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LETTERS TO THE EDITOR

Reaction of 2,2,2-trichloro-1,2,3-dioxaphospholo[4,5-*b*]pyridine with 4-Bromophenylacetylene

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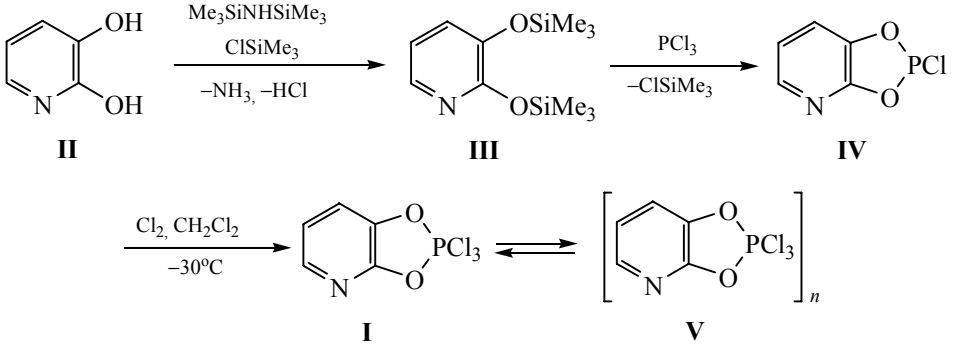
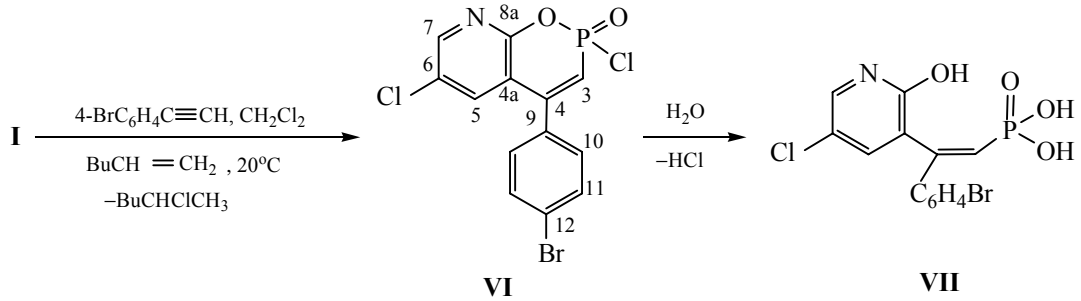
A simple transformation of dioxaphospholene fragment into the oxaphosphorinine we found earlier studying the reaction of 2,2,2-trihalogenobenzo[*d*]-1,3,2-dioxaphosphols with arylacetylenes [1] opens a way to preparation of phosphorus-containing analogs of coumarins, benzo[*e*]-1,2-oxaphosphorinine derivatives [2–4].

In this work 2,2,2-trichloro-1,3,2-dioxaphospholo-[4,5-*b*]pyridine **I** was brought into the reaction with acetylene. Compound **I** was obtained starting from 2,3-dihydroxypyridine **II** in several stages: a silylation using hexamethyldisilazane to form compound **III**, the reaction of the latter with phosphorus trichloride to give phosphol **IV**, and chlorination of the latter. The selected way to phosphol **I** allows maximally to avoid possible complexation processes of the base nitrogen with phosphorus atom or hydrogen chloride in the intermediate synthesis stages. However phosphorane **I** proper is in the equilibrium with hexacoordinated form **V** (δ_P –160.7 ppm).



The reaction of trichlorophosphorane **I** with 4-bromophenylacetylene in the presence of equimolar amount of hexene, which was used to bind the released hydrogen chloride, under mild conditions (CH_2Cl_2, 20°C) proceeds also to the formation of oxaphosphorinane derivatives. The ^{31}P NMR spectrum of the reaction mixture contains characteristic doublet of the main compound **VI** at δ_P 16.6 ppm ($^2J_{PCH}$ 23.1 Hz) and the signal of the starting phosphorus derivative as the ate-complex **V**, which precipitates due to the poor solubility. The removal of compound **V** and the solvent followed by evacuating the residue (150°C, 15 mm Hg) to remove hexene and styrenes results in a glassy substance, which was dissolved in chloroform, treated with water, and crystallized to obtain phosphonic acid **VII**. The structure of the latter was proved by the ^{13}C, $^{13}C–\{^1H\}$ NMR spectra. The observed signal multiplicity for the nuclei C^{8a} (d.d) and C^{4a} (d.d) and the coupling constants values are in accordance with the *ipso*-substitution of the oxygen atom in the *meta*-position relative to the nitrogen atom and with the chlorination into the position 6 of the

heterocycle. The formation of 2,3,5-trisubstituted pyridine is also in good agreement with the ^{1}H NMR spectrum, where the protons H^5 and H^7 resonate as singlets.



Thus, the reaction of phospholopyridine **I** with 4-bromophenylacetylene proceeds to form exclusively compounds of the phosphirine nature. The reaction makes it possible to extend the synthesis method of oxaphosphorinine heterocycle to the derivatives, in which the latter is fused with pyridine that opens prospects for using other hydroxy substituted *N*-heterocycles, including alkaloids.

2,3-Bis(trimethylsiloxy)pyridine (III). A mixture of 10 g of 2,3-dihydroxypyridine **II**, 39 ml of hexamethyldisilazane, and some drops of trimethylchlorosilane was refluxed for 4 h. Then the hexamethyldisilazane excess was removed by distillation. The residual colorless clear liquid was distilled in a vacuum. Yield 19.1 g (68.6%), bp 119°C (25 mm Hg), n_D^{20} 1.512. IR spectrum, ν, cm^{-1}: 412, 579, 597, 624, 695, 739, 766, 795, 847, 906, 933, 1063, 1107, 1201, 1251, 1284, 1305, 1372, 1462, 1584, 1623, 1655, 1872, 1959, 2555, 2901, 2959, 3058, 3462.

2-Chloro-1,3,2-dioxaphospholo[4,5-*b*]pyridine (IV). A mixture of 45.9 g (0.18 mol) of compound **III** and 26 ml (0.30 mol) of phosphorus trichloride was heated to boiling. The residue was distilled. Yield 13.1 g (41.4%), bp 90–100°C (15 mm Hg), colorless clear liquid. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$), δ_P 171.2 ppm.

2,2,2-Trichloro-1,3,2-dioxaphospholo[4,5-*b*]pyridine (I). To a solution of 3.7 g (0.055 mol) of phosphite **IV** in 10 ml of methylene chloride was added 1.5 g (0.058 mol) of chlorine in 30 ml of CH_2Cl_2 at –30°C (the bath temperature). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P –40 ppm. The obtained compound was used without further purification.

Reaction of compound (I) with 4-bromophenylacetylene. To a suspension of phosphorane **I** in CH_2Cl_2 (20 ml) was added a solution of 3.6 g of 4-bromophenylacetylene and 5 ml of hexene in 15 ml of CH_2Cl_2. We observed HCl release and dissolution of the phosphorane precipitate. After 24 h the solvent was removed and the reaction mixture was kept in a vacuum (15 mm Hg) for 2 h at 120°C (the external heating temperature). The obtained glassy brown residue containing predominantly compound **VI** was washed with anhydrous hexane (2×20 ml) to remove the formed styrenes and dissolved in 15 ml of chloroform. The solution was treated with 1 ml of water. The formed white precipitate was filtered off, washed with acetone, and dried in air. Yield of phosphonate **VII** 1.03 g (12.6%), bp 190–191°C. IR spectrum, ν, cm^{-1}: 3447, 3232, 3069, 2955, 2925, 2855, 2289, 1634, 1614, 1548, 1488, 1455, 1378, 1313, 1204, 1132, 1077, 1007, 933, 868, 803, 787, 761, 666, 510. ^{1}H NMR spectrum, δ, ppm: 6.28 d (1H, H^3, $^2J_{PCH}$ 13.0 Hz), 7.46 d (1H, H^5, $^4J_{HCCCH}$ 2.9 Hz), 7.63 d (1H, H^7, $^4J_{HCCCH}$ 2.9 Hz), 7.26 d (H^{10}, $^3J_{HCCH}$ 8.6 Hz), 7.53 d (H^{11}, $^3J_{HCCH}$ 8.6 Hz). ^{13}C NMR spectrum, δ, ppm (the signal multiplicity in the ^{13}C–{^{1}H} spectrum is given in the brackets): 123.21 d.d (d) (C^3, $^1J_{PC^3}$ 182.1, $^1J_{HC^3}$ 150.3 Hz), 148.75 m (d) (C^4, $^3J_{PCCC^4}$ 4.6, $^2J_{HCC^4}$ 2.2 Hz), 124.12 d.d (d) (C^{4a}, $^3J_{PCCC^{4a}}$ 15.2, $^3J_{HCCC^{4a}}$ 9.5 Hz), 131.35 d.d (s) (C^5, $^1J_{HC^5}$ 184.1, $^3J_{HCCC^5}$ 3.7 Hz), 110.68 br.s (s) (C^6), 141.09 d.d (s) (C^7, $^1J_{HC^7}$ 167.0, $^3J_{HCCC^7}$ 5.3 Hz), 159.31 d.d.d (d) (C^{8a}, $^3J_{HCCC^{8a}}$ 8.6, $^3J_{HCCC^{8a}}$ 7.3, $^3J_{PCCCC^{8a}}$ 1.0 Hz), 138.73 d.d.d (d) (C^9, $^3J_{PCCCC^9}$ 20.8, $^3J_{HCCC^9}$ 7.0, $^3J_{HCCC^9}$ 7.0 Hz), 121.94 d.d (s) (C^{10}, $^1J_{HC^{10}}$ 161.1, $^3J_{HCCC^{10}}$ 7.0 Hz), 128.44 d.d (s) (C^{11}, $^1J_{HC^{11}}$ 166.9, $^3J_{HCCC^{11}}$ 5.7 Hz), 121.94 d.d.d.d (s) (C^{12}, $^3J_{HCCC^{12}}$ 11.2, $^3J_{HCCC^{12}}$ 11.2, $^3J_{HCCC^{12}}$ 3.0, $^3J_{HCCC^{12}}$ 3.0 Hz). ^{31}P–{^{1}H} NMR spectrum: δ_P 10.0 ppm.

The ^{1}H and ^{31}P NMR spectra were recorded on

Bruker Avance-400 (400 MHz, ^{1}H; 100.6 MHz, ^{13}C) and Bruker CXP-100 (36.48 MHz, ^{31}P) spectrometers in DMSO-d_6 relative to the solvent or external reference (H_3PO_4) signal. The IR spectra were registered on a Bruker Vector-22 instrument (mineral oil, KBr).

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