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SHORT COMMUNICATIONS

Reaction of 2-Chloro-1,3,2-benzodioxaphosphinin-4-one with 2-(Arylmethylideneamino)phenols. Stereoselective Formation of 10-Aryl-3,4 : 8,9-dibenzo-5,7-dioxa-1-aza-6-phosphabicyclo[4.3.1]decane-2,6-diones

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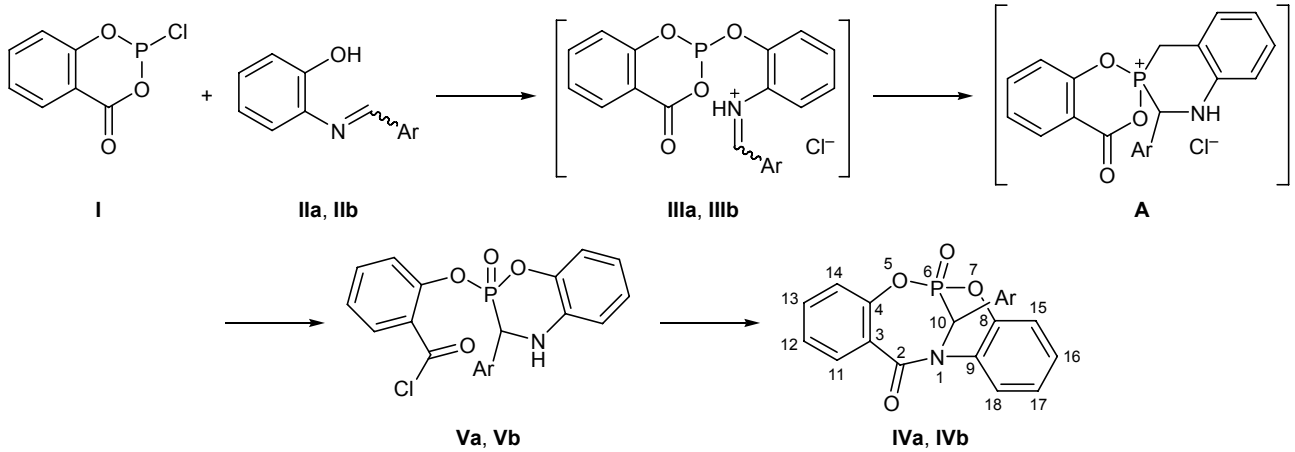
Cyclic mixed anhydrides derived from hydroxy carboxylic and phosphorous acids (2-R-1,3,2-benzodioxaphosphinin-4-ones or "salicyl phosphites") contain a highly reactive macroergic POC(O) moiety and are convenient intermediate products for regio- and stereoselective syntheses of various phosphorus-containing heterocyclic (including bridged polycyclic) systems which are difficult to obtain by other methods [1–4].

We previously reported on stereoselective synthesis of a 1,4,2-benzoxazaphosphepine derivative via intramolecular expansion of the six-membered ring in salicyl phosphite possessing a 2-(benzylideneamino)-ethoxy group [5]. In the present communication we describe intramolecular cyclization processes in the system 2-chloro-1,3,2-benzodioxaphosphinin-4-one (**I**)–2-(arylmethylideneamino)phenol **II** in the absence of a base. Taking into account lower nucleophilicity of the nitrogen atom in aromatic Schiff bases and conformational rigidity of the aromatic ring, which should not favor intramolecular cyclization, we believed that the imine fragment in initially formed phosphite **III** (THF, 20°C) may act as a base. However, we failed to



R = Ph (**a**), naphthalen-2-yl (**b**).

detect intermediate **III** in the reaction mixture. After treatment of the reaction mixture with triethylamine in the final step, we isolated the corresponding intramolecular cyclization products, stable cage-like phosphorus-containing heterocycles, 10-aryl-3,4:8,9-dibenzo-5,7-dioxa-1-aza-6-phosphabicyclo[4.3.1]decane-2,6-diones **IV**, which were formed as the only diastereoisomer. A probable reaction scheme includes transformation of initially formed phosphite **III** into quasiphosphonium salt **A** which is readily converted into 3,4-dihydro-2*H*-1,4,2λ^5-benzoxazaphosphinine **V** with a 2-chlorocarbonylphenoxy substituent on the phosphorus atom via the Arbuzov reaction. The ^{31}P NMR spectra of compounds **Va** and **Vb** contained doublet signals at δ_P 12.0 ($^2J_{PH}$ = 15.7 Hz) and 11.9 ppm ($^2J_{PH}$ = 14.7 Hz), respectively. Addition of triethylamine promotes cyclization of **V** to cage-like heterocycles **IV**.

The structure of compounds **IV** was proved by ^{1}H, ^{13}C, and ^{31}P NMR, IR, and MALDI and ESI mass spectra. In the ^{1}H NMR spectra of **IVa** and **IVb** we observed a doublet signal in the region δ 5.7–5.9 ppm ($^2J_{PH}$ = 14.7 Hz), corresponding to the PCHN proton; the same coupling constant was found for the phosphorus signal. The mass spectra of **IVa** and **IVb** contained strong peaks of their molecular ions with *m*/*z* 363 and 413, respectively.

3,4:8,9-Dibenzo-10-phenyl-5,7-dioxa-1-aza-6-phosphabicyclo[4.3.1]decane-2,6-dione (IVa). A solution of 4.61 g (23.40 mmol) of aminophenol **IIa** in 25 mL of anhydrous THF was added dropwise over a period of 30 min under stirring at 20°C in an argon atmosphere to a solution of 4.74 g (23.40 mmol) of compound **I** in 20 mL of anhydrous THF. The mixture was stirred for 30 min, 2.60 g (25.74 mmol) of triethylamine was added dropwise over a period of 10 min (20°C), and the mixture was stirred for 1 h and left overnight. The precipitate was filtered off, the solvent was removed under reduced pressure, and the residue, a light brown oily liquid, was treated with anhydrous diethyl ether to obtain a light gray powder. The product was filtered off, washed with diethyl ether, and dried under reduced pressure. Yield 6.37 g (75%), mp 117°C. IR spectrum, ν, cm^{-1}: 1694 (C=O), 1285 (P=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.73 d (10-H, $^2J_{HP}$ = 14.8), 6.97 d.d (18-H, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.7), 7.07 d.d.d (16-H, $^3J_{HH}$ = 7.7, 7.7, $^4J_{HH}$ = 1.7), 7.12 d.d.d.d (17-H, $^3J_{HH}$ = 8.0, 7.7, $^4J_{HH}$ = 1.9, $^5J_{HP}$ = 1.4), 7.14–7.16 m (*m*-H, *p*-H), 7.29 br.d (14-H, $^3J_{HH}$ = 8.4), 7.33 br.d.d (12-H, $^3J_{HH}$ = 7.6, 7.6), 7.48 br.d (*o*-H, $^3J_{HH}$ = 7.2), 7.54 d.d.d.d (13-H, $^3J_{HH}$ = 7.6, 8.4, $^4J_{HH}$ = 1.7, $^5J_{HP}$ = 1.4), 7.65 d.d (15-H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.9), 7.76 d.d (11-H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.7). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm (*J*, Hz): 50.62 d (C^{10}, $^1J_{CP}$ = 125.2), 118.37 d (C^{14}, $^3J_{CP}$ = 6.6), 121.67 d (C^{15}, $^3J_{CP}$ = 4.0), 124.35 s (C^{18}), 125.38 d (C^{i}, $^2J_{CP}$ = 6.1), 125.89 d (C^3, $^3J_{CP}$ = 1.8), 126.92 d (C^{16}, $^4J_{CP}$ = 1.6), 127.40 d (C^{o}, $^3J_{CP}$ = 7.7), 128.25 d (C^{12}, $^5J_{CP}$ = 2.2), 128.64 s (C^{p}), 128.73 s (C^{m}), 128.92 d (C^9, $^2J_{CP}$ = 5.5), 128.98 (C^{17}), 130.50 s (C^{11}), 134.35 s (C^{13}), 146.33 d (C^8, $^2J_{CP}$ = 11.9), 147.29 d (C^4, $^2J_{CP}$ = 8.0), 168.12 d (C^2, $^3J_{CP}$ = 1.6). ^{31}P NMR spectrum: δ_P 11.6 ppm, d ($^2J_{PH}$ = 14.7 Hz). MALDI mass spectrum: *m*/*z* 364 [*M* + H]$^+$. ESI mass spectrum: *m*/*z* 364 [*M* + 1]$^+$. Found, %: C 65.71; H 3.67; N 4.10; P 8.15. $C_{20}H_{14}NO_4P$. Calculated, %: C 66.12; H 3.86; N 3.86; P 8.54.

3,4:8,9-Dibenzo-10-(2-naphthyl)-5,7-dioxa-1-aza-6-phosphabicyclo[4.3.1]decane-2,6-dione (IVb) was synthesized in a similar way. Yield 78%, light yellow powder, mp 123°C. IR spectrum, ν, cm^{-1}: 1689 (C=O), 1290 (P=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.92 d (10-H, $^2J_{HP}$ = 14.1), 7.05 br.d.d (18-H, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.7), 7.12–7.15 m (16-H, 17-H), 7.43–7.45 m and 7.71–7.75 m (13-H, $C_{10}H_7$), 7.56 br.d (14-H, $^3J_{HH}$ = 8.4), 7.63 br.d.d (12-H, $^3J_{HH}$ = 7.6, 7.6), 7.89 d.d (15-H, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.9), 8.00 br.d (11-H, $^3J_{HH}$ = 8.0). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm (*J*, Hz): 51.09 d (C^{10}, $^1J_{CP}$ = 125.6), 118.81 d (C^{14}, $^3J_{CP}$ = 6.6), 121.98 d (C^{15}, $^3J_{CP}$ = 4.3), 124.59 s (C^{18}), 124.59 d (C$^{1'}$, $^3J_{CP}$ = 9.3), 125.29 d (C$^{2'}$, $^2J_{CP}$ = 6.1), 126.08 d (C^3, $^3J_{CP}$ = 1.9), 126.72 s (C$^{6'}$), 126.99 s (C$^{7'}$), 127.17 d (C^{16}, $^4J_{CP}$ = 1.1), 127.60 s (C$^{8'}$), 127.24 d (C$^{3'}$, $^3J_{CP}$ = 6.4), 128.32 s (C$^{5'}$), 128.54 d (C^{12}, $^5J_{CP}$ = 2.1), 129.00 (C^{17}), 129.15 s (C$^{4'}$), 130.73 d (C^{11}, $^4J_{CP}$ = 1.2), 132.90 s (C$^{8a'}$), 132.97 s (C$^{4a'}$), 133.18 d (C^9, $^2J_{CP}$ = 5.2), 134.62 s (C^{13}), 146.65 d (C^8, $^2J_{CP}$ = 11.9), 147.58 d (C^4, $^2J_{CP}$ = 8.1), 168.39 d (C^2, $^3J_{CP}$ = 1.7). ^{31}P NMR spectrum: δ_P 11.4 ppm, d ($^2J_{PH}$ = 14.1 Hz). MALDI mass spectrum: *m*/*z* 414 [*M* + H]$^+$. ESI mass spectrum: *m*/*z* 414 [*M* + 1]$^+$. Found, %: C 69.27; H 4.19; N 3.49; P 7.68. $C_{24}H_{16}NO_4P$. Calculated, %: C 69.73; H 3.87; N 3.39; P 7.59.

The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400, 162.0, and 100.6 MHz, respectively, using $CDCl_3$ as solvent and reference for ^{1}H and ^{13}C; the ^{31}P chemical shifts were measured relative to H_3PO_4 (external reference). The IR spectra were recorded on a Bruker Vector-22 spectrometer from samples dispersed in mineral oil and placed between KBr plates. The MALDI (matrix-assisted laser desorption/ionization) mass spectra were

obtained on a Bruker Ultraflex time-of-flight mass spectrometer. The ESI (electrospray ionization) mass spectra were obtained on a Bruker Daltonik Amazon instrument with positive ion detection.

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