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LETTERS TO THE EDITOR

Phosphorylation of Optically Pure Salicylal-1,2-diphenylethanediamine with Alkylene Chlorophosphites

L. K. Kibardina, A. R. Burilov, and M. A. Pudovik

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Akademy of Sciences,
ul. Arbuzova 8, Kazan, 420088 Russia
e-mail: pudovik@iopc.knc.ru

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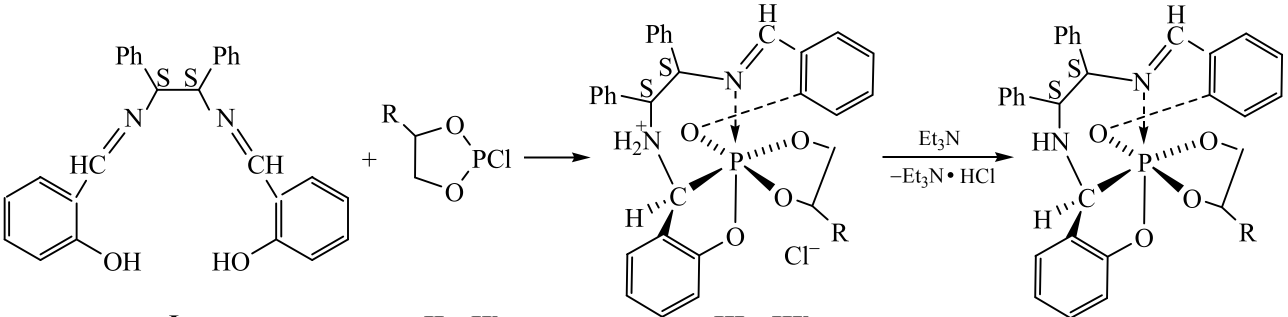
The reaction of salicylalethylenediimine with 2-chloro-1,3,2-dioxaphospholane was found to be a cascade process, resulting in the framework derivatives of hexacoordinated phosphorus atom involving the intramolecular transannular N→P bond (by X-ray data) [1]. It is important that the reaction is highly stereoselective and gives rise to a single diastereomer. Aiming to obtain the optically pure derivative of hexacoordinated phosphorus atom, diimine **I** {obtained in the reaction of 1*S*,2*S*(–)-diphenylethanediimine with salicylaldehyde [2]} was introduced into the reaction with ethylene chlorophosphite. Diimine **I** reacts with ethylene chlorophosphite **IIa** to give an optically pure diastereomer **IIIa** in 82% yield. Its phosphorus chemical shift is δ_P –113.32 ppm, which is characteristic of P(VI) derivatives. The optical rotation of compound **IIIa** is $[\alpha]_D^{20}$ –28.1° (*c* 0.3739, CH_2Cl_2).



I **IIa, IIb** **IIIa, IIIb** **IVa**

R = H (**IIa, IIIa, IVa**); Me (**IIb, IIIb**).

Under the treatment with triethylamine, compound **IIIa** undergoes dehydrochlorination to form phosphorate **IVa** of a neutral structure {δ_P –101.52 ppm, $[\alpha]_D^{20}$ –29.4° (*c* 0.3989, CH_2Cl_2)}.

The reaction with 1,2-propylene chlorophosphite **IIb** leads to the appearance of another chiral center and to the formation of diastereomers mixture **IIIb** (δ_P –112.34, 112.99 ppm) in 1:1.4 ratio.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonium-7,8-diphenyl-2,13-dioxa-1-phospha-[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIa). A mixture of 0.42 g of diimine **I** and 0.13 g of chloride **IIa** in 10 ml of methylene chloride was kept for 7 days at 20°C. The solvent was removed and the residue was washed with diethyl ether. Yield 0.45 g (82%), mp 164–167°C, $[\alpha]_D^{20}$ –28° (*c* 0.3739, CH_2Cl_2). IR spectrum, ν, cm^{-1}: 1624 (C=N), 2415–2678 (NH_2^+). ^{31}P NMR spectrum

($CDCl_3$): δ_P –113.32 ppm. Mass spectrum (MALDI-TOF), *m*/*z*: 510 [M^+ – HCl]. Found, %: N 5.31; P 6.02. $C_{30}H_{28}ClN_2O_4P$. Found, %: N 5.12; P 5.67.

1,1-(1,2-Propylenedioxy)-3,4,11,12-dibenzo-6-aza-9-ammonium-7,8-diphenyl-2,13-dioxa-1-phospha-[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIb) was similarly obtained from 0.42 g of diimine **I** and 0.14 g of chloride **IIa**. Yield 0.46 g (89%), mp 149–151°C. IR spectrum, ν, cm^{-1}: 1628 (C=N), 2413–2669 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –112.34, –112.99. Mass spectrum (MALDI-TOF), *m*/*z*: 524 [M^+ – HCl]. Found, %: N 5.01; P 5.34. $C_{31}H_{30}ClN_2O_4P$. Calculated, %: N 4.99; P 5.52.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6,9-diaza-7,8-diphenyl-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene (IVa). A mixture of 0.14 g of compound **IIIa** and 0.06 g of triethylamine in 10 ml of methylene chloride was refluxed for 2 h. After the removal of the solvent the reaction mixture was diluted with benzene, filtered off from triethylamine hydrochloride, and concentrated. Yield 0.26 g (71%), mp 146°C. IR spectrum, ν, cm^{-1}: 1635 (C=N), 3317 (NH). ^{31}P NMR spectrum ($CDCl_3$): δ_P –101.52 ppm. Mass spectrum (MALDI-TOF), *m*/*z*: 510. Found, %: N 5.22; P 6.13. $C_{30}H_{27}N_2O_4P$. Calculated, %: N 5.49; P 6.07.

The IR spectra were recorded on a Bruker Vector 22 Fourier-spectrometer from KBr pellets in a range of 400–4000 cm^{-1}. The ^{31}P NMR spectra were registered on a Bruker MSL-400 Fourier-spectrometer (100.62 MHz). The mass spectra (MALDI-TOF) were taken on a Ultraflex III TOF/TOF Bruker instrument using *p*-nitroaniline as a matrix.

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