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LETTERS TO THE EDITOR

Synthesis of Thiophosphoryl-Containing Bisazomethines

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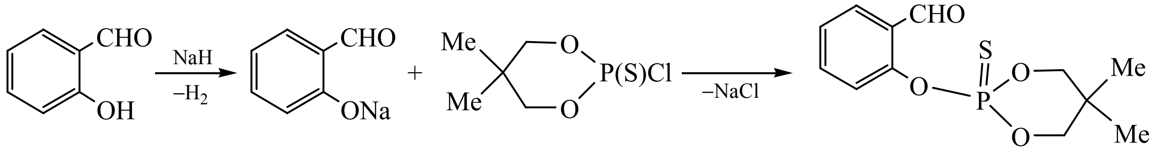
In recent years, the metal complex compounds based on the hydroxyl containing diimines and a wide range of the metal salts attracted much interest. The metal complexes of this type show the catalytic activity in various chemical processes [1–6]. Some metal complexes have a high fungicidal, antibacterial, antimicrobial [7–11], and anti-cancer activity [12]. *O*,*O*-Diphosphorylated bisazomethines are of some interest as the effective tetradentate ligands. The data on these compounds are scarce. The reaction of *O*-thiophosphorylated salicylaldehyde with diamines is the simplest approach to the synthesis of compounds of this type. The phosphorylated aldehyde **III** was obtained in high yield by a sequential reaction of salicylaldehyde with sodium hydride and 2-chloro-2-thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinane **II**.



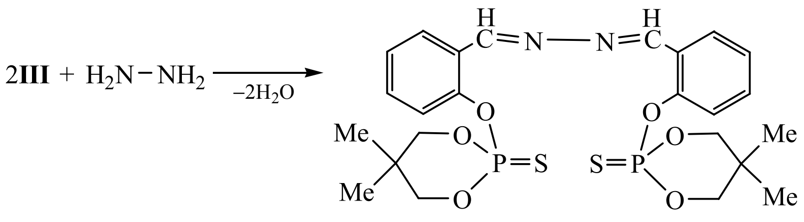
I **II** **III**

According to the XRD data, the bond and torsion angles in the molecule of **III** lie within the values range characteristic of each type of linking. The tetra-coordinated phosphorus atom is part of the six-membered ring, which is in a *chair* conformation. In the crystal of compound **III** there are no any significant intermolecular interactions.

Another method for the synthesis of compound **III** is the reaction of salicylaldehyde **I** with acid chloride **II** in the presence of a base. However, in this case aldehyde **III** was obtained in a lower yield.

$$\mathbf{I} + \mathbf{II} \xrightarrow[-\mathrm{Et_3N{\bullet}HCl}]{\mathrm{Et_3N}} \mathbf{III}$$

The reaction of aldehyde **III** with hydrazine results in the tetradentate ligand **IV** containing a combination of two azomethine and two thiophosphoryl fragments.



IV

2-Thioxo-2-(2-formylphenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane (III). *a*. To a suspension of 0.96 g of sodium hydride in 70 ml of THF at 10°C was added dropwise a solution of 4.87 g of 2-hydroxybenz-aldehyde **I** in 35 ml of THF. The mixture was stirred for 1 h at 20°C. After adding a solution of 8.0 g of chlorothiophosphate **II** in 100 ml of THF, the mixture was heated with stirring under nitrogen atmosphere (24 h, 65°C). After cooling, the precipitate was separated, and the solvent was removed. The residue was purified by the column chromatography on a silica gel (*n*-hexane–diethyl ether, 1:1). Yield 8.9 g (78%), white crystals, mp 82–83°C. IR spectrum, ν, cm^{-1}: 825 (P=S), 1602 (Ph), 1694 (C=O). ^{1}H NMR spectrum, (CDCl$_3$), δ_H, ppm (*J*, Hz): 0.95 s (3H, CH$_3$), 1.32 s (3H, CH$_3$), 4.08 m (2H, OCH$_2$), 4.37 m (2H, OCH$_2$), 7.35 m (2H, CH$_{Ar}$), 7.61 t (1H, CH$_{Ar}$, $^3J_{HH}$ 7.7), 7.92 d (1H, CH$_{Ar}$, $^3J_{HH}$ 8.6), 10.36 s (1H, CHO). ^{31}P NMR spectrum, (CDCl$_3$): δ_P 54.22 ppm. Mass spectrum (MALDI-TOF), *m/z*: 287 $[M + H]^+$. Found, %: C 50.45; H 5.21; P 10.87; S 11.11. $C_{12}H_{15}O_4PS$. Calculated, %: C 50.35; H 5.24; P 10.84; S 11.19.

b. To a mixture of 1.71 g of aldehyde **I** and 1.45 g of triethylamine in 30 ml of anhydrous benzene was added dropwise a solution of 2.81 g of chlorothiophosphate **II** in 10 ml of benzene. The reaction mixture was refluxed for 62 h. After cooling, triethylamine hydrochloride was separated, and the solvent was removed. The residue was purified by the column chromatography on silica gel (eluent methylene chloride–ethanol, 40:1). Yield 1.51 g (38%), mp 81–83°C. IR spectrum, ν, cm^{-1}: 825 (P=S), 1602 (Ph), 1694 (C=O). ^{31}P NMR spectrum, (CDCl$_3$): δ_P 54.24 ppm. Found, %: P 10.77; S 11.06. $C_{12}H_{15}O_4PS$. Calculated, %: P 10.84; S 11.19.

Bis[2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinyloxy)benzal]hydrazine (IV). A mixture of 0.28 g of aldehyde **III** and 0.02 g of hydrazine hydrate in 5 ml of ethanol was refluxed for 1 h. Yield 0.18 g (64%), mp 141–144°C. IR spectrum, ν, cm^{-1}: 827 (P=S), 1602 (Ph), 1630 (C=N). ^{1}H NMR spectrum, (CDCl$_3$), δ_H, ppm (*J*, Hz): 0.94 s (3H, CH$_3$), 1.30 s (3H, CH$_3$), 4.05 d (2H, OCH$_2$, $^2J_{HH}$ 10.9), 4.11 d (2H, OCH$_2$, $^2J_{HH}$ 10.9), 4.27 d (2H, OCH$_2$, $^2J_{HH}$ 6.9), 4.29 d (2H, OCH$_2$, $^2J_{HH}$ 6.9), 7.44 m (8H, CH$_{ar}$), 8.04 s (2H, CH=N). ^{31}P NMR spectrum, (CDCl$_3$): δ_P 54.68 ppm. Mass spectrum (MALDI-TOF), *m/z*: 569 $[M + H]^+$. Found, %: P 11.26; S 11.30. $C_{24}H_{30}N_2O_6P_2S_2$. Calculated, %: P 10.84; S 11.19.

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 an Avance 600 spectrometer in CDC1$_3$ operating at 600.13 MHz. The ^{31}P NMR spectra were recorded on a Bruker MSL-400 Fourier spectrometer (100.62 MHz). The mass spectra (MALDI-TOF) were obtained on a Ultraflex III TOF/TOF Bruker instrument (*p*-nitroaniline matrix). The X-ray diffraction analysis was carried out on a Bruker SMART Apex II diffractometer (graphite monochromator, λMoK_α 0.71073 Å).

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