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LETTERS TO THE EDITOR

Hexacoordinated Phosphorus Derivatives in the Reaction of Alkylenechlorophosphites with Hydroxylated Bisazomethines

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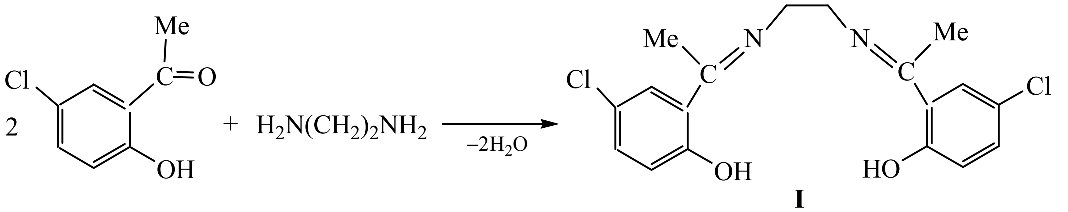
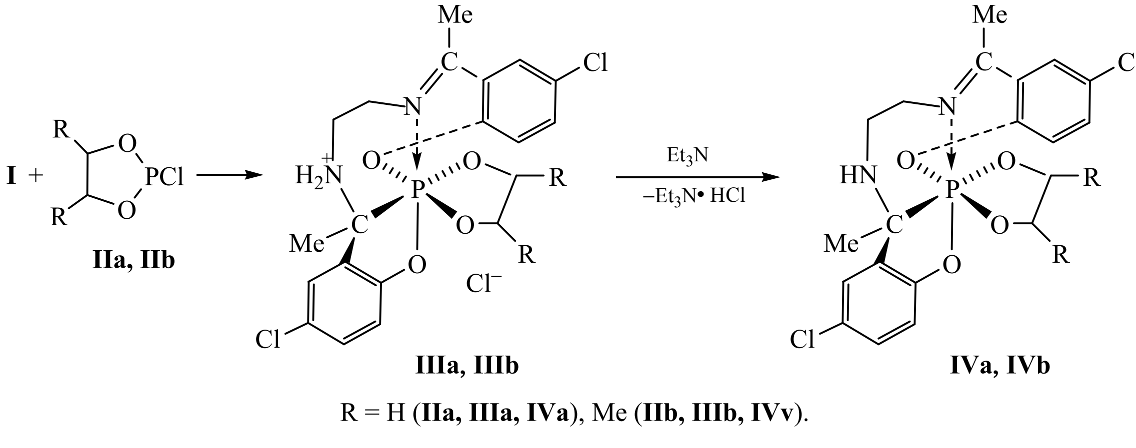
We found previously that the reaction of equimolar amounts of hydroxylated bisazomethines with alkylenechlorophosphites in the absence of a base leads to the formation of the hexacoordinated phosphorus derivatives [1, 2]. In addition, the studied reactions were characterized by the high stereoselectivity, which allows obtaining P(VI)-derivatives in an optically pure form, with the phosphorus atom as a stereogenic center [3]. In order to study the limits of applicability of this reaction we involved diimine **I** derived from the 2-hydroxy-5-chloroacetophenone and diaminoethane in the reaction with the hydroxylated alkylenechlorophosphites.



I

The reaction of equimolar amounts of diimine **I** with ethylenechlorophosphite **IIa** in a methylene chloride solution in the absence of a base leads to the formation of polycyclic derivative of the hexacoordinated phosphorus atom of the salt structure **IIIa**. Its structure is formed with the participation of the P–O, P–C bonds and N–P transannular bond. The ^{31}P NMR spectrum of the reaction mixture contains two signals of different intensity (–106.63, –107.49 ppm), which indicates the formation of the product as a diastereomeric mixture.



IIa, IIb **IIIa, IIIb** **IVa, IVb**

R = H (**IIa, IIIa, IVa**), Me (**IIb, IIIb, IVv**).

A similar result was obtained when butylenechlorophosphite **IIb** was used as a phosphorylating agent. In this case, the ^{31}P NMR spectrum also contains two singlet signals (δ_P –109.11, –109.65 ppm). We failed to obtain a high-quality proton spectra due to a very poor solubility of the reaction products in organic solvents. The salt products **IIIa** and **IIIb** undergo dehydrochlorination at the treating with triethylamine to give phosphorates **IVa** and **IVb** of a neutral structure. They were recrystallized to yield the diastereomerically homogeneous products.

***N,N'*-Bis[1-(2-hydroxy-5-chlorophenyl)ethylidene]-ethylenediamine** (**I**). A mixture of 5.0 g of 5-chloro-2-hydroxyacetophenone and 0.9 g of ethylenediamine in 30 ml of ethanol was heated at reflux for 2 h. After cooling the precipitated crystals were separated and washed with diethyl ether. Yield 5.1 g (95 %), mp 254–255°C. IR spectrum, ν, cm^{-1}: 1614 (C=N). Found, %: C 59.63; H 4.83; Cl 19.71; N 7.66. $C_{18}H_{18}Cl_2N_2O_2$. Calculated, %: C 59.17; H 4.93; Cl 19.45; N 7.67.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-5,10-dimethyl-6-aza-9-ammonium-2,13-dioxa-1-phospha-[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIa). A mixture of 0.5 g of diimine **I** and 0.17 g of ethylenechlorophosphite **IIa** in 10 ml of methylene chloride was stirred for 2 h at 25°C. The crystalline product was separated, washed with diethyl ether, and dried in air. Yield 0.6 g (89%), mp 209–211°C. IR spectrum, ν, cm^{-1}: 1605 (C=N), 2368–2705 (NH_2^+). ^{31}P NMR spectrum (d_6-DMSO), δ_P, ppm: –106.63, –107.49. Mass spectrum (MALDI-TOF), *m/z*: 455 [M^+ – HCl]. Found, %:C 48.62; H 4.37; N 5.59; P 5.94. $C_{20}H_{22}Cl_3N_2O_4P$. Calculated, %: C 48.83; H 4.48; N 5.69; P 6.30.

1,1-(2,3-Butylene)-3,4,11,12-dibenzo-5,10-dimethyl-6-aza-9-ammonium-2,13-dioxa-1-phospha[8.3.0^{1,10}]-tridecatri-3,5,11-ene chloride (IIIb) was prepared similarly from 0.5 g of diimine **I** and 0.40 g of butylenechlorophosphite **IIb**. Yield 0.8 g (57%), mp 220–223°C. IR pectrum, ν, cm^{-1}: 1605 (C=N), 2368–2705 (NH_2^+). ^{31}P NMR spectrum (d_6-DMSO), δ_P, ppm: –109.11, –109.65. Found, %: Cl 20.78; N 5.58; P 5.95. $C_{20}H_{26}Cl_3N_2O_4P$. Calculated, %: Cl 20.70; N 5.38; P 5.96.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-5,10-dimethyl-6,9-diaza-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene (IVa). A mixture of 0.50 g of salt **IIIa** and 0.10 g of triethylamine in 15 ml of methylene chloride was boiled for 2 h. After 1 day, triethylamine hydrochloride was separated, methylene chloride was removed, and the residue was treated with diethyl ether. Yield 0.3 g (65 %), mp 192–195°C. IR spectrum (KBr), ν, cm^{-1}: 1606 (C=N), 3343 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.41 d (3H, CH_3CP $^3J_{HP}$ 18.72), 2.69 s (3H, CH_3C=N), 3.29–4.47 m (8H, CH_2N, CH_2O), 6.78–7.54 m (6H, Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P –95.73 ppm. Mass spectrum (MALDI-TOF), *m/z*: 455. Found, %: N 6.07; P 6.51. $C_{20}H_{21}Cl_2N_2O_4P$. Calculated, %: N 6.15; P 6.81.

1,1-(2,3-Butylenedioxy)-3,4,11,12-dibenzo-5,10-dimethyl-6,9-diaza-2,13-dioxa-1-phospha[8.3.0^{1,10}]-tridecatri-3,5,11-ene (IVb) was prepared similarly from 0.8 g of the salt **IIIb** and 0.16 g of triethylamine in 15 ml of methylene chloride. Yield 0.45 g (61%), mp 180–182°C. ^{31}P NMR spectrum ($CDCl_3$): δ_P –98.53 ppm. Found, %: N 5.77; P 6.43. $C_{22}H_{25}Cl_2\cdot N_2O_4P$. Calculated, %: N 5.80; P 6.41.

The IR spectra were recorded on a Bruker Vector-22 spectrometer in the range of 400–3600 cm^{-1} from mulls in mineral oil. The ^{1}H NMR spectra were registered on an Avance 600 instrument operating at 600.13 MHz with the residual proton signals of solvent ($CDCl_3$) serving as reference. The ^{31}P NMR spectra were taken on a Bruker MSL-400 Fourier-spectrometer (100.62 MHz).

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