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LETTERS TO THE EDITOR

Regiochemistry of Reaction of Benzo[*d*]-1,3,2-dioxaphosphorin-2-ylisocyanate with *ortho*-Halophenylcarbonyldiethylphosphonates

L. M. Burnaeva[a], V. F. Mironov[a,b], A. T. Gubaidullin[b], G. A. Ivkova[a], and A. B. Dobrynin[b]

[a] *Kazan (Volga Region) Federal University, Kazan, Tatarstan, Russia*
ul. Kremlevskaya 18, Kazan, Tatarstan, 142008 Russia
e-mail: liliya.burnaeva@ksu.ru, mironov@iopc.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre,*
Russian Academy of Sciences, Kazan, Tatarstan, Russia

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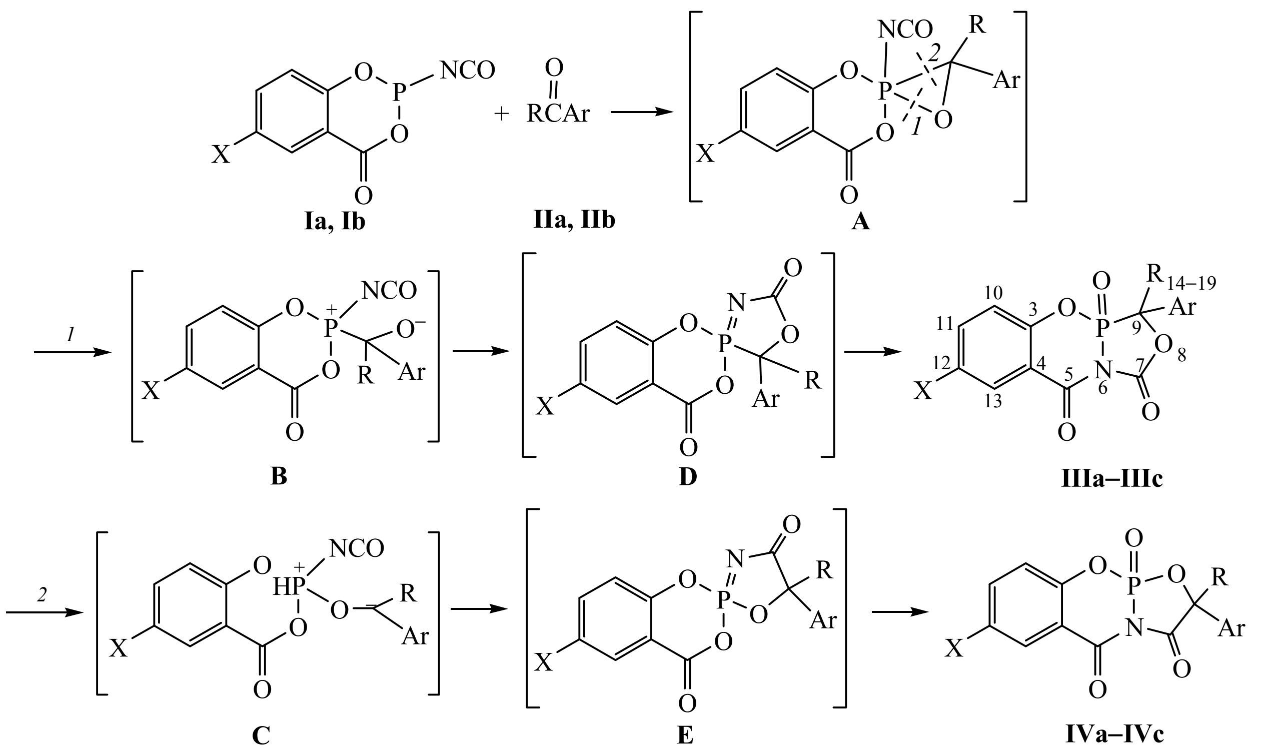
Functionally substituted P(III) derivatives containing an isocyanate group react readily with the activated carbonyl compounds to give a variety of difficultly accessible P-heterocycles: spirophosphoranes [1], diazadiphosphetidines, 1,3,2-dioxaphosphepines [2]. Thus, the reactions involving perfluoro-*para*-quinone [3] and *para*-substituted arylcarbonylphosphonates [4] result in the substituted phosphabicyclononanes containing phosphorus–oxygen, phosphorus–nitrogen, and phosphorus–carbon bonds.

In this report the isocyanatophosphite **I** is shown to react with *ortho*-bromo- and *ortho*-chlorophenylcarbonyl diethylphosphonates **II** to give tricyclic compounds, like substituted phosphabicyclononanes **III** and **IV** containing the P–C and P–OC bonds. According to the ^{31}P–{^{1}H} NMR data, the reactions of isocyanatophosphite **Ia** with *ortho*-chloro- and *ortho*-bromophenylcarbonylphosphonates **IIa** and **IIb** as well as the reaction of isocyanatophosphite **Ib** with compound **IIa** give rise to isomeric mixtures of four biphosphorus compounds **III** and **IV**. The spectra of each mixture contain four doublets in the range of δ_P 7.8–17.3 ppm corresponding to the phosphonate phosphorus atoms of compound **III** and two doublets at δ_P in the range –0.6 to –1.0 and 9.7 to 11.1 ppm corresponding to the phosphate and phosphonate phosphorus atoms of compound **IV**.

Apparently, the reaction starts with the formation of intermediate spirophosphorane **A**, which is a product of the cheletropic interaction of the phosphorus atom with the carbonyl group. The cyclization process involving isocyanate group proceeds probably through the formation of bipolar ions **B** and **C** owing to the cleavage of P–O or P–C bond of oxaphosphirane intermediate **A**. The intramolecular attack of the alkoxide anion or carbanion intermediate results in the oxazaphospholines **D** and **E** that undergo intramolecular acylation at the nitrogen atom to form the target compounds **III** and **IV**.

The individual crystalline phosphonates **IIIb** and **IIIc** were isolated from the mixtures of regioisomers **III** and **IV**. Their structure was confirmed by the NMR and XRD analysis. The conformation of six-membered heterocycles **IIIb** and **IIIc** is a distorted *boat*: the fragment conjugated with the benzene ring is planar; the P and N atoms are deflected to one side of the fragment by different distances. The phosphonate substituent is axially positioned. The conformation of the five-membered heterocycle is a *twist*: the C and P atoms lie on the opposite sides of the N–C–O fragment plane.

9-(*o*-Chlorophenyl)-9-diethoxyphosphoryl-6-aza-3,4-benzo-2,8-dioxa-1-phosphabicyclo[4.3.0$^{1.6}$]nonane-1,5,7-trione (IIIa) and 8-(*o*-chlorophenyl)-8-diethoxyphosphoryl-6-aza-3,4-benzo-2,9-dioxa-1-phosphabicyclo[4.3.0$^{1.6}$]nonane-1,5,7-trione (IVa). A mixture of 6.81 g (0.03 mol) of isocyanatophosphite **Ia** and 9.1 g (0.03 mol) of *ortho*-chlorophenylcarbonyldiethylphosphonate **IIa** was kept in a sealed tube at 120–130°C for 10 h. A thick oily substance was



X = H (**Ia**), Cl (**Ib**); X = H, Ar = 2-ClC$_6$H$_4$ (**IIa–IVa**), 2-BrC$_6$H$_4$ (**IIb–IVb**); X = Cl, Ar = 2-ClC$_6$H$_4$ (**IIIc, IVc**); R = P(O)(OEt)$_2$.

obtained, consisting of a mixture of the isomeric compounds **IIIa** and **IVa** in a ratio of 10.3 (7.8 d_1, 2.5 d_2): 21.3 (14.2 d_3, 7.1 d_4). ^{31}P–{^{1}H} NMR spectrum (161.9 MHz, CH$_2$Cl$_2$), δ_P, ppm (*J*, Hz): 7.8 and 9.1 two d ($^2J_{PCP}$ 27.5), d_1, 8.3 and 16.3 two d ($^2J_{PCP}$ 22.9), d_2 **IIIa**; –0.4 and 10.4 two d ($^2J_{POCP}$ 6.1), d_3, –0.9 and 9.9 two d ($^2J_{POCP}$ 9.2), d_4 IVa. Reprecipitation from a CH$_2$Cl$_2$ solution into pentane gives a light yellow powder in 80% yield, mp 145°C (mixture of **IIIa** and **IVa**). IR spectrum, ν, cm^{-1}: 1750, 1660, 1600, 1520, 1490, 1460, 1250, 1160, 1030, 970, 760. ^{1}H NMR spectrum (300 MHz, acetone-d_6), δ_H, ppm (*J*, Hz): 1.59 q ($^3J_{HCCH}$ 5.3), 4.3–3.8 br.m, 8.25–7.2 br.m. Found, %: C 46.70; H 3.60; P 12.40. C$_{19}$H$_{18}$ClNO$_8$P$_2$. Calculated, %: C 46.96; H 3.70; P 12.77.

9-(*o*-Bromo)phenyl-9-diethoxyphosphoryl-6-aza-3,4-benzo-2,8-dioxa-1-phosphabicyclo[4.3.0$^{1.6}$]nonane-1,5,7-trione (IIIb) and 8-(*o*-bromo)phenyl-8-diethoxyphosphoryl-6-aza-3,4-benzo-2,9-dioxa-1-phosphabicyclo[4.3.0$^{1.6}$]nonane-1,5,7-trione (IVb). A mixture of 9.9 g (0.05 mol) of isocyanatophosphite **Ia** and 15.2 g (0.05 mol) of *o*-bromophenylcarbonyldiethylphosphonate **IIb** was kept in a sealed tube at 120–130°C for 10 h. The obtained thick oil [**IIIb** + **IVb** in the ratio of 18.6 (16.1 d_1, 2.4 d_2):10.9 (6.8 d_3, 4.1 d_4)] was characterized by the spectroscopic methods. ^{31}P–{^{1}H} NMR spectrum (161.9 MHz, CH$_2$Cl$_2$), δ_P, ppm (*J*, Hz): 7.5 and 9.1 two d ($^2J_{PCP}$ 27.5), d_1, 8.3 and 16.7 two d ($^2J_{PCP}$ 24.7), d_2 **IIIb**; –0.6 and 11.1 two d ($^2J_{POCP}$ 6.9), d_3, –1.1 and 10.1 two d ($^2J_{POCP}$ 9.2), d_4 **IVb**. Reprecipitation of this oily substance from a CH$_2$Cl$_2$ solution into pentane gives a mixture of compounds **IIIb** and **IVb** as a pale yellow powder in 80% yield, mp 130°C. The maintaining of the pale yellow powder in CH$_2$Cl$_2$ solution for 10 days yields the crystals of **IIIb** as a mixture of two diastereomers d_1, d_2 in the ratio of 1:1.2. IR spectrum, ν, cm^{-1}: 1830, 1720, 1605, 1460, 1290, 1030, 760, 570. ^{1}H NMR spectrum (acetone-d_6), δ_H, ppm (*J*, Hz): 1.15–1.41 br.t, 4.8–3.7 br.m, 8.5–7.0 br.m. ^{31}P–{^{1}H} NMR spectrum (161.9 MHz, CH$_2$Cl$_2$), δ_P, ppm. (*J*, Hz): 7.9 and 9.7 two d ($^2J_{PCP}$ 27.5), d_1, 7.8 and 13.8 two d ($^2J_{PCP}$ 22.9), d_2. Found, %: C 42.86; H 3.41; P 11.59. C$_{19}$H$_{18}$Br·NO$_8$P$_2$. Calculated, %: C 43.02; H 3.40; P 11.70.

9-(*o*-Chlorophenyl)-9-diethoxyphosphoryl-6-aza-2,8-dioxa-3,4-(4-chloro)benzo-1-phosphabicyclo-[4.3.0$^{1.6}$]nonane-1,5,7-trione (IIIc) and 8-(*o*-chlorophenyl)-8-diethoxyphosphoryl-6-aza-2,9-dioxa-3,4-

(4-chloro)benzo-1-phosphabicyclo[4.3.0$^{1.6}$]nonane-1,5,7-trione (IVc). A mixture of 8.1 g (0.03 mol) of isocyanatophosphite **Ib** and 9.1 g (0.03 mol) of *o*-chlorophenylcarbonyldiethylphosphonate **IIa** was kept in a sealed tube at 120–130°C for 10 h. The obtained thick oily substance was characterized by the spectroscopic methods. ^{31}P–{^{1}H} NMR spectrum (161.9 MHz, CH_2Cl_2), δ_P, ppm. (J, Hz): 7.6 and 9.0 two d ($^{2}J_{PCP}$ 27.5), d_1, 8.2 and 17.4 two d ($^{2}J_{PCP}$ 24.7), d_2 **IIIc**; –1.0 and 10.9 two d ($^{2}J_{POCP}$ 5.5), d_3, –1.4 and 9.7 two d ($^{2}J_{POCP}$ 9.2), d_4 **IVc**. Reprecipitation of this oily substance from a CH_2Cl_2 solution into pentane gives a mixture of compounds **IIIc** and **IVc** in a ratio of 23 (13 d_1, 10 d_2):11 (7 d_3, 3 d_4) in 80% yield, yellow powder, mp 140°C. The maintaining of the pale yellow powder in CH_2Cl_2 solution for 10 days gives the crystalline diphosphonate **IIIc**, mp 148°C. IR spectrum, ν, cm^{-1}: 1827, 1710, 1617, 1600, 1515, 1467, 1450, 1370, 1246, 1211, 1165, 1094, 1025, 998, 965, 820, 760, 670, 540. ^{1}H NMR spectrum (600 MHz, $CDCl_3$), δ_H, ppm (J, Hz): 7.37 d (H^{10}, $^{3}J_{H^{11}CCH^{10}}$ 8.8), 7.68 d.d (H^{11}, $^{3}J_{H^{10}CCH^{11}}$ 8.8, $^{4}J_{H^{13}CCCH^{11}}$ 2.7), 8.17 d (H^{13}, $^{4}J_{H^{11}CCCH^{13}}$ 2.7), 7.51 m (H^{16}), 7.42 m (H^{17,18}), 7.73 d.d.d.d (H^{19}, $^{3}J_{H^{18}CCH^{19}}$ 7.2, $^{4}J_{H^{17}CCCH^{19}}$ 2.3, $^{4}J_{P^{1}CCCH^{19}}$ 1.6, $^{4}J_{P^{2}CCCH^{19}}$ 1.6), 4.16 m (H^{20AB}, $^{3}J_{POCH}$ 7.4, $^{3}J_{HCCH}$ 7.1), 4.16 d. q (OCH_2, $^{3}J_{HCCH}$ 7.1, $^{3}J_{HCCH}$ 7.1), 4.03 m [OCH_AH_B, B-part of ABM_3X system, $^{2}J(H_AH_B)$ 10.1, $^{3}J(POCH_B)$ 7.8, $^{3}J(H_BCCH_M)$ 7.1], 3.96 m [OCH_2, A-part of ABM_3X system, $^{2}J(H_BH_A)$ 10.1, $^{3}J(POCH_A)$ 9.6, $^{3}J(H_ACCH_M)$ 7.1], 1.19 t (CH_3, $^{3}J_{HCCH}$ 7.1), 1.18 t (CH_3, $^{3}J_{HCCH}$ 7.1). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm. (J, Hz) (the multiplicity of the signal in the ^{13}C–{^{1}H} spectrum is given in the brackets): 149.76 d.d.d.d (d) (C^{3}, $^{3}J_{HC^{11}CC^{3}}$ 11.2, $^{2}J_{P^{1}OC^{3}}$ 9.2, $^{3}J_{HC^{13}CC^{3}}$ 8.6, $^{2}J_{HC^{10}C^{3}}$ 4.6), 118.81 d.d (d) (C^{4}, $^{3}J_{HC^{10}CC^{4}}$ 5.0, $^{3}J_{P^{1}OCC^{4}}$ 1.5), 155.60 d.d.d (d) (C^{5}, $^{3}J_{HC^{13}CC^{5}}$ 4.5, $^{2}J_{P^{1}NC^{5}}$ 3.4, $^{4}J_{HC^{10}CCC^{5}}$ 2.0), 144.07 d (d) (C^{7}, $^{2}J_{P^{1}NC^{7}}$ 25.1), 83.39 br.d.d (d.d) (C^{9}, $^{1}J_{P^{1}C^{9}}$ 153.0, $^{1}J_{P^{2}C^{9}}$ 117.5), 121.67 d.d (d) (C^{10}, $^{1}J_{HC^{10}}$ 169.2, $^{3}J_{P^{1}OCC^{10}}$ 9.4), 137.27 d.d (s) (C^{11}, $^{1}J_{HC^{11}}$ 169.2, $^{3}J_{HC^{13}CC^{11}}$ 6.5), 132.37 d.d.d (s) (C^{12}, $^{3}J_{HC^{10}CC^{12}}$ 11.1, $^{2}J_{HC^{13}C^{12}}$ 3.9, $^{2}J_{HC^{11}CC^{12}}$ 3.9), 130.34 d.d (s) (C^{13}, $^{1}J_{HC^{13}}$ 172.6, $^{3}J_{HC^{11}CC^{13}}$ 5.7), 126.57 m (d.d) (C^{14}, $^{2}J_{PCC^{14}}$ 4.2, $^{2}J_{PCC^{14}}$ 4.3), 131.83 m (d.d) (C^{15}, $^{2}J_{PCCC^{15}}$ 5.7, $^{2}J_{PCCC^{15}}$ 4.2), 130.57 d.d.m (br.s) (C^{16}, $^{1}J_{HC^{16}}$ 166.7, $^{3}J_{HC^{18}CC^{16}}$ 6.5), 131.26 br. d.d (br.s) (C^{17}, $^{1}J_{HC^{17}}$ 164.9, $^{3}J_{HC^{19}CC^{17}}$ 8.7), 127.72 d.d.d (d) (C^{18}, $^{1}J_{HC^{18}}$ 164.4, $^{3}J_{HC^{16}CC^{18}}$ 7.9, $^{4}J_{PC^{9}CCC^{18}}$ 1.5), 129.18 d.m (d.d) (C^{19}, $^{1}J_{HC^{19}}$ 162.5, $^{3}J_{HC^{17}CC^{19}}$ 7.5, $^{3}J_{PCCC^{19}}$ 7.3, $^{3}J_{PCCC^{19}}$ 3.6), 66.02 t.d.q (d) (OCH_2, $^{1}J_{HC}$ 150.1, $^{2}J_{POC}$ 7.5, $^{2}J_{HCC}$ 4.2), 65.84 t.d.q (d) (OCH_2, $^{1}J_{HC}$ 150.2, $^{2}J_{POC}$ 7.3, $^{2}J_{HCC}$ 4.3), 16.25 q.d.t (d) (CH_3, $^{1}J_{HC}$ 127.7, $^{3}J_{POCC}$ 5.2, $^{2}J_{HCC}$ 2.5), 16.21 q.d.t (d) (CH_3, $^{1}J_{HC}$ 127.8, $^{3}J_{POCC}$ 5.6, $^{2}J_{HCC}$ 2.5). ^{31}P–{^{1}H} NMR spectrum (242.9 MHz, $CDCl_3$), δ_P, ppm (J, Hz): 7.7 and 9.0 two d ($^{2}J_{PCP}$ 27.5). Found, %: C 42.70; H 3.27; P 11.80. $C_{19}H_{17}Cl_2NO_8P_2 \cdot H_2O$. Calculated, %: C 42.38; H 3.16; P 11.52.

The ^{1}H, ^{31}P, ^{13}C NMR spectra were recorded on a Varian Unity-300 and Bruker Avance-600 instruments. The IR spectra were taken on a Bruker Vector-22 instrument from the suspension of the substance in mineral oil.

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