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LETTERS TO THE EDITOR

Dedicated to the 110th anniversary of M.I. Kabachnik's birth

Trimethylchlorosilane-Catalyzed Intramolecular Cyclization of 2-(2-Benzylideneaminoethyloxy)-1-phenylbenzo[*e*]-1,3,2-azaoxaphosphorin-4-one

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Abstract—A catalytic effect of trimethylchlorosilane on the intramolecular cyclization of 2-(2-benzylideneaminoethyloxy)-1-phenylbenzo[*e*]-1,3,2-azaoxaphosphorin-4-one into 3,4-benzo-5,10-diphenyl-1,5-diaza-7-oxabicyclo[4.3.1^{1,6}]decane-2,6-dione, formed as two diastereomers in a 1 : 1 ratio, was studied.

Keywords: oxazaphosphorin, benzylideneaminoethanol, cage aminophosphonate, trimethylchlorosilane

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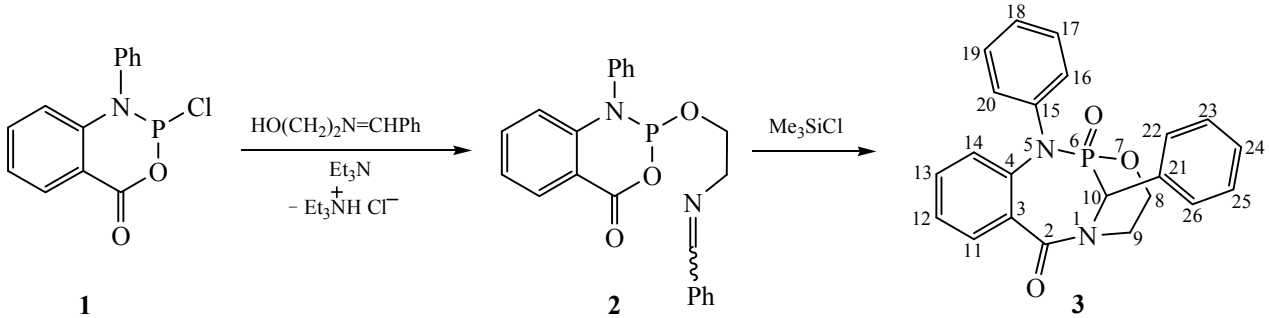
1-Aminophosphonic acids derivatives are of interest due to their diverse biological activity [1, 2] and complexing properties [3]. Various approaches have been used for the synthesis of these compounds, based on the Kabachnik–Fields and Pudovik reactions [4–7]. We have previously proposed to use the ring expansion reaction of 2-R-benzo[*d*]-1,2,3-dioxaphosphorin-4-ones by imines to produce 1-aminophosphonic acid esters. The reaction led to the formation of 2-R-benzo[*f*]-1,4,2-oxazaphosphorin-2,5-diones with high stereoselectivity [8–10]. Later, an intramolecular version of this reaction has been carried out using 2-(2-arylideneaminophenoxy)benzo[*d*]-1,2,3-dioxaphosphorin-4-ones, which underwent cyclization into the cage 1-aminophosphonates [11]. Here this approach to the synthesis of cage aminophosphonates was extended to 2-(2-benzylideneaminoethyloxy)-1-phenylbenzo[*e*]-1,3,2-azaoxaphosphorin-4-one **2** obtained by reacting benzylideneaminoethanol with 1-phenyl-2-chlorobenzo[*e*]-1,3,2-azaoxaphosphorin-4-one **1** in the presence of a base to avoid the opening of the anhydride moiety. Compound **2** is stable at 25°C and does not show any tendency to intramolecular transformations (Scheme 1).

We found that in the presence of trimethylchlorosilane as a catalyst the intramolecular cyclization into

Scheme 1.



1 **2** **3**

the cage aminophosphonate **3** occurred readily in a benzene–dichloromethane mixture at 25°C within 5–7 h. It should be noted that catalytic effect of trimethylchlorosilane has been previously observed in the addition reactions of diethylphosphite [12] and triethyl phosphite [13–16] to carbonyl compounds and imines. However, an equimolar or rather significant amount of trimethylchlorosilane was used; in some cases the process was carried out by boiling in polar acetonitrile.

The structure of the resulting mixture of diastereomers was established from ^{1}H, ^{13}C, ^{31}P NMR and mass spectra. The large difference in the chemical shifts of the carbon of the phenyl substituent at the C^{10} atom is apparently due to the magnetic anisotropy of the 3,4-benzo fragment in one of the isomers in which this phenyl substituent is close to the benzo fragment.

In conclusion, we developed a mild method for the synthesis of cage aminophosphonates through the intramolecular interaction of an imino group with a P(III) atom promoted with trimethylchlorosilane.

3,4-Benzo-5,10-diphenyl-1,5-diaza-7-oxa-6-phosphabicyclo[4,3,1^{1,6}]decane-2,6-dione (3). A solution of 2.18 g (7.85 mmol) of 4,5-benzo-2-chloro-3-phenyl-6-oxo-1,3,2-oxazaphosphorin **1** in 10 mL of anhydrous dichloromethane was added to a mixture of 1.17 g (7.85 mmol) of 2-benzylideneaminoethanol and 0.86 g (8.51 mmol) of triethylamine in 20 mL of anhydrous benzene at 10°C under argon atmosphere. The precipitate was filtered off, and 0.085 g (0.79×10^{-3} mmol) of trimethylchlorosilane was added to the filtrate containing compound **2** (δ_P 120.3 ppm, $^{3}J_{PH}$ = 8.0 Hz). After 1 day, the solvent was removed in a vacuum, and the residue was treated with diethyl ether. Yield 2.48 g (81%), pale red powder, mp 257–261°C (mixture of diastereomers d_1 : d_2 = 1 : 1). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 3.26 d.d.d (1H, NCH, $^{2}J_{HH}$ = 14.2, $^{3}J_{HH}$ = 12.9, $^{3}J_{HH}$ = 3.7), 3.57 d.d.d (1H, NCH, $^{2}J_{HH}$ = 14.0, $^{3}J_{HH}$ = 12.2, $^{3}J_{HH}$ = 3.7), 4.04 d.d.d (1H, POCH, $^{3}J_{PH}$ = 19.5, $^{2}J_{HH}$ = 11.3, $^{3}J_{HH}$ = 3.7), 4.20 d.d.d (1H, POCH, $^{3}J_{PH}$ = 20.2, $^{2}J_{HH}$ = 11.4, $^{3}J_{HH}$ = 3.7), 4.10–4.30 m (2H, POCH, NCH), 4.88 d.d (1H, NCH, $^{2}J_{HH}$ = 14.2, $^{3}J_{HH}$ = 2.9, d_1), 5.38 d (1H, PCH, $^{2}J_{PH}$ = 21.0, d_2), 5.49 d (1H, PCH, $^{2}J_{PH}$ = 12.1, d_1); 6.84 m, 6.96 m, 7.01 m, 7.12 m, 7.19 m, 7.30–7.34 m, 7.38–7.45 m (28H, $H^{11–14}$, $H^{16–20}$, $H^{22–26}$). $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz), δ_C, ppm (*J*, Hz): 40.55 br.t.d.t (d) (C^{9}, $^{1}J_{HC}$ = 142.1, $^{3}J_{HC}$ = 3.5, $^{2}J_{HC}$ = 3.5, $^{2}J_{PC}$ = 1.5), 50.53 br.t.t (s) (C^{9}, $^{1}J_{HC}$ = 142.0, $^{2}J_{HC}$ = 2.7), 55.77 d.d.m (d) (C^{10}, $^{1}J_{HC}$ = 137.0, $^{1}J_{PC}$ = 126.0, $^{3}J_{HC}$ = 4.9), 62.28 d.d.m (d) (C^{10}, $^{1}J_{HC}$ = 128.0, $^{1}J_{PC}$ = 125.1, $^{3}J_{HC}$ = 4.9), 71.54 t.d.d.d (d) (C^{8}, $^{1}J_{HC}$ = 150.1, $^{2}J_{PC}$ = 11.2, $^{2}J_{HC}$ = 4.8, $^{2}J_{HC}$ = 2.4), 71.65 t.d.d.d (d) (C^{8}, $^{1}J_{HC}$ = 150.2, $^{2}J_{PC}$ = 11.8, $^{2}J_{HC}$ = 4.3, $^{2}J_{HC}$ = 2.3), 172.32 m (s) and 172.73 m (s) (C^{2}), 141.95 m (d) and 142.01 m (d) (C^{4}, $^{2}J_{PC}$ = 1.8, 1.7), 138.58 m (d) and 141.27 m (d) (C^{15}, $^{2}J_{PC}$ = 5.1, 3.7), 130.92 m (d) and 133.72 m (d) (C^{21}, $^{2}J_{PC}$ = 4.2, 2.0), 131.89 br.d.d (s) and 132.87 br.d.d (s) (C^{13}, $^{1}J_{HC}$ = 164.1 and 162.3, $^{3}J_{HC}$ = 8.2 and 8.5), 124.49 d.m (d) and 125.15 d.m (d) ($C^{16,20}$, $^{1}J_{HC}$ = 161.9 and 161.4, $^{3}J_{HC}$ = 7.5 and 7.8, $^{3}J_{HC}$ = 7.4, $^{3}J_{PC}$ = 3.2 and 3.0), 125.46 d.t (s) and 125.71 d.t (s) (C^{18}, $^{1}J_{HC}$ = 163.0 and 162.5, $^{3}J_{HC}$ = 7.2 and 7.5), 127.13 br.d.d (d) (C^{14}, $^{1}J_{HC}$ = 163.1, $^{3}J_{HC}$ = 7.5, $^{3}J_{PC}$ = 1.5), 127.58 br.d.d (br.s) (C^{14}, $^{1}J_{HC}$ = 162.5, $^{3}J_{HC}$ = 7.7), 127.32 d.t (s) and 128.95 d.t (s) (C^{24}, $^{1}J_{HC}$ = 161.3 and 162.0, $^{3}J_{HC}$ = 7.2), 128.07 br.d.d (s) and 128.29 br.d.d (s) (C^{12}, $^{1}J_{HC}$ = 162.5, $^{3}J_{HC}$ = 7.6), 128.30 d.d (s) and 129.18 d.d (s) ($C^{17,19}$, $^{1}J_{HC}$ = 162.4 and 160.4, $^{3}J_{HC}$ = 7.8), 129.65 d.d (s) and 129.73 d.d (s) ($C^{23,25}$, $^{1}J_{HC}$ = 161.8 and 161.9, $^{3}J_{HC}$ = 7.8 and 8.1), 126.16 d.m (d) and 128.99 d.m (d) ($C^{22,26}$, $^{1}J_{HC}$ = 159.4 and 162.2, $^{3}J_{PC}$ = 7.8 and 7.9). $^{31}P\{^{1}H\}$ (^{31}P) NMR spectrum (162.0 MHz), δ_P, ppm (*J*, Hz): 15.3 d.d (s) (d_1, $^{3}J_{PH}$ = 19.3, $^{2}J_{PCH}$ = 12.5), 18.5 d.d (s) (d_2, $^{3}J_{PH}$ = 21.1, $^{2}J_{PH}$ = 20.2). Mass spectrum (EI), *m*/*z* (I_{rel}, %), *m*/*z*: 390 (83.9) $[M]^{\cdot+}$, 362 (19.4) $[M - C_2H_4]^{+}$, 313 (66.8) $[M - C_6H_5]^{+}$, 299 (18.6) $[M - P(O)OC_2H_4]^{+}$, 285 (2.9) $[C_{20}H_{17}N_2]^{+}$, 195 (100.0) $[C_8H_8N_2O_2P]^{+}$, 167(58.9) $[C_7H_8N_2OP]^{+}$, 91 (23.5) $[C_6H_5CH_2]^{+}$, 77 (28.4) $[C_6H_5]^{+}$. Found, %: N 6.82; P 8.21. $C_{22}H_{19}N_2O_3P$. Calculated, %: N 7.18; P 7.95.

NMR spectra were recorded on a Bruker Avance-400 instrument [^{1}H, ^{13}C, $^{13}C\{^{1}H\}$, DEPT, ^{31}P] from $CDCl_3$ solutuions. Mass spectrum was registered on a DFS Thermo Electron Corporation instrument (USA), the energy of ionizing electrons is 70 eV.

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CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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