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LETTERS TO THE EDITOR

To the 80th Anniversary of B.I. Ionin

Interaction of Ethylenechlorophosphite with Hydroxyl-Containing Azomethines

R. Kh. Bagautdinova[a], M. A. Pudovik[a], E. M. Pudovik[b], and A. R. Burilov[a]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, Tatarstan, 420088 Russia*
e-mail: pudovik@iopc.ru

[b] *Kazan (Volga Region) Federal University, Kazan, Tatarstan, Russia*

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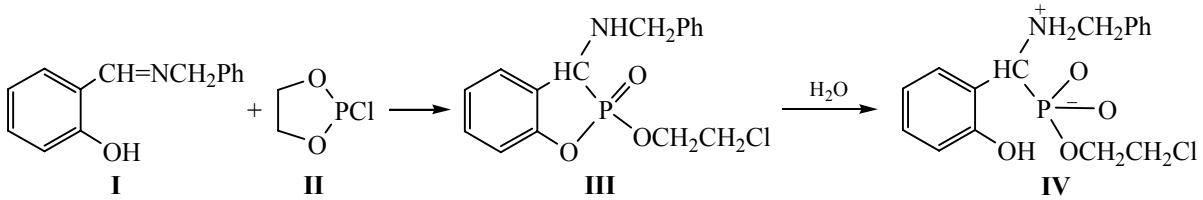
Recently it has been shown that phosphorylation of salicylalalkylene diimines with 2-chloro-1,3,2-dioxaphospholanes in the absence of a base yields polycyclic derivatives of hexacoordinate phosphorus atom containing a transannular intramolecular bond N→P [1–3]. Extending these studies, we performed a reaction of ethylenechlorophosphite with monoazomethines containing phenolic group.

The reaction of imine **I** with ethylenechlorophosphite **II** afforded cyclic phosphonate **III** as a mixture of diastereomers (δ_P 15.92, 16.13 ppm) in the 70:30 ratio. Hydrolysis of **III** gave aminophosphonate **IV** (δ_P 10.41 ppm). The reaction proceeded via phosphorylation of imine **I** at the hydroxyl group with elimination of hydrogen chloride. The latter protonated the imine nitrogen atom, increasing electrophilicity of the C=N bond. Attack of the trivalent phosphorus atom was accompanied by formation of an activated imino spirocyclic moiety which was converted into **III** as a result of attack of chloride anion at the carbon atom of dioxaphospholane fragment (Scheme 1).

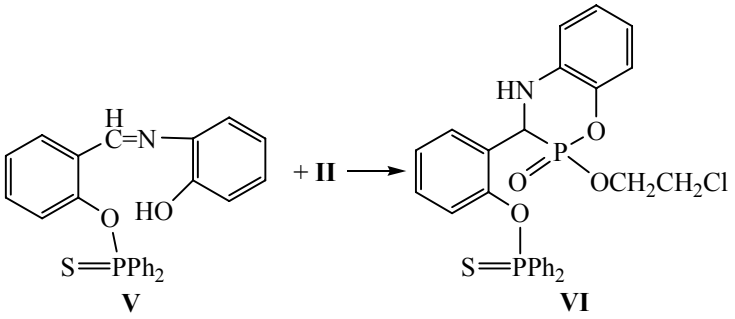
Similar reaction of azomethine **V** with ethylenechlorophosphite afforded six-membered cyclic phosphonate **VI** as a mixture of diastereomers (δ_P 80.86, 9.45 and 80.70, 9.36 ppm) in a ratio of 44 : 56 (Scheme 2).

***O*-Chloroethyl[benzylamino-2-hydroxyphenyl]-methylphosphonate (IV).** A solution of 0.63 g of ethylenechlorophosphite **II** in 10 mL of dichloromethane was added dropwise to a solution of 1.06 g of imine **I** in 50 mL of anhydrous dichloromethane upon stirring. After 12 h, the solvent was removed, and 50 mL of distilled water was added to the residue. After 24 h, the precipitate was filtered off and washed three times with hexane. Yield 1.4 g (79%), mp 285–288°C. IR spectrum (KBr), ν, cm^{-1}: 1458, 1606 (Ph), 2436, 2591, 2745, 2852 (NH_2^+), 3416 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.48 d (1H,

Scheme 1.



Scheme 2.



V **VI**

CH_2, $^2J_{HH}$ 5.8), 3.50 d (1H, CH_2, $^2J_{HH}$ 5.8), 3.67 m (2H, CH_2Cl), 4.00 d (1H, PCH, $^2J_{PH}$ 13.4), 4.24 m (2H, OCH_2), 6.81–7.43 m (9H, Ph). ^{31}P NMR spectrum (DMSO-d_6): δ_P 10.41 ppm. Mass spectrum (MALDI-TOF): m/z 356 $[M + H]^+$. Found, %: C 53.88; H 5.31; Cl 9.69; N 3.73; P 8.52. $C_{16}H_{19}ClNO_4P$. Calculated, %: C 54.01; H 5.39; Cl 9.96; N 3.94; P 8.71.

2-(2-Chloroethoxy)-2-oxo-3-(2-diphenylthioxophosphinyloxy)phenyl-3,4-dihydro-2*H*-benzo[*e*][1,4,2]oxazaphosphinine (VI). A solution of 0.17 g of ethylenechlorophosphite in 10 mL of dichloromethane was added dropwise to a solution of 0.59 g of imine **V** [4] in 50 mL of anhydrous dichloromethane. The mixture was incubated during 12 h, and then the solvent was removed. 50 mL of hexane was added to the residue. After 24 h, the precipitate was separated and washed three times with hexane. Yield 0.66 g (87%), mp 101–104°C. IR spectrum (KBr), ν, cm^{-1}: 1586, 1606 (Ph), 3275 (NH). ^1H (acetone-d_6), δ, ppm (J, Hz): 3.65 m (2H, CH_2Cl), 4.24 m (2H, OCH_2), 5.28 d (1H, PCH, $^2J_{PH}$ 10.7), 5.38 d (1H, PCH, $^2J_{PH}$ 22.3), 6.75–8.28 m (18H, Ph). ^{31}P NMR spectrum (acetone-d_6), δ_P, ppm: 80.86, 9.45 and 80.70, 9.36 (diastereomers ratio 44 : 56). Mass spectrum (MALDI-TOF), m/z: 556 $[M + H]^+$, 579 $[M + Na]^+$, 594 $[M + K]^+$. Found, %: C 58.11; H 4.00; Cl 6.17; N 2.44; P 11.36; S 5.54. $C_{27}H_{24}ClNO_4P_2S$. Calculated, %: C 58.32; H 4.36; Cl 6.38; N 2.52; P 11.14; S 5.77.

IR spectra were recorded with a Bruker Vector-22 spectrometer (400–4000 cm^{-1}, KBr pellets). ^1H NMR spectra were registered using a Bruker MSL-400 instrument operating at 400.13 MHz using residual proton signals of the deuterated solvent as reference. ^{31}P NMR spectra were obtained with a Bruker MSL-400 spectrometer (100.62 MHz). Mass spectra (MALDI-TOF) were taken with an Ultraflex III TOF/TOF Bruker instrument (*p*-nitroaniline as matrix).

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