

LETTERS
TO THE EDITORReaction of 2-Bromo-1,3,2-Dioxaphospholane
with Salicylaethanediamine

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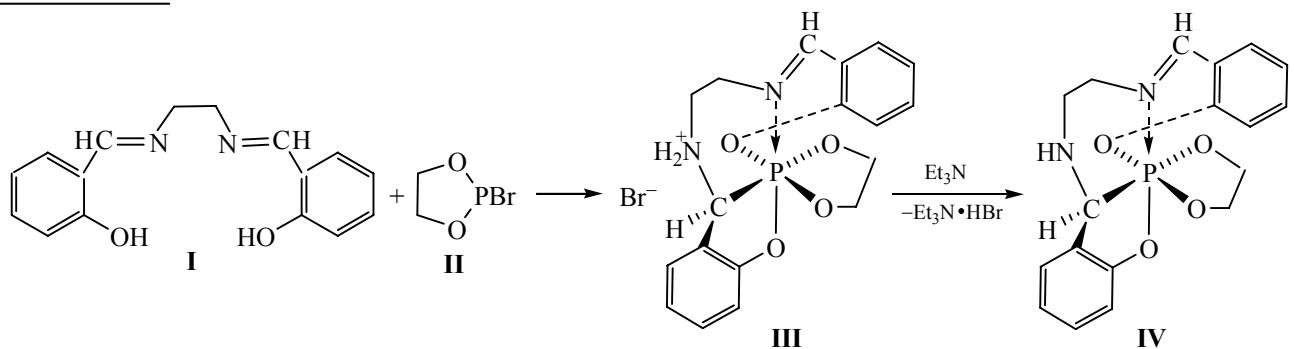
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We have previously shown that the reaction of salicylaethanediamine with some cyclic chlorphosphites results in hexacoordinated phosphorus atom derivatives involving the intramolecular transannular N→P bond (according to the X-ray diffraction method) [1]. Aiming to study the synthetic opportunities of this reaction, we carried out for the first time the reaction

of ethylenebromophosphite **II** with bisazometine **I**. According to the ^{31}P NMR data, the reaction occurs with a high stereoselectivity to form diastereomerically pure product **III** in almost quantitative yield. The phosphorus chemical shift of this product is $\delta_{\text{P}} -118.05$ ppm, which is characteristic for the P(VI) derivatives.



At treating with triethylamine, product **III** undergoes dehydrobromination to transform into a neutral phosphate **IV** ($\delta_{\text{P}} -101.52$ ppm). The structure of the compounds obtained was confirmed by the ^1H and ^{31}P NMR, IR spectroscopy, mass spectrometry and elemental analysis data.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonium-2,13-dioxo-1-phospha[8.3.0] 1,10 tridecatri-3,5,11-ene bromide (III). To a solution of 0.27 g diimine **I** in 5 ml of methylene chloride was added 0.17 g of bromide **II**. A self-heating of the reaction mixture was observed. After 4 h, the precipitate formed was separated and washed with diethyl ether. Yield 0.42 g (96%), mp 282°C. IR spectrum, ν , cm^{-1} : 1625 (C=N), 2415–2678 (NH_2^+). ^1H NMR spectrum (CD_3Cl), δ ,

ppm: 3.54–4.07 m (8H, NCH_2 , OCH_2), 4.46 d (1H, PCH, $^2J_{\text{HP}}$ 7.85), 6.86–7.71 m (8H, CH_{Ar}), 8.72 d (1H, CHN= , $^3J_{\text{PH}}$ 7.62). ^{31}P NMR spectrum ($\text{DMSO}-d_6$): $\delta_{\text{P}} -118.05$ ppm. Mass spectrum (MALDI-TOF), m/z : 358 [$M^+ - \text{HBr}$]. Found, %: N 6.01; P 7.06. $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{PBr}$. Calculated, %: N 6.38; P 7.05.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6,9-diaza-2,13-dioxo-1-phospha[8.3.0] 1,10 tridecatri-3,5,11-ene (IV). A mixture of 0.44 g of compound **III** and 0.1 g of triethylamine in 10 ml of methylene chloride was refluxed for 2 h. The solvent was distilled off, the reaction mixture was dissolved in benzene, and triethylamine hydrochloride was filtered off. The resulting solution was evaporated. Yield 0.27 g (74%), mp 177°C. IR, ν , cm^{-1} : 1635 (C=N), 3345 (NH). Mass

spectrum (MALDI-TOF), m/z : 358.3. ^{31}P NMR spectrum (CD_3Cl): δ_{P} -105.48 ppm. Found, %: N 7.49; P 8.31. $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4\text{P}$. Calculated, %: N 7.81; P 8.53.

The ^1H NMR spectra were recorded on an Avance 600 spectrometer (600.13 MHz, CDCl_3). The ^{31}P NMR spectra were recorded on a Bruker Fourier MSL-400 spectrometer (100.62 MHz). The IR spectra were recorded on a Vector 22 Fourier spectrometer (Bruker) in the range 400–3600 cm^{-1} from KBr pellets. The mass spectra (MALDI-TOF) were obtained on an

Ultraflex III TOF/TOF Bruker instrument (matrix *p*-nitroaniline).

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