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LETTERS TO THE EDITOR

Phosphacyclanes in Reactions of Bis(*ortho*-formylphenyl)phenylthioxophosphonate with Diamines

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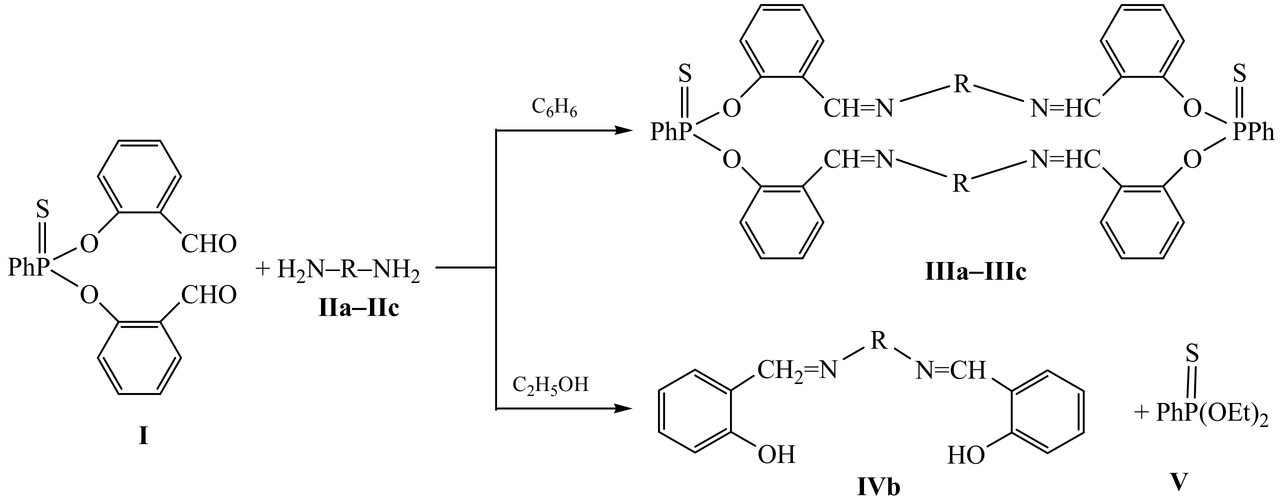
Phosphorus-containing macrocycles are widely used in supramolecular chemistry for studying the molecular recognition processes and complex formation [1–4]. Macromolecules containing azomethine fragments, which are usually involved into complex formation, are of particular interest. As a rule, their synthesis is carried out by reacting hydrazides of thiophosphonic and phosphonic acids with dialdehydes [5–8].

We prepared macrocycles containing phosphorus atoms and azomethine fragments via the reaction of bis(*o*-formylphenyl)phenylthioxophosphonate **I** with aromatic diamines **IIa–IIc** in benzene under heating. When the reaction was performed in ethanol, bisazomethine **IVb** and diethylthioxophenylphosphonate **V** were obtained. Apparently, this was due to ethanolysis of macrocycle **IIIb**. However, it is not improbable that the formation of **IVb** is caused by the reaction of thiophosphonates with ethanol to give salicylaldehyde, which reacts with diamines. A possibility of dialdehyde **I** ethanolysis under heating was found in a special experiment. The starting

Scheme 1.



R = C_6H_4-*para* (**a**), $C_6H_4CH_2C_6H_4$-*para* (**b**), $(CH_2)_4$ (**c**).

dialdehyde **I** was obtained by reacting phenyldichlorothiophosphonate with salicylaldehyde in the presence of a base (Scheme 1).

The composition and structures of the reaction products were confirmed by elemental analysis, mass spectrometry, IR, ^{1}H and ^{31}P NMR spectroscopy.

Bis(*o*-formylphenyl)phenylthioxophosphonate (I). To a solution of 4.9 g of salicylaldehyde and 4.1 g of triethylamine in 50 mL of diethyl ether was added dropwise a solution of 4.2 g of phenyldichlorothioxophosphonate. After 24 h the precipitated triethylamine hydrochloride was filtered off. Next, the solvent was removed, and the residue was chromatographed on silica gel eluting with a hexane-–ethyl acetate mixture (2 : 1). Yield 4.9 g (66%), mp 72°C. ^{31}P NMR spectrum: δ_P 86.53 ppm. Mass spectrum (MALDI-TOF), *m/z*: 421 $[M + K]^+$. Found, %: P 8.59; S 7.94. $C_{20}H_{15}O_4PS$. Calculated, %: P 8.11; S 8.37.

2,12-Dithioxa-2,12-diphenyl-2,12-diphospha-1,3,-11,13-tetraoxa-6,8,16,18-tetraaza-4,10,14,20-tetra(1,2)-phentylene-7,17-bis(1,4)phenylenecyclocosaphan-5,8,15,18-tetraene (IIIa). A mixture of 1.9 g of aldehyde **I**, 0.54 g of diamine **IIa**, and 15 mL of benzene was refluxed for 1 h with water separation. The solvent was removed, and the residue was recrystallized from methylene chloride. Yield 1.51 g (67%), mp 123–125°C. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{31}P NMR spectrum (DMSO-d_6): δ_P 85.33 ppm. Mass spectrum (MALDI-TOF), *m/z*: 910 $[M + 1]^+$. Found, %: P 6.83; S 7.17. $C_{50}H_{38}O_4P_2S_2$. Calculated, %: P 7.06; S 7.10.

2,14-Dithioxa-2,14-diphenyl-2,14-diphospha-1,3,13,15-tetraoxa-6,10,18,22-tetraaza-4,12,16,24-tetra(1,2)phenylene-7,9,19,21-tetra(1,4)phenylene-cyclocosaphan-5,10,17,22-tetraene (IIIb). A mixture of 2.4 g of aldehyde **I**, 1.24 g of diamine **IIb** and 20 mL of benzene was refluxed for 1 h with water separation. The solvent was removed, and the residue was treated with petroleum ether. After 12 h, the precipitated product was separated. Yield 2.7 g (78%), mp 138–140°C. IR spectrum, ν, cm^{-1}: 1618 (C=N). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 3.85 br.s (4H), 8.45 s (4H). ^{31}P NMR spectrum (DMSO-d_6): δ_P 85.01 ppm. Mass spectrum (MALDI-TOF), *m/z*: 1089 $[M + H]^+$. Found, %: N 4.87; P 5.74; S 5.59. $C_{66}H_{50}N_4O_4P_2S_2$. Calculated, %: N 5.14; P 5.69; S 5.88.

2,15-Dithioxa-2,15-diphenyl-2,15-diphospha-1,3,14,16-tetraoxa-6,11,19,24-tetraaza-4,13,17,26-tetra(1,2)phenylenecyclohexacosaphan-5,11,18,24-tetraene (IIIc). A mixture of 3.8 g of aldehyde **I**, 0.88 g of diamine **IIc**, and 30 mL of benzene was heated for 0.5 h at 60°C. The solvent was removed, and the residue was washed with cold petroleum ether. Yield 6.6 g (77%). IR spectrum, ν, cm^{-1}: 1621 (C=N). ^{31}P NMR spectrum (DMSO-d_6): δ_P 84.35 ppm. Mass spectrum (MALDI-TOF), *m/z*: 869 $[M + H]^+$.

Reaction of dialdehyde I with 4,4'-diaminodiphenylmethane IIb in ethanol. A mixture of 0.7 g of **I**, 0.4 g of diamine **IIb** and 20 mL of ethanol was heated for 1 h at 60°C to yield 0.43 g (89%) of **IVb** (mp 221°C [9]) and 0.34 g (81%) of phosphonate **V**. ^{31}P NMR spectrum (DMSO-d_6): δ_P 85.25 ppm.

The IR spectra were recorded on a Bruker Vector-22 spectrometer in the range of 400–3600 cm^{-1} from KBr pellets. The ^{1}H NMR spectra were registered on a Bruker Avance 600 instrument operating at 600.13 MHz relative to the signals of residual protons of the deuterated solvent (CDCl$_3$). The ^{31}P NMR spectra were taken on a Bruker MSL-400 Fourier spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were obtained on a Ultraflex III TOF/TOF Bruker instrument using *p*-nitroaniline as a matrix.

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