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LETTERS TO THE EDITOR

Synthesis of Phosphorus-Containing Polycyclic Derivatives by Phosphorylation of Hydroxyl-Containing Diimines

S. A. Terent'eva, L. K. Kibardina, A. R. Burilov, and M. A. Pudovik

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
fax: (8432)752253
e-mail: pudovik@iopc.knc.ru

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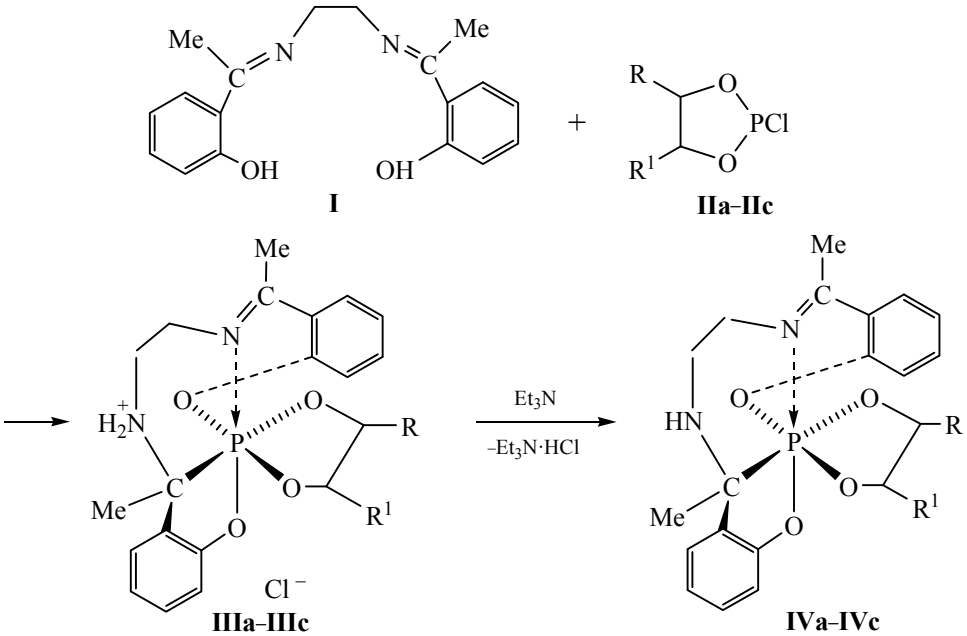
On studying phosphorylation of diimine **I** by cyclic chlorophosphites **IIa–IIc** it was established that the reaction products are polycyclic derivatives of hexacoordinated phosphorus atom **IIIa–IIIc**, which involve a transannular nitrogen–phosphorus bond. Their structure was proved by mass-spectrometry, ^{1}H, ^{31}P and IR spectroscopy, X-ray analysis, and composition by elemental analysis data. Chemical shifts of the phosphorus nuclei for compounds **IIIa–IIIc** are in the range of –109 to –112 ppm, that is characteristic for hexacoordinated phosphorus nuclei.

We believe that primarily the phosphorylation of one of diimine **I** hydroxyl groups occurs to form phosphate and to release hydrogen chloride. The latter protonates one of imine nitrogen atoms to increase electrophilicity of C=N bond. The following nucleophilic attack of phosphorus P(III) atom on the activated imine-group is accompanied with P–C bond formation. The reaction accomplished by the cyclization as a result of attack of the second phenol hydroxyl on phosphorus atom, which leads to appearance of two chiral centers in the molecule (in the reaction of



IIa, IIIa, IVa: R = R^1 = H; **IIb, IIIb, IVb**: R = Me, R^1 = H; **IIc, IIIc, IVc**: R = R^1 = Me.

diimine **I** with ethylene chlorophosphite **IIa**). This process is stereo-selective since according to ^{1}H and ^{31}P NMR spectral data only one diastereomer is formed. On use of chlorophosphites **IIb** and **IIc** as phosphorylating agents the products molecules **IIIb** and **IIIc** contain several chiral centers. As a result, they are formed as a diastereomeric mixture.

On treating the salt products **IIIa–IIIc** with triethylamine they undergo dehydrochlorination to give phosphorates **IVa–IVc** of neutral structure (δ_P from –99 to –102 ppm). Silicon hexacoordinated derivatives were earlier obtained by reaction of diimines of type **I** with tetrachlorosilane [1].

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIa). To a solution of 0.5 g of diimine **I** in 10 ml of methylene chloride was dropwise added 0.22 g of chlorophosphite **IIa**. The mixture was kept for 24 h at 20°C. To the reaction mixture was added 25 ml of diethyl ether. The precipitate was separated and washed with ether. Yield 0.65 g (90%), mp 154°C. IR spectrum (KBr), ν, cm^{-1}: 1604 (C=N), 2498–2729 (NH_2^+). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.64 d (3H, CH_3CP, $^3J_{HP}$ 18.4 Hz), 2.73 s (3H, CH_3C=N), 3.02 br.s (2H, NH_2^+), 3.39–4.53 m (8H, CH_2N, CH_2O), 6.87–7.99 m (8H, Ph). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –109.65. Found, %: N 6.43; P 7.25. $C_{20}H_{24}ClN_2O_4P$. Calculated, %: N 6.62; P 7.32

1,1-(1,2-Propylenedioxy)-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIb) was prepared similarly from 2.96 g of diimine **I** and 1.41 g of chlorophosphite **IIb**. Yield 3.0 g (69%), mp 145°C. IR spectrum (KBr), ν, cm^{-1}: 1604 (C=N), 2500–2733 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –109.72, 109.97. Found, %: N 5.96; P 7.01. $C_{21}H_{26}ClN_2O_4P$. Calculated, %: N 6.40; P 7.09.

1,1-(2,3-Butylenedioxy)-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIc) was prepared similarly from 1.5 g of diimine **I** and 0.8 g of chlorophosphite **IIc**. Yield 2.1 g (93%), mp 159°C. IR spectrum (KBr), ν, cm^{-1}: 1605 (C=N), 2458–2727 (NH_2^+). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 d (3H, C*H*$_3$CH, $^3J_{HH}$ 5.80 Hz), 1.03 d (3H, C*H*$_3$CH, $^3J_{HH}$ 6.15 Hz), 1.15 d (3H, C*H*$_3$CH, $^3J_{HH}$ 5.80 Hz), 1.20 d (3H, C*H*$_3$CH, $^3J_{HH}$ 6.15 Hz), 1.68 d. d (6H, CH_3CP, $^3J_{HP}$ 3.76, 4.09 Hz), 2.01 br.s (1H, NH), 2.59 s (3H, CH_3C=N), 3.02–4.84 m (8H, NH_2^+, CH_2N, CHO), 6.79–7.92 m (8H, Ph). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –110.95, –111.59, –112.24 (diastereomer ratio 5:45:50%). MS (MALDI–TOF), *m/z*: 414 [M^+ – HCl]. Found, %: C 58.24; H 6.79; N 6.30; P 6.82. $C_{22}H_{31}ClN_2O_4P$. Calculated, %: C 58.33; H 6.87; N 6.20; P 6.87.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-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 0.20 g of triethylamine in 3 ml of methylene chloride was heated for 2 h at reflux. After 1 day triethylamine hydrochloride was separated, the solvent was removed and the residue was treated with diethyl ether. Yield 0.3 g (66%), mp 136–138°C. IR spectrum (KBr), ν, cm^{-1}: 1610 (C=N), 3358 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.64 d (3H, CH_3CP $^3J_{HP}$ 18.45 Hz), 2.71 s (3H, CH_3C=N), 3.31–4.51 m (8H, CH_2N, CH_2O), 6.87–7.89 m (8H, Ph). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –99.72. Found, %: N 7.61; P 8.29. $C_{20}H_{23}N_2O_4P$. Calculated, %: N 7.25; P 8.03.

1,1-(1,2-Propylenedioxy-3,4,11,12-dibenzo-6,9-diaza-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene (IVb) was prepared similarly from 1.0 g of salt **IIIb** and 0.35 g of triethylamine. Yield 0.65 g (72%), mp 136°C. IR spectrum (KBr), ν, cm^{-1}: 1604 (C=N), 3343 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 d (3H, CH_3CHO, $^3J_{HH}$ 5.46 Hz), 1.52 d (3H, CH_3CHO, $^3J_{HH}$ 5.46 Hz), 2.36 d (3H, CH_3CP $^3J_{HP}$ 3.1 Hz), 2.40 s (3H, CH_3C=N), 3.91–4.51 m (2H, CHO), 6.73–7.60 m (8H, Ph). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –99.72. MS (MALDI–TOF), *m/z*: 400. Found, %: C 54.07; H 5.13; N 6.97; P 7.71. $C_{21}H_{25}N_2O_4P$. Calculated, %: C 54.00; H 5.70; N 7.00; P 7.75.

1,1-(2,3-Butylenedioxy)-3,4,11,12-dibenzo-6,9-diaza-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene (IVc) was prepared similarly from 1.8 g of salt **IIIc** and 0.60 g of triethylamine. Yield 0.80 g (50%), mp 95–100°C. IR spectrum (KBr), ν, cm^{-1}: 1605 (C=N), 3343 (NH). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –102.60. Found, %: N 6.19; P 7.35. $C_{22}H_{27}N_2O_4P$. Calculated, %: N 6.76; P 7.48.

The IR spectra were recorded on a Vector-22 spectrometer (Bruker) in the range of 400–3600 cm^{-1}

in vaseline oil. ^{1}H NMR spectra were registered on a Avance 600 instrument (600.13 MHz) relative to residual protons of deuterated solvent (chloroform-d_3). ^{31}P NMR spectra were taken on a NMR-Fourier spectrometer Bruker MSL-400 (100.62 MHz). The mass spectra (MALDI–TOF) were obtained on an ULTRAFLEX III instrument (matrix *p*-nitroaniline).

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