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LETTERS TO THE EDITOR

Phosphorus-Containing Azomethines Based on Salicylaldehyde and Thiosemicarbazide

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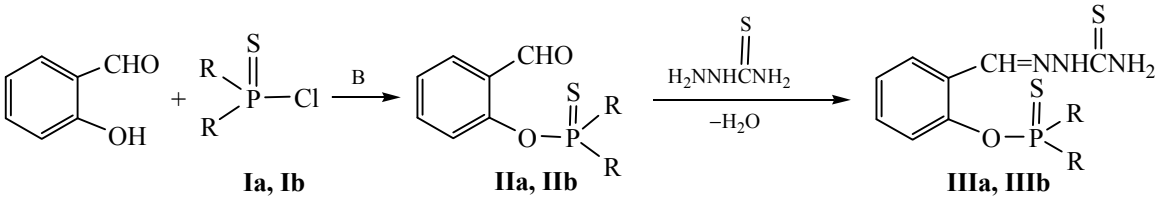
Recently, azomethines derived from aromatic aldehydes and thiosemicarbazide and their metal complex compounds with a wide range of metal salts were intensively studied. Some thiosemicarbazones of aromatic aldehydes possess melanin inhibitory [1] and high antibacterial activity [2]. They can be used as inhibitors of carbon steel in salt water [3], inhibitors of decomposition of cumene hydroperoxide [4] and as components of the high-sensitive copper membranes [5]. Their nickel complexes are effective catalysts for C–C coupling [6]. Some of the copper and nickel complexes showed antibacterial [2], and palladium complexes anti-malarial and anti-tumor properties [7]. Also they are catalysts in the cyclopropanation reactions of unactivated olefins [8].

In our opinion, thiosemicarbazones containing thiophosphoryl, thiocarbonyl, and azomethine moieties can serve as effective tridentate ligands. Synthesis of compounds of this type was performed using thiophosphorylated salicylaldehyde derivatives. The latter were prepared by reacting salicylaldehyde with diphenylchlorothiophosphinate or 2-chloro-1,3,2-dioxaphosphorinane in the presence of a base.



Ia, Ib **IIa, IIb** **IIIa, IIIb**

R = Ph (**a**); R = $OCH_2CMe_2CH_2O$ (**b**).

Compounds **IIa** and **IIb** are crystalline substances, the structure of which was confirmed by a complex of physical methods. Heating of a mixture of **IIa** or **IIb** with thiosemicarbazide in ethanol for 12 h results in the desired product, azomethines **IIIa** or **IIIb**. Structure and composition of the latter were confirmed by the IR, ^1H and ^{31}P NMR spectroscopy, mass spectrometry, X-ray diffraction and elemental analysis.

According to XRD data, compound **IIIb** crystallizes in the space group *P*21/*n*. In the unit cell there are two independent molecules, which differ from each other by reversing the phenyl moiety relative to the double P=S bond: $\angle S^{2A}P^{2A}O^{9A}C^{10A}$ 63.7(4)°, $\angle S^{2B}P^{2B}O^{9B}C^{10B}$ 53.8(3)°. Phosphorus atom has a tetragonal configuration, the six-membered heterocyclic ring was in a *chair* conformation. A crystal contains a water molecule.

Diphenyl 2-formylphenoxythiophosphinate (IIa). To a solution of 1.27 g of salicylaldehyde and 1.05 g of triethylamine in 20 mL of anhydrous benzene was added with stirring 2.63 g of diphenylchlorothiophosphinate. After 12 h the precipitated triethylamine hydrochloride was filtered off. The solvent was removed, and the residue was washed with diethyl

ether. Yield 2.13 g (61%), mp 98–100°C. IR spectrum (KBr), ν, cm^{-1}: 1599 (Ph), 1692 (C=O). ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 7.52–8.15 m (14H, Ph), 10.33 s (1H, PhCH). ^{31}P NMR spectrum [$(CD_3)_2CO$]: δ_P 85.26 ppm. Mass spectrum, *m*/*z*: 338. Found, %: P 9.27; S 9.21. $C_{19}H_{15}O_2PS$. Calculated, %: P 9.16; S 9.48.

2-Thioxo-2-(2-formylphenoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane (IIb). 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 chlorothiophosphinate **II** in 10 mL of benzene. After 12 h the precipitated triethylamine hydrochloride was filtered off. The solvent was removed, the residue was purified by column chromatography (silica gel, eluent a methylene chloride–ethanol mixture, 40:1). Yield 1.51 g (38%), mp 81–83°C. IR spectrum (KBr), ν, cm^{-1}: 825 (P=S), 1602 (Ph), 1694 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95 s (3H, CH_3), 1.32 s (3H, CH_3), 4.08 m (2H, OCH_2), 4.32–4.42 m (2H, OCH_2), 7.30–7.48 m (2H, CH_{Ar}), 7.61 t (1H, CH_{Ar}, $^3J_{HH}$ 7.74), 7.92 d (1H, CH_{Ar}, $^3J_{HH}$ 8.68), 10.36 s (1H, CHO). ^{31}P NMR spectrum ($CDCl_3$): δ_P 54.27 ppm. Mass spectrum (MALDI-TOF), *m*/*z*: 287 $[M + H]^+$. Found, %: C 50.55; H 5.29; P 10.91; S 11.08. $C_{12}H_{15}O_4PS$. Calculated, %: C 50.35; H 5.24; P 10.84; S 11.19.

2-Diphenylthiophosphinyloxybenzalthio-semicarbazide (IIIa). A mixture of 0.25 g of aldehyde **I**, 0.07 g of thiosemicarbazide and 5 mL of anhydrous ethanol was heated at reflux for 6 h. After cooling the precipitate was separated. Yield 0.25 g (83%), mp 198–201°C. IR spectrum (KBr), ν, cm^{-1}: 1598 (Ph), 1603 (C=N), 3109, 3164, 3250, 3342 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.05–8.1 m (14H, Ph), 8.49 s (1H, PhCH). ^{31}P NMR spectrum [$(CD_3)_2CO$]: δ_P 83.35 ppm. Mass spectrum, *m*/*z*: 412. Found, %: P 7.42; S 15.38. $C_{20}H_{18}N_3OPS_2$. Calculated, %: P 7.53; S 15.59.

2-Thioxo-1,3,2-dioxaphosphorinyloxybenzalthio-semicarbazide (IIIb). A mixture of 0.32 g of aldehyde **II**, 0.1 g of thiosemicarbazide in 5 mL of ethanol was heated at reflux for 0.5 h. After cooling the precipitate was separated. Yield 0.32 g (80%), mp 209–212°C. IR spectrum (KBr), ν, cm^{-1}: 1600 (Ph), 1603 (C=N), 3162, 3266, 3376, 3411 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 s (3H, CH_3), 1.33 s (3H, CH_3), 4.10–4.19 m (2H, OCH_2), 4.51–4.55 m (2H, OCH_2), 7.26–7.48 m (4H, Ph), 8.48 s (1H, PhCH). ^{31}P NMR spectrum [$(CD_3)_2CO$]: δ_P 54.10 ppm. Mass spectrum, *m*/*z*: 359. Found, %: P 8.33; S 17.40. $C_{13}H_{18}N_3O_3PS_2$. Calculated, %: P 8.62; S 17.84.

The IR spectra were recorded on a Bruker Vector-22 spectrometer in the range of 400–3600 cm^{-1} from KBr pellets. ^1H NMR spectra were registered on an Avance 600 instrument operating at 600.13 MHz relative to the residual proton signals of the deuterated solvents ($CDCl_3$). ^{31}P NMR spectra were taken on a Bruker MSL-400 FT-NMR spectrometer (100.62 MHz). Mass spectrum MALDI-TOF was obtained on a Ultraflex III TOF/TOF Bruker instrument (*p*-nitroaniline matrix). Electron impact mass spectra were recorded on a DFS Thermo Electron Corporation instrument (ionizing electron energy 70 eV, ion source temperature 280°C, direct input of the sample into the source, evaporator temperature varied from 50 to 350°C).

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