of the carbon atoms of the C=N group of hexaimine **I** (δ_C 160.4 ppm).

The mass spectrum of compound **III** contains a peak with *m*/*z* 1872.7638 corresponding to the ion $[M - Na]^+$ and confirming the molecular weight of the nitrogen-containing macrocycle with six diphenylphosphine groups. There are also peaks at *m*/*z* 1670.6935, 1467.6256, 1265.5615, 1061.6718, 849.5355, and 637.4048 corresponding to the fragments with split-off one, two, three, four, five, and six diphenylphosphine groups, respectively.

Hexaimine **I** was obtained by reacting terephthalaldehyde (Acros Organics, 98%) with 1,2-diaminocyclohexane (Acros Organics, 98%, a mixture of *cis*- and *trans*-isomers) according to [4] at an increased reaction time. Diphenylphosphine oxide **II** was obtained by hydrolysis of diphenylchlorophosphine (Acros Organics, 98%) with 1 N hydrochloric acid under argon atmosphere [5]. Methylene chloride was purchased from JSC "Vekton" (purum, TU 2631-019-44493179-98).

Compound (III). A mixture of 2.02 g (10 mmol) of diphenylphosphine oxide **II** in 5 mL of anhydrous methylene chloride and 1.05 g (1.66 mmol) of hexaimine **I** in 17 mL of methylene chloride was refluxed for 35 h under argon. Then the solvent was removed on a rotary evaporator. Yield 3.03 g (98.6%), a yellowish cream solid, mp > 230°C. IR spectrum, ν, cm^{-1}: 3428 (NH), 1190 (P=O). ^1H NMR spectrum, δ, ppm: 1.2–1.6 m (12H, CH_2), 2.1–2.4 m (6H, $NCH_{cyclohexyl}$), 4.6 m (6H, PCH), 6.8–8.0 m (72H, Ar). ^{13}C NMR spectrum, δ_C, ppm: 24.4, 29.6, 33.1 ($12CH_2$); 54.1, 56.9 ($6NCH_{cyclohexyl}$); 58.7, 61.0 (6PCH), 128.3–132.6 (Ar). ^{31}P NMR spectrum, δ_P, ppm: 31.1, 31.6. Found, %: C 73.87; H 6.42; N 4.51; P 9.78. $C_{114}H_{114}N_6O_6P_6$. Calculated, %: C 74.01; H 6.21; N 4.54; P 10.05.

^1H, ^{13}C and ^{31}P NMR spectra ($CDCl_3$) were recorded on a Bruker Avance-400 spectrometer operating at 400.13, 100.61, and 161.98 MHz, respectively. ^{31}P chemical shifts were measured with respect to 85% H_3PO_4. IR spectrum was taken on a Shimadzu FTIR-8400S instrument from KBr pellets. Mass spectrum (ESI) was obtained on a Bruker Customer Microtof 10223 instrument using methanol as solvent. Elemental analysis was performed on an automated CHNS-analyzer Vario Microcube Elementar; phosphorus content was determined by spectrophotometry.

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