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LETTERS TO THE EDITOR

Phosphorus-containing Salicylalalkylene(arylene)diamines

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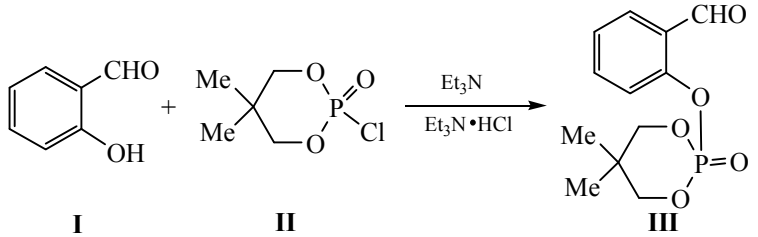
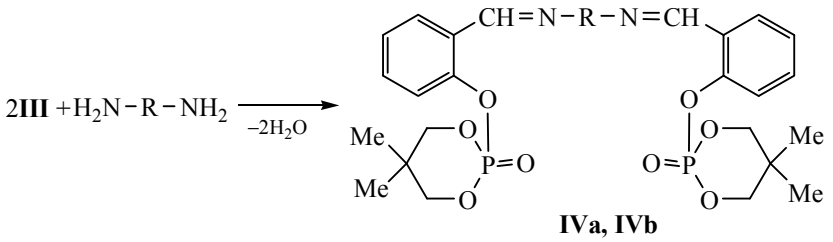
In recent years the metal complex compounds on the basis of hydroxyl diimines and a wide range of the metal salts were intensively studied. The metal complexes of this type showed catalytic properties in various chemical processes [1–6]. Some metal complexes possess a high fungicidal, antibacterial, antimicrobial, and anti-cancer activity [7–12]. The hydroxy-containing bisazomethines are promising starting substances for the synthesis of the pincer phosphorus-containing compounds. The pincer complexes of various types are used in versatile applications, predominantly as the catalysts and biologically active compounds [13]. There are poor data on phosphorylation of the hydroxylated bisazomethines. We developed a method for the synthesis of diphosphorylated diimines including the preliminary preparation of phosphorylated salicylaldehyde **III** via the reaction of salicylaldehyde **I** with cyclic chlorophosphate **II**. Then compound **III** reacts with aliphatic and aromatic diamines to give the phosphorylated diimines **IVa** and **IVb**. The structure of the latter was confirmed by the IR, ^{1}H and ^{31}P NMR spectroscopy, and mass spectrometry; the composition was proved by the elemental analysis data.



I **II** **III**



IVa, IVb

IV: R = $(CH_2)_4$ (**a**); *para*-C_6H_4 (**b**).

The IR spectra of diimines **IVa** and **IVb** contain the absorption bands at 1300 and 1614–1640 cm^{-1} belonging to the phosphoryl and C=N moieties, respectively. The chemical shift of the phosphorus nuclei of compounds **IVa** and **IVb** is characteristic of the phosphate derivatives (δ_P –14 ppm).

2-Oxo-2-(2-formylphenoxy)-(5,5-dimethyl-1,3,2-dioxaphosphorinane (III). To a solution of 2.15 g of salicylaldehyde and 2.61 g of triethylamine in 20 ml of anhydrous benzene was added a solution of 3.26 g of the acid chloride **II** in 10 ml of anhydrous benzene. After 6 days, the precipitated triethylamine hydro-

chloride was filtered off, and the solvent was removed in a vacuum. Yield 2.37 g (91%), viscous substance. IR spectrum (KBr), ν, cm^{-1}: 1602 (Ph), 1695 (C=O). ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 0.95 s (3H, CH_3), 1.32 s (3H, CH_3), 4.08–4.16 m (2H, OCH_2), 4.55 d (2H, OCH_2, $^2J_{HH}$ 11.03), 7.37–7.90 m (4H, Ph), 10.41 s (1H, CH=O). ^{31}P NMR spectrum [$(CD_3)_2CO$]: δ_P –14.60 ppm. Mass spectrum (MALDI-TOF), *m/z* : 613. Found P, %: 11.04. $C_{12}H_{15}O_5P$. Calculated P, %: 11.46.

1,4-Bis[2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinyloxy)benzal]-1,4-diaminobutane (IVa). To a mixture of 0.55 g of aldehyde **III** and 0.80 g of anhydrous magnesium sulfate in 5 ml of anhydrous chloroform was added dropwise 0.09 g of 1,4-butanediamine. After 1 day, magnesium sulfate hydrate was separated. The solvent was removed in a vacuum, and the residue crystallized on standing. Yield 0.17 g (28%), yellow powder, mp 108–111°C. IR spectrum (KBr), ν, cm^{-1}: 1604 (Ph), 1640 (C=N). ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 0.95 s (6H, CH_3), 1.30 s (6H, CH_3), 1.80–1.82 m (4H, CH_2), 3.67–3.72 s (4H, NCH_2), 4.05–4.13 s (4H, OCH_2), 4.43 d (4H, OCH_2, $^2J_{HH}$ 10.0), 7.20–8.03 m (8H, Ph), 8.74 s (2H, CH=N). ^{31}P NMR spectrum [$(CD_3)_2CO$]: δ_P – 14.55 ppm. Mass spectrum (MALDI-TOF), *m/z* : 592. Found, %: N 4.96; P 10.56. $C_{28}H_{38}N_2O_8P_2$. Calculated, %: N 4.73; P10.45.

1,4-Bis[2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinyloxy)benzal]-1,4-diaminobenzene (IVb). To a mixture of 0.43 g of aldehyde **III** and 0.80 g of anhydrous magnesium sulfate in 5 ml of anhydrous ethanol was added 0.09 g of *p*-phenylenediamine. After 1 day, to the reaction mixture was added 5 ml of anhydrous chloroform. Then magnesium sulfate was filtered off, and the solvent was removed in a vacuum. To the residue was added 5 ml of anhydrous diethyl ether, and the resulting precipitate was separated and washed with ether. Yield 0.24 g (49%), yellow powder, mp 248–252°C. IR spectrum (KBr), ν, cm^{-1}: 1600 (Ph), 1614 (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 s (6H, CH_3), 1.33 s (6H, CH_3), 4.02–4.11 m (4H, OCH_2), 4.26–4.30 m (4H, OCH_2), 6.76–8.20 m (12H, Ph), 8.88 s (2H, CH=N). ^{31}P NMR spectrum ($CDCl_3$): δ_P –14.08 ppm. Mass spectrum (MALDI-TOF), *m/z* : 613. Found, %: C 59.03; H 5.57; N 4.41; P 10.13. $C_{30}H_{34}N_2O_8P_2$. Calculated, %: C 58.81; H 5.61; N 4.57; P 10.11.

The IR spectra were recorded on a Bruker Vector-22 spectrometer in the range of 400–3600 cm^{-1} for the dispersion of samples in mineral oil. The ^1H NMR spectra were taken on an Avance 600 instrument (600.13 MHz), the residual protons signals of $CDCl_3$ serving as internal reference. The ^{31}P NMR spectra were registered on a Bruker MSL-400 NMR Fourier spectrometer (100.62 MHz). The MALDI-TOF mass spectra were obtained on a ULTRAFLEX III spectrometer using p-nitroaniline as a matrix.

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