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LETTERS TO THE EDITOR

Azomethines Based on *O*-Phosphorylated Derivatives of Salicylaldehyde and *orto-*/*para*-Aminophenols

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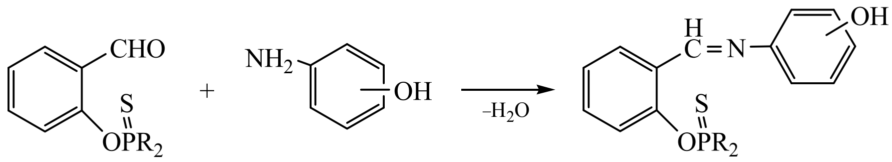
In recent years azomethines derived from Salicylaldehyde and aminophenols and their metal complexes attract increasing interest of researchers. Some of these compounds possess high antimicrobial, antibacterial, tuberculocidal, and antioxidant activities [1–6], catalyze the olefins epoxidation [7] and inhibit steel corrosion [8]. In view of the above, their derivatives containing thiophosphoryl group instead of hydroxy group may be promising tridentate ligands. Synthesis of Schiff bases of this type was carried out by reacting salicylaldehyde thiophosphorylated derivatives with *ortho*- and *para*-aminophenols. Compounds **Ia** and **Ib** were obtained via reaction of salicylaldehyde with diphenylchlorothiophosphinate and 2-chloro-2-thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinane [9] in the presence of a base.



Ia, Ib **IIa, IIb** **IIIa–IIId**

I, R = Ph (**a**); $OCH_2CMe_2CH_2O$ (**b**); **II**, OH-*ortho* (**a**); OH-*para* (**b**); **III**, R = Ph, OH-*ortho* (**a**); R = Ph, OH-*para* (**b**); R = $OCH_2CMe_2CH_2O$, OH-*ortho* (**c**); R = $OCH_2CMe_2CH_2O$, OH-*para* (**d**).

The structure and composition of the obtained imines were confirmed by IR, ^1H and ^{31}P NMR spectra, mass spectrometry, and elemental analysis. According to the ^1H NMR spectral data, the desired products **IIIa**–**IIId** were obtained as mixtures of *syn*/*anti*-isomers.

Diphenylthiophosphinyloxybenzal-2-*ortho*-aminophenol (IIIa). A mixture of 0.8 g of aldehyde **Ia**, 0.26 g of aminophenol **IIa** and 5 mL of ethanol was refluxed for 2 h. After cooling the precipitate was filtered off. Yield 0.8 g (79%), mp 183–186°C. IR spectrum (KBr), ν, cm^{-1}: 1622 (C=N), 3311 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.79–8.06 m (18H, Ph), 8.22 s and 8.24 s (1H, PhCH), 8.91 s (1H, OH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 84.60 ppm. Mass spectrum, *m*/*z*: 430. Found, %: P 7.31; S 7.39. $C_{25}H_{20}NO_2PS$. Calculated, %: P 7.21; S 7.47.

Diphenylthiophosphinyloxybenzal-2-*para*-aminophenol (IIIb) was prepared similarly from a mixture of 0.22 g of aldehyde **Ia** and 0.07 g of aminophenol **IIb** in 5 mL of ethanol. After cooling, the solvent was removed, and 10 mL of hexane was added to the residue. Then the precipitate was filtered off. Yield 0.23 g (82%), mp 138–141°C. IR spectrum (KBr), ν, cm^{-1}: 1619 (C=N), 3325 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.78–8.03 m (18H, Ph), 8.19 s and 8.21 s (1H, PhCH), 8.69 s (OH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 84.51 ppm. Mass spectrum, *m*/*z*: 430. Found, %: P 7.31; S 7.52. $C_{25}H_{20}NO_2PS$. Calculated, %: P 7.21; S 7.47.

2-Thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinylbenzal-*ortho*-aminophenol (IIIc) was prepared similarly from a mixture of 0.36 g of aldehyde **Ib** and 0.14 g of aminophenol **IIa** in 10 mL of ethanol. Yield 0.34 g (72%), mp 162–165°C. IR spectrum (KBr), ν, cm^{-1}: 1621 (C=N), 3420 (OH). ^{1}H 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 and 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-Thioxo-5,5-dimethyl-1,3,2-dioxaphosphorinylbenzal-*para*-aminophenol (IIId) was prepared similarly from a mixture 0.2 g of aldehyde **Ib** and 0.08 g of aminophenol **IIb** in 10 mL of ethanol. Yield 0.24 g (92%), mp 214–217°C. IR spectrum (KBr), ν, cm^{-1}: 1616 (C=N), 3340 (OH). ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 1.00 s (3H, CH_3), 1.37 s (3H, CH_3), 4.16–4.24 m (2H, OCH_2), 4.57–4.60 m (2H, OCH_2), 6.95–7.65 m (8H, Ph), 8.87 s (1H, PhCH), 9.39 s (OH). ^{31}P NMR spectrum [$(CD_3)_2SO$]: δ_P 54.75 ppm. Mass spectrum, *m*/*z*: 377. Found, %: P 8.13; S 8.61. $C_{18}H_{20}NO_4PS$. Calculated, %: P 8.21; S 8.50.

IR spectra were recorded on a Bruker Vector-22 spectrometer from KBr pellets. ^{1}H NMR spectra were registered on an Avance 600 instrument operating at 600.13 MHz using as internal reference the signals of residual protons of the deuterated solvent ($CDCl_3$). ^{31}P NMR spectra were taken on a Bruker MSL-400 NMR Fourier spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were obtained on a Ultraflex III TOF/TOF Bruker instrument (matrix *p*-nitroaniline).

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