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LETTERS TO THE EDITOR

Intramolecular Transformation of 2-Benzylideneaminoethoxybenzo[*d*]-1,3,2-dioxaphosphorin-4-one into 3,4-Benzo-10-phenyl-1-aza-5,7-dioxa-6-phosphabicyclo-[4.3.1]decane-2,6-dione

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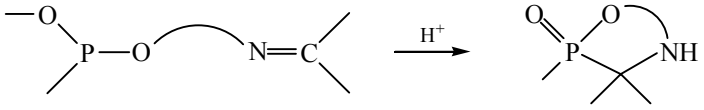
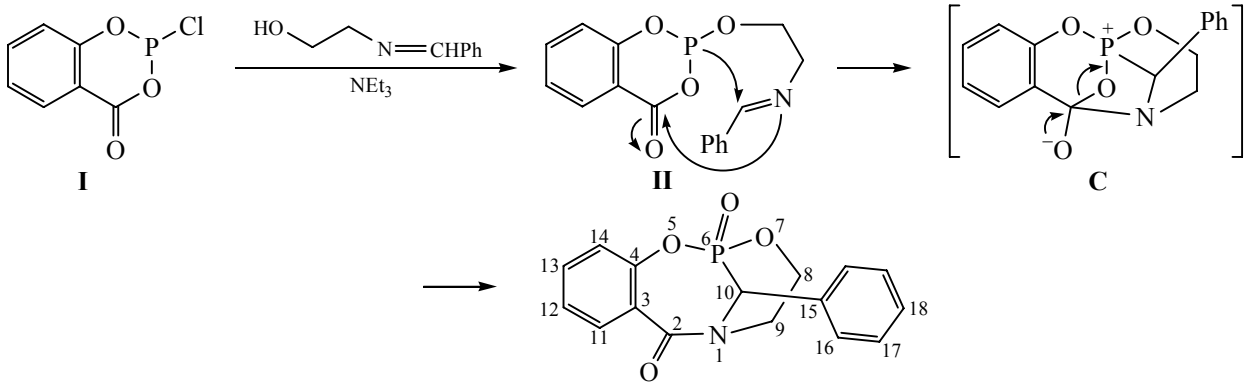
Alkylideneaminoalkoxy derivatives of P(III) **A** readily undergo cyclization in the presence of proton-donating reagents to form 1,4,2-oxazaphosphacyclanes **B** [1–3], which are difficultly accessible by other methods. The derivatives **A** obtained from chlorophosphites, β- or γ-iminoalcohols in the presence of a base are stable and some of them are distilled under reduced pressure [4]. This behavior of the iminophosphites **A** is due to the formation of immonium derivatives in the presence of the proton donor leading to the increase in electrophilic properties of the imino group carbon atom and to the intramolecular cyclization of the phosphites **A** by the nucleophilic attack of the atom P(III) on the imino group.



A **B**

The similar intramolecular cyclization to form P–C bond can be initiated not only by the proton-donating reagents, but by any suitable electrophilic group, which is present in the iminophosphite molecule. The acylphosphite fragment POC(O), which is capable of suffering the nucleophilic attack, proved to be such electrophilic group [5]. Thus, P-cyclic derivative of salicylic acid **II** containing benzylideneaminoethoxyl group as an exocyclic substituent, which was obtained by the reaction of 2-chlorobenzo[*d*]-1,3,2-dioxa-



I **II** **C**

III

phosphorin-4-one **I** with 2-benzylideneaminoethanol in benzene in the presence of triethylamine (δ_P 137.5 ppm), was capable of the intramolecular cyclization into the bicyclic structure **III** (δ_P 20.0 ppm). Apparently, this process includes the nitrogen atom attack on the endocyclic carbonyl carbon atom with the subsequent (or simultaneous) attack of the phosphorus atom on the imino group carbon atom. In this case the intermediate bipolar ion **C** is formed, which further is transformed into the end reaction product **III**.

This transformation is completed in 3 days and is characterized by the high stereoselectivity (one diastereomer is formed). The structure of compound **III** was proved by the ^{1}H, ^{31}P NMR and IR spectroscopy, mass-spectrometry (MALDI, EI) methods. The IR spectrum contains the absorption band at 1673 cm^{-1} belonging to the amide carbonyl group. The corresponding absorption bands originating from the groups P=O (1220 cm^{-1}) and POC (1036 cm^{-1}) are also present.

Compound (III). To a mixture of 0.82 g of 2-benzylideneaminoethanol and 0.84 g of triethylamine in 20 ml of anhydrous benzene was dropwise added at stirring within 20 min a solution of 1.12 g of compound **I** in 5 ml of anhydrous benzene at room temperature under argon atmosphere. After the phosphite addition the reaction mixture was stirred for 30 min and kept for 3 days under argon. The precipitate was filtered off and washed with diethyl ether. The solvent was removed. The residue was viscous colorless oily liquid. Yield 1.5 г (87%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.74 m (1H, NC^9H, $^2J_{HH}$ 14.1, $^3J_{HH}$ 6.9–7.0, $^3J_{HH}$ 6.8), 4.18 m (1H, NC^9H, $^2J_{HH}$ 14.1, $^3J_{HH}$ 6.7, $^3J_{HH}$ 6.7), 4.32 m (1H, OC^8H), 4.43 m (1H, OC^8H), 5.18 d (1H, $^2J_{PH}$ 15.8 Hz), 7.15 br. d (1H, H^{12}, $^3J_{HH}$ 8.3), 7.21 br. d. d (1H, H^{14}, $^3J_{HH}$ 7.6, $^3J_{HH}$ 7.7), 7.27 m, 7.40 m, 7.68 m (*7H*, $H^{11,13}$, $H^{16–18}$). ^{31}P NMR spectrum, δ, ppm (*J*, Hz): 19.9 ($^2J_{PCH}$ 16.0). Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 317 (18.6), 316 (100.0) $[M + H]^+$. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 315 (68.4) $[M]^{+\cdot}$, 287 (34.7) $[M – CO]^+$, 258 (28.7) $[M – CO – COH]^+$, 210 (68.9) $[M – PhCO]^+$, 184 (73.1) $[C_9H_{13}O_2P]^+$, 120 (100.0) $[C_6H_4CO_2]^+$, 91 (76.9) $[PhCH_2]^+$, 77 (19.4) $[Ph]^+$. Found, %: N 4.51; P 10.01. $C_{16}H_{14}NO_4P$. Calculated, % : N 4.44; P 9.84.

The 1H and ^{31}P NMR spectra were recorded on Bruker Avance-600 (600 MHz, ^{1}H) and Bruker CXP-100 (36.48 MHz, ^{31}P) spectrometers in $CDCl_3$ relative to the residual signal of the solvent or to external H_3PO_4. The IR spectrum was registered on a Bruker Vector-22 instrument (from thin film on KBr plates). The mass spectrum MALDI was obtained on a TOF mass spectrometer ULTRAFLEX (Bruker, Germany). Laser desorption was performed with a pulse UV laser (λ 337 nm). Dihydroxybenzoic acid was used as a matrix. The sample was prepared by the “dry drop” method: a mixture of matrix ethanol solution (1 wt %) and THF solution of the analyzed substance (0.1 wt %) was applied on the support and dried at 40°C. The mass spectrum EI was registered on a DFS Thermo Electron Corporation instrument (USA) at the ionization electrons energy 70 eV and ion source temperature 280°C. The capillary column DB-5MS 30 m × 0.254 mm) was used. Gas-carrier helium. The processing of mass spectral data was carried out with the use of Xcalibur program.

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