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LETTERS TO THE EDITOR

O,O-Diphosphorylated Azomethines

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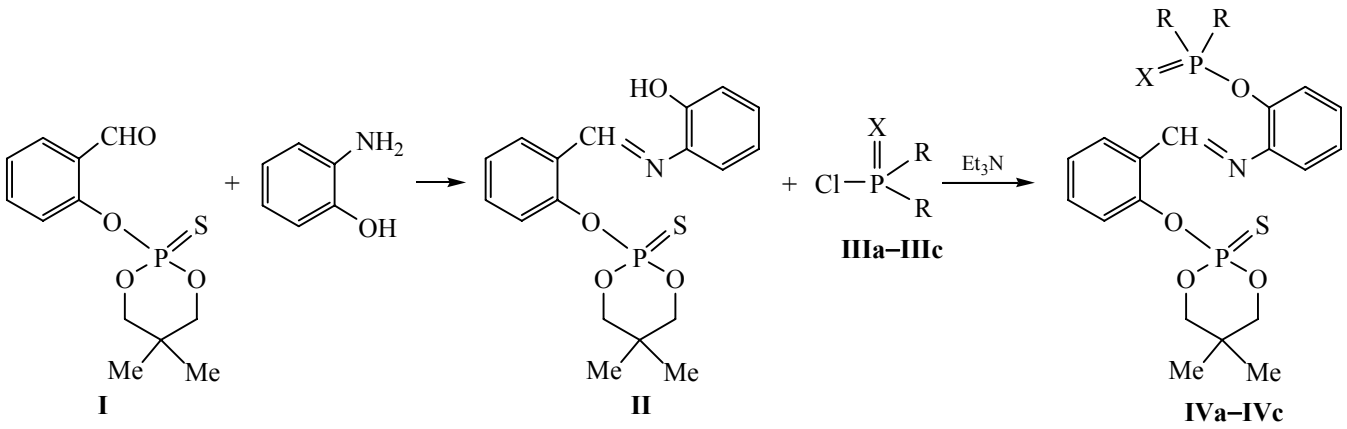
Hydroxyl-containing azomethines and the derived chelating agents have recently attracted increased interest. A wide range of metals including biogenic Zn(II), Cu(II), Cd(II), Co(II), Ni(II), Fe(III), Pd(II), Zr(IV), U(II), and others have been used to obtain metal complexes, applicable as catalysts for enantioselective epoxidation of non-functionalized olefins and allyl alcohols [1–4] as well as chemosensors of aluminum ions [5] and showing magnetic properties [6].

A number of aldimines and metal complexes have shown pronounced fungicidal, antibacterial, and antimicrobial [7, 8] activity. However, we have failed to find any information on the *O*-phosphorylated azomethines which are of definite interest as ligands for metal complexes design. In this work we obtained azomethine **II** via reaction of the phosphorylated salicylic aldehyde **I** with *ortho*-aminophenol. Further phosphorylation of **II** with P(IV) acid chlorides **IIIa**–**IIIc** in the presence of bases resulted in diphosphorylated derivatives **IVa**–**IVc**, promising tridentate ligands. Compounds **IVa**–**IVc** were crystalline substances, their composition and structure were confirmed by elemental analysis, mass spectrometry, and IR and NMR spectroscopy (Scheme 1).

2-Thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinyloxybenzal-*ortho*-aminophenol (II). A mixture of 0.36 g

Scheme 1.



R = –$OCH_2CMe_2CH_2O$–, X = S(**a**); R= –$OCH_2CMe_2CH_2O$–, X = O (**b**); R = Ph, X = S (**c**).

of aldehyde **I**, 0.14 g of aminophenol, and 10 mL of ethanol was refluxed during 2 h. After cooling, the precipitate was filtered off and washed with diethyl ether. Yield 0.34 g (72%), mp 162–165°C. IR spectrum (KBr), ν, cm^{-1}: 1621 (C=N), 3420 (OH). ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 0.98 s (3H, CH_3), 1.32 s (3H, CH_3), 4.09–4.17 m (2H, OCH_2), 4.31–4.35 m (2H, OCH_2), 6.91–7.52 m (8H, Ph), 8.22 s, 8.24 s (1H, PhCH), 9.04 s (OH). ^{31}P NMR spectrum, ($CDCl_3$), δ_P: 55.18 ppm. Mass spectrum, *m*/*z*: 377. Found, %: P 8.15; S 8.41. $C_{18}H_{20}NO_4PS$. Calculated, %: P 8.21; S 8.50.

2-(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzylidene-2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphineoxy)aniline (IVa). A mixture of 0.46 g of imine **II**, 0.08 g of anhydrous potassium carbonate, and 0.24 g of acid chloride **IIIa** in 30 mL of anhydrous acetone was refluxed during 33 h. The precipitate of potassium chloride was separated, the solvent was evaporated, and the residue was washed with diethyl ether. Yield 0.3 g (38%), mp 73–76°C. IR spectrum (KBr), ν, cm^{-1}: 1605 (Ph), 1622 (C=N). ^1H NMR spectrum, [$(CD_3)_2CO$], δ, ppm: 0.94 s (3H, CH_3), 0.99 s (3H, CH_3), 1.30 s (3H, CH_3), 1.34 s (3H, CH_3), 4.07–4.21 m (4H, OCH_2), 4.44–4.60 m (4H, OCH_2), 6.59–7.91 m (8H, Ph), 10.37 s (1H, PhCH). ^{31}P NMR spectrum, [$(CD_3)_2CO$], δ_P, ppm: 55.68, 55.84. Mass spectrum, *m*/*z*: 542. Found, %: C 50.71; H 5.77; N 2.45; P 11.15; S 12.10. $C_{23}H_{29}NO_6P_2S_2$. Calculated, %: C 51.00; H 5.41; N 2.59; P 11.44; S 11.84.

2-(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzylidene-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinyloxy)aniline (IVb). 0.12 g of acid chloride **IIIb** in 2 mL of anhydrous benzene was added to 0.24 g of imine **II** and 0.08 g of triethylamine in 10 mL of anhydrous benzene upon stirring. The mixture was incubated during 12 h at room temperature. The precipitated triethylamine hydrochloride was separated, the solution was evaporated, and the residue was washed with diethyl ether. Yield 0.2 g (61%), mp 53–56°C. IR spectrum (KBr), ν, cm^{-1}: 1599 (Ph), 1623 (C=N). ^1H NMR spectrum, [$(CD_3)_2CO$], δ, ppm: 0.94 s (3H, CH_3), 1.00 s (3H, CH_3), 1.29 s (3H, CH_3), 1.33 s (3H, CH_3), 4.07–4.21 m (4H, OCH_2), 4.44–4.60 m (4H, OCH_2), 6.90–8.42 m (8H, Ph), 9.08 s (1H, PhCH). ^{31}P NMR spectrum, [$(CD_3)_2CO$], δ_P, ppm: 54.72, –21.57. Mass spectrum, *m*/*z*: 526. Found, %: C 52.34; H 5.39; N 2.94; P 11.99; S 5.69. $C_{23}H_{29}NO_7P_2S$. Calculated, %: C 52.56; H 5.57; N 2.67; P 11.79; S 6.10.

2-(5,5-Dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzylidene-2-(diphenylthioxophosphorinyloxy)aniline (IVc). 0.21 g of acid chloride **IIIb** in 2 mL of benzene was added to a suspension of 0.31 g of imine **II** and 0.1 g of triethylamine in 10 mL of anhydrous benzene upon stirring. The mixture was incubated during 4 days. The precipitated triethylamine hydrochloride was separated, the solvent was evaporated, and the precipitate was washed with diethyl ether. Yield 0.4 g (82%), mp 41–45°C. IR spectrum (KBr), ν, cm^{-1}: 1591 (Ph), 1623 (C=N). ^1H NMR spectrum, [$(CD_3)_2CO$], δ, ppm: 0.96 s (3H, CH_3), 1.31 s (3H, CH_3), 4.12–4.17 m (2H, OCH_2), 4.53–4.55 m (2H, OCH_2), 7.14–8.15 m (18H, Ph), 8.74 s (1H, PhCH). ^{31}P NMR spectrum, [$(CD_3)_2CO$], δ_P, ppm: 54.50, 81.99. Mass spectrum, *m*/*z*: 594. Found, %: C 60.41; H 4.77; N 2.45; P 10.45; S 10.69. $C_{30}H_{29}NO_4P_2S_2$. Calculated, %: C 60.69; H 4.93; N 2.36; P 10.44; S10.80.

IR spectra (KBr pellets) were recorded with a Bruker Vector-22 spectrometer at 400–3600 cm^{-1}. ^1H NMR spectra were registered with an Avance 600 spectrometer (600.13 MHz) relative to residual proton signals of the deuterated solvent ($CDCl_3$). ^{31}P NMR spectra were obtained using a Bruker MSL-400 Fourier spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were obtained with a ULTRAFLEX III spectrometer (*para*-nitroaniline as matrix).

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