ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2283–2285. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © R.Kh. Bagautdinova, E.M. Pudovik, A.R. Burilov, M.A. Pudovik, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 11, pp. 1925–1926.

LETTERS TO THE EDITOR

Phosphorus-Containing Bisazomethines as Promising Tetradentate Ligands

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Received August 11, 2014

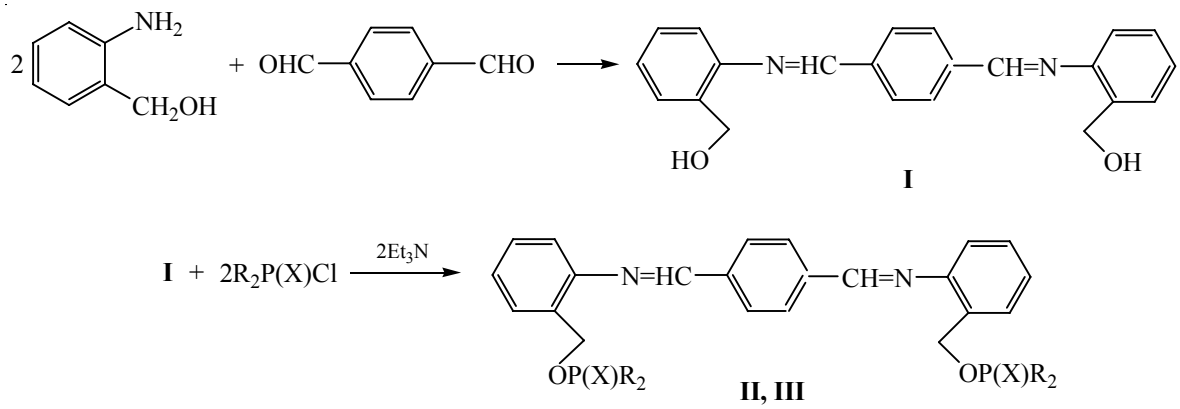
Keywords: bisazomethine, pentavalent phosphorus acids chlorides, phosphorylation, tetradentate ligands

DOI: 10.1134/S1070363214110449

Recently, metal complexes based on hydroxyl bisazomethines have become of emerging interest. Some of these compounds catalyze enantioselective epoxidation of non-functionalized olefins [1, 2], selective *ortho*-hydroxylation of phenols [3], epoxidation of styrene [4], oxidation of styrenes to carbonyl compounds under the action of hydrogen peroxide [5], oxidation of alcohols to carbonyl compounds [6], oxidation of organic sulfides to sulfoxides [7], heterogeneous hydrogenation of alkenes and alkynes [8], and polymerization of butadiene [9]. A number of metal complexes showed pronounced fungicidal, antibacterial, antimicrobial [10–14], and anticancer activity [15].

There have been no published data on *O*-phosphorylated bisazomethines, peculiar ligands for synthesis of metal complexes. Interaction of tere-phthalaldehyde with *ortho*-aminobenzyl alcohol resulted in formation of bisazomethine **I** having two hydroxymethyl groups. Its phosphorylation with tetracoordinated phosphorus acids chlorides in the presence of triethylamine gave diphosphorylated bisazomethines **II** and **III**. The resulting compounds were crystalline materials; their composition and structure were confirmed by elemental analysis, mass spectrometry, IR, ^{1}H, and ^{31}P NMR spectroscopy (Scheme 1).

Scheme 1.



R = Ph, X = S (**II**); R_2 = $OCH_2CMe_2CH_2O$, X = O (**III**).

1,4-Phenylenebis(methanylidene)bis(azanylidene)-bis(2,1-phenylene)dimethanol (I). A mixture of 2.02 g of terephthalaldehyde and 3.71 g of *ortho*-aminobenzyl alcohol in 30 mL of ethanol was refluxed for 0.5 h. The formed precipitate was filtered off and washed with ethanol. Yield 4.57 g (88%), mp 153–155°C. IR spectrum (KBr), ν, cm^{-1}: 1592 (OPh), 1612 (C=N), 3332 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, (*J*, Hz): 4.72 d (2H, CH_2O, $^2J_{HH}$ 14.67), 4.96 d (1H, CH_2O, $^2J_{HH}$ 14.67), 5.57 s (1H, PhCH), 5.58 s (1H, PhCH), 6.29 s (1H, OH), 6.30 s (1H, OH), 6.61–6.99 m (8H, Ph), 7.53 c (4H, Ph). Mass spectrum (MALDI-TOF): *m*/*z* 344. Found, %: C 77.01; H 5.81; N 7.55. $C_{22}H_{20}N_2O_2$. Calculated, %: C 76.71; H 5.86; N 8.13.

***O*,*O*-(1,4-Phenylene)bis(methanylidene)bis(azanylidene)bis(2,1-phenylene)bis(methylene)bis(diphenylphosphinothioate) (II).** A solution of 0.44 g of diphenylchlorothiophosphinate in 5 mL of benzene was added dropwise to a suspension of 0.3 g of diimine **I** and 0.2 g of triethylamine in 10 mL of anhydrous benzene. The reaction mixture was refluxed for 33 h. Ttriethylamine hydrochloride was filtered off; the solvent was removed in vacuum. The residue was treated with 10 mL of hexane, and the formed precipitate was filtered off. Yield 0.23 g (33%), mp 137–140°C. IR spectrum (KBr), ν, cm^{-1}: 1590 (OPh), 1611 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, (*J*, Hz): 4.76–4.82 m (2H, CH_2O), 4.99–5.05 m (2H, CH_2O), 5.64 s (2H, PhCH), 6.54–7.85 m (32H, Ph). ^{31}P NMR spectrum (DMSO-d_6): δ_P 78.70 ppm. Mass spectrum (MALDI-TOF): *m*/*z* 777. Found, %: P 7.70; S 8.36. $C_{46}H_{38}N_2O_2P_2S_2$. Calculated, %: P 7.97; S 8.25.

***O*,*O*-(1,4-Phenylene)bis(methanylidene)bis(azanylidene)bis(2,1-phenylene)bis(methylene)bis(oxy)bis-(5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide) (III)** was prepared similarly from 0.3 g of diimine **I**, 0.2 g of triethylamine and 0.32 g of 2-chloro-2-thioxo-4,5-dimethyl-1,3,2-dioxaphosphinane; reaction time was 24 h. Yield 0.26 g (46%), mp 148–149°C. IR spectrum (KBr), ν, cm^{-1}: 1590 (OPh), 1611 (C=N). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm, (*J*, Hz): 0.92 s (3H, CH_3), 1.35 s (3H, CH_3), 3.97–4.04 m (4H, CH_2O), 4.50 d (4H, CH_2O, $^2J_{HH}$ 10.52), 6.44–7.53 m (12H, Ph) 8.08 s (2H, PhCH). ^{31}P NMR spectrum (C_6D_6): δ_P –21.10 ppm. Mass spectrum (MALDI-TOF): *m*/*z* 641. Found P, %: 9.82. $C_{32}H_{38}N_2O_8P_2$. Calculated P, %: 9.67.

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

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 12-03-00204).

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