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LETTERS TO THE EDITOR

Cyclic P(III)-Phosphorylated Derivatives of Pamoic Acid. The Reaction of 4,4'-Methylene-bis(2-phenylnaphtho[2,3-*d*]-1,3,2-dioxaphosphorin-4-one) with Chloral

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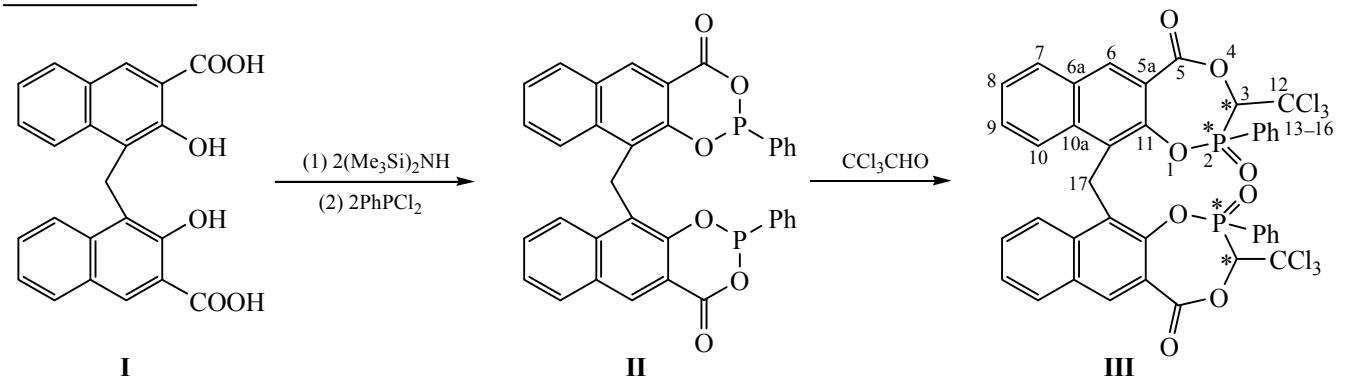
The mixed cyclic anhydride derivatives of natural hydroxycarbocylic acids, as well as of phosphorous or phosphonous acids are convenient reagents for the synthesis of heterocycles with predefined structure. Such acids react with activated unsaturated compounds under mild conditions, readily cleaving the macroergic RO–C(O) fragment and forming the products of cyclic and acyclic structures [1–3]. Recently, by an example of hexafluoroacetone we demonstrated the possibility to involve also more complex objects in such processes, the P(III)-cyclic derivatives derived from the natural substance, 4,4'-methylene-bis(3,2-hydroxynaphthoic) (pamoic) acid (**I**) [4], interesting due to their biological properties [5–7]. In this paper we attempted to prepare the products of expansion of a six-membered ring to a seven-membered one by an example of reaction of chloral with a phosphorylated derivative of the pamoic acid containing phosphorus–carbon bond, 4,4'-methylene-bis(2-phenylnaphtho[2,3-*d*]-1,3,2-dioxaphosphorin-4-one) (**II**). Direct phosphorylation of acid **I** with PCl_3 did not give an unambiguous result [8], so we synthesized compound **II** in two steps: The silylation of acid **I** with hexamethyldisilazane followed by the reaction of the acid **I** *O*-trimethylsilyl derivative with dichlorophenylphosphine.



I **II** **III**

Compound **II** reacts with the prochiral chloral under mild conditions with the formation of six stereoisomeric bis(naphtho-1,4,2-dioxaphosphepines) (**III**) (δ_P 33.6, 32.5, 31.6, 31.2, 29.3, 28.7 ppm) in the ratio 4:5:5:33:4:9. This reaction gives rise to four chiral center resulting in the formation of a mixture of diastereomers. However, one of them (δ_P 31.2 ppm) dominates. In a similar reaction of the cycle expansion of 2-phenylnaphtho[*d*]1,3,2-dioxaphosphepine at the action of chloral [9] the stereoselectivity is very high: of the two possible 2-phenyl-2,5-dioxo-3-(trichloromethyl)naphtho[2,3-*e*]1,4,2-dioxaphosphepine dia-

stereomers only one is formed. The difference in the solubility in methylene chloride of the diastereomers obtained provided a possibility to separate the dominating one. The remaining isomers were isolated as mixtures by reprecipitation of the reaction mixture from methylene chloride to pentane. Structure of individual diastereoisomers of compound **III** is proved by spectral methods.

Compound II. *a*. To a solution of pamoic acid (8.25 g, 21.3 mmol) was added hexamethyldisilazane (18.0 g, 11.0 mmol). The reaction mixture was heated at 120°C for 30 h until the ammonia liberation ceased. The resulting orange precipitate of methylene-bis(2-trimethylsiloxycarbonyl-3-trimethylsiloxynaphthalene) was filtered off, dried in a vacuum (0.1 mm Hg at 60°C), and used further without additional purification, yield 97%.

b. A mixture of methylene-bis(2-trimethylsiloxycarbonyl-3-trimethylsiloxynaphthalene) (12.49 g, 20.1 mmol), CH_2Cl_2 (30 ml) and phenyldichlorophosphine (7.2 g, 40.2 mmol) was maintained at 20°C for 5 days, then the volatile compounds were removed by a vacuum distillation (12 mm Hg). The residue was dried in a vacuum (0.1 mm Hg, 60–70°C). Compound **II** was obtained as a dense vitreous substance of light-cream color, which was used further without additional purification. ^{31}P-$\{^1H\}$ NMR spectrum ($CDCl_3$): δ_P 158.5 ppm (δ_1), 157.7 ppm (δ_2).

Compound (III). A mixture of phosphonite **II** (2.28 g, 3.8 mmol), CH_2Cl_2 (10 ml), and chloral (1.51 g, 10.2 mmol) was maintained at 20°C for 4 days. During this period occurred a partial formation of compound **III**, which was filtered off, washed with diethyl ether, and dried in a vacuum (12 mm Hg). Yield 20%, mp 243-245°C. Found, %: C 51.97, H 2.49, P 7.11. $C_{39}H_{24}Cl_6O_8P_2$. Calculated, %: C 52.29, H 2.68, P 6.93. IR spectrum, cm^{-1}: 3435, 3057, 2894, 1742, 1623, 1594, 1504, 1448, 1440, 1369, 1344, 1285, 1257, 1206, 1160, 1143, 1122, 1077, 1056, 999, 932, 897, 875, 837, 821, 809, 783, 750, 690, 661, 644, 615, 536. The ^1H NMR spectrum (DMF-d_7, δ , ppm, *J*, Hz): 8.58 c (H^6), 8.14 br.d (H^7, $^3J_{H^8CCH^7}$ 8.4), 7.84–7.92 and 7.68, two m (H^{14-16}), 7.79 br.d (H^{10}, $^3J_{H^9CCH^{10}}$ 8.6), 7.64 m (H^9), 7.56 m (H^8), 6.80 d (H^3, $^2J_{PCH^3}$ 4.1), 3.66 m (H^{17}). The ^{13}C NMR spectrum (in parentheses is shown the multiplicity of the signal in ^{13}C–$\{^1H\}$ NMR spectrum) (DMF-d_7, δ_C, ppm, *J*, Hz): 79.98 d.d (d) (C^3, $^1J_{HC^3}$ 151.1, $^1J_{PC^3}$ 96.1), 165.08 d.d (s) (C^5, $^3J_{HC^3OC^5}$ 4.0–5.0, $^3J_{HC^6CC^5}$ 4.0–5.0), 121.04 br.s (s) (C^{5a}), 135.32 d.d (s) (C^6, $^1J_{HC^6}$ 166.6, $^3J_{HC^7CC^6}$ 5.1), 131.35 m (s) (C^{6a}), 130.62 br. d.d. d (br. s) (C^7, $^1J_{HC^7}$ 163.0, $^3J_{HC^9CC^7}$ 8.5, $^3J_{HC^6CC^7}$ 5.0–6.0), 130.62 d.d (s) (C^8, $^1J_{HC^8}$ 163.6, $^3J_{HC^{10}CC^8}$ 8.1), 130.23 d.d (s) (C^9, $^1J_{HC^9}$ 163.6, $^3J_{HC^7CC^9}$ 7.3), 123.92 d.d (s) (C^{10}, $^1J_{HC^{10}}$ 161.8, $^3J_{HC^8CC^{10}}$ 7.3), 134.43 m (s) (C^{10a}), 128.40 m (d) (C^{11}, $^3J_{POCC^{11}}$ 4.8), 141.46 m (d) (C^{11a}, $^2J_{POC^{11a}}$ 9.2), 94.40 d (d) (C^{12}, $^2J_{PCC^{12}}$ 6.2), 127.92 d.m (d) (C^{13}, $^1J_{PC^{13}}$ 128.7, $^3J_{HC^{15}CC^{13}}$ 7.3), 131.86 d.d.d.d (d) (C^{14}, $^1J_{HC^{14}}$ 165.8, $^2J_{PCC^{14}}$ 10.3, $^3J_{HC^{14'}CC^{14}}$ 7.7, $^3J_{HC^{16}CC^{14}}$ 7.7), 129.40 d.d.d (d) (C^{15}, $^1J_{HC^{15}}$ 165.1, $^3J_{PCCC^{15}}$ 13.6, $^3J_{HC^{15'}CC^{15}}$ 7.7), 134.21 br.d.t (br.s) (C^{16}, $^1J_{HC^{16}}$ 164.5, $^3J_{HC^{14}CC^{16}}$ 7.7), 22.66 t (s) (C^{17}, $^1J_{HC^{17}}$ 130.7). The ^{31}P–$\{^1H\}$ NMR spectrum (DMSO-d_6): δ_P 31.2 ppm (s).

The NMR spectra were recorded on a Bruker Avance-400 instrument (^1H, 400 MHz, ^{13}C, 100.6 MHz, ^{31}P, 162.0 MHz). The IR spectrum was recorded on a Bruker Vector-22 instrument from a suspension of the substance in mineral oil.

REFERENCES

1. Mironov, V.F., Gubaidullin, A.T., Konovalova, I.V., Ivkov, G.A, Litvinov, I.A., Burnaeva, L.M., Zyablikova, T.A., Romanov, S.V., and Mavleev, R.A., *Zh. Obsch. Khim*., 2000, vol. 70, no. 11, p. 1812.
2. Burnaeva, L.M., Mironov, V.F., Romanov, S.V., Ivkova, G.A., Shulaeva, I.L., and Konovalova, I.V., *Zh. Obsch. Khim*., 2001, vol. 71, no. 3, p. 525.
3. Mironov, V.F., Zagidullina, E.R., Ivkova, G.A., Dobrynin, A.B., Gubaidullin, A.T., Latypov, Sh.K., Musin, R.Z., Litvinov, I.A., Balandina, A.A., and Konovalova, I.V., *Arkivoc,* 2004, part 12, p. 95.
4. Burnaeva, L.M., Mironov, V.F., Abdrakhmanova, L.M., Ivkova, G.A., Balandina, A.A., Latypov, Sh.K., Konovalova, I.V., and Pudovik, A.N., *Zh. Obsch. Khim*., 2006, vol. 76, no. 8, p. 1394.
5. Reetz, M., Merk, C., and Mehler, G., *Chem. Comm*., 1998, no. 19, p. 2075.
6. Hu, H.-Y., Horton, J.K., Gryk, M.R., Prasad, R., Naron, J.M., Sun, D.-A., Hecht, S.M., Wilson, S.H., and Mullen, G.P., *J. Biol. Chem*., 2004, vol. 279, no. 38, p. 39736.
7. Fei, Z., Slavin, A., and Woollins, D., *Polyhedron*, 2001, vol. 20, no. 28, p. 3355.
8. Fonge, H., Chitneni, S.K., Lixin, J., Vunckx, K., Prinsen, K., Nuyts, J., Mortelmans, L., Bormans, G., Ni, Y., and Verbruggen, A., *Bioconjugate Chem*., 2007, vol. 18, no. 6, p. 1924.
9. Burnaeva, L.M., Mironov, V.F., Abdrakhmanova, L.M., Gubaidullin, A.T., Musin, R.Z., Ivkova, G.A., Litvinov, I.A., Latypov, Sh.K., Balandina, A.A., and Konovalova, I.V., *Zh. Obsch. Khim*., 2007, vol. 77, no. 4, p. 578.