ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 1005–1007. © Pleiades Publishing, Inc., 2006.
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LETTERS TO THE EDITOR

New Example of the Application of Trivalent Phosphorus Derivatives in a Synthetic Chemistry of Carbohydrates

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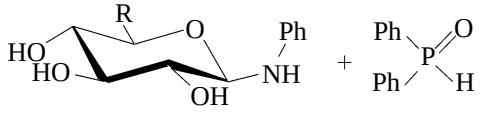
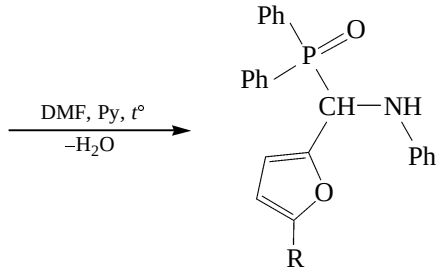
Received September 7, 2005

DOI: 10.1134/S1070363206060284

We found that reaction of β-pyranosylaminobenzenes with diphenylphosphinous acid in the presence of weak bases leads to formation of tertiary phosphine oxides containing aniline and α-furyl fragments in their structures.



I, II **III**



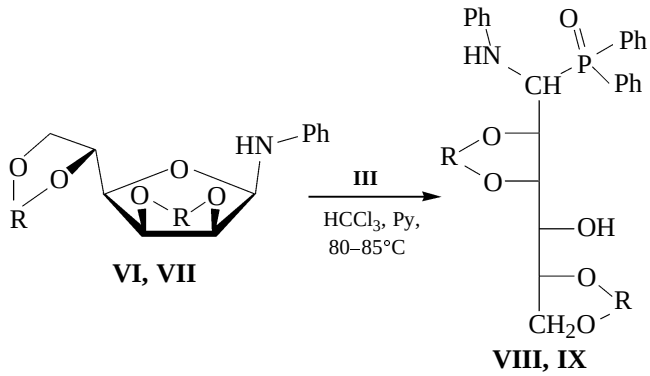
IV, V

R = H (**I, IV**), CH_2O (**II, V**).

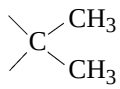
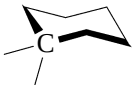
The synthesis of compound **IV** was performed at 20–25°C, and compound **V** was synthesized at 50–55°C. The structures of the obtained compounds were proved by ^1H, ^{13}C and, ^{31}P NMR spectroscopy and X-ray diffraction.

Thus, we suggested a new original synthetic approach to representatives of the class of tertiary β-aminofurfurylphosphine oxides. Taking into account the data in [1] we expect that these compounds will present interest as receptors of α-hydroxy acids.

The reaction of glycosylamines with compound **III** probably combines two processes: Kabachnik–Fields phosphorylation [2, 3] and aromatization of the initially formed phosphine oxides containing polyol fragments. This assumption is confirmed by the results of the reaction of compound **III** with partially protected glycosylamines **VI** and **VII**.



VI, VII **VIII, IX**

R =  (**VI, VIII**),  (**VII, IX**).

Tertiary phospine oxides IV and V *(general procedure).* *N*-Phenylglycoside **I** or **II**, 5 mmol, was dissolved in 5 ml of DMF and then 1 ml of pyridine and 5 mmol of compound **III** were added. The mixture was stirred for 5–6 h at 20–25°C (with **I**) or 50–

55°C (with **II**). The solvents were evaporated, and the residue was washed with benzene and subjected to chromatography on silica gel in ethanol–acetone (4 : 1).

***N*-[(Diphenylphosphinoyl)(2-furyl)methyl]aniline (IV).** Yield 50%, mp 238–240°C (sublimes at 240°C), R_f 0.75. ^{1}H NMR spectrum (DMSO, δ, ppm): 5.85–6.02 m (2H, NCHP, NH); furan fragment: 6.21 m (H, H4, $^3J_{HH}$ 3.3 Hz); 6.30 m (H, H^3, $^4J_{H,NCHP}$ 2.7 Hz); 7.35 m (H, H^5); aniline fragment: 6.57 d.d (H, H^4); 6.89 d (2H, H^2, H^6, $^3J_{HH}$ 7.6 Hz); 7.02 d.d (2H, H^3, H^5, $^3J_{HH}$ 8.5 Hz); diphenylphosphinoyl fragment: 7.43–7.52 m (6H, 2H^3, 2H^4, 2H^5); 7.75–7.98 m (4H, 2H^2, $^3J_{HH}$ 9.9 Hz, $^3J_{HP}$ 59.3 Hz, 2H^6, $^3J_{HH}$ 10.4 Hz, $^3J_{HP}$ 58.7 Hz). ^{13}C NMR spectrum (DMSO, δ_C, ppm): 50.3 d (NCHP, $^1J_{CP}$ 81.6 Hz); furan fragment: 109.5 d (C^3, $^3J_{CP}$ 5.0 Hz); 110.4 (C^4); 142.4 (C^5); 149.9 (C^2); aniline fragment: 113.9 (C^2, C^6); 117.5 (C^4); 128.6 (C^3, C^5); 147.1 d (C1, $^3J_{CP}$ 10.9 Hz); diphenylphosphinoyl fragment: 128.1–128.4 m (2C^3, 2C^5); 130.3–133.2 m (2C^1, 2C^4, 2C^2, 2C^6). ^{31}P NMR spectrum (DMSO): δ_P 29.1 ppm.

{5-[(Diphenylphosphinoyl)(phenylamino)methyl]-2-furyl}methanol (V). Yield 38%, mp 197–198°C, R_f 0.70. ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 5.97–6.04 m (3H, NCHP, NH, H^4 furan); furan fragment: 4.11 m (2H, CH_2); 5.07 t [1H, OH, ^3J(H,CH_2) 6.0 Hz]; 6.28 m (1H, H^3); aniline fragment: 6.57 d.d (1H, H^4, $^3J_{HH}$ 6.4 Hz); 6.93 d (2H, H^2, H^6, $^3J_{HH}$ 7.6 Hz); 7.02 d.d (2H, H^3, H^5, $^3J_{HH}$ 7.2 Hz); diphenylphosphinoyl fragment: 7.43–7.50 m (6H, 2H^3, 2H^4, 2H^5); 7.77–8.01 m (4H, 2H^2, 2H^6). ^{13}C NMR spectrum (DMSO, δ_C, ppm): 50.2 d (NCHP, $^1J_{CP}$ 82.2 Hz); furan fragment: 55.3 (CH_2); 107.3 (C^3); 109.9 d (C^4, $^4J_{CP}$ 5.0 Hz); 148.7 (C^5); 154.6 (C^2); aniline fragment: 113.7 (C^2, C^6); 117.2 (C^4); 128.6 (C^3, C^5); 146.8 d (C^1, $^3J_{CP}$ 11.3 Hz); diphenylphosphinoyl fragment: 127.8–128.5 m (2C^3, 2C^5); 130.6–132.4 m (2C^1, 2C^4, 2C^2, 2C^6). ^{31}P NMR spectrum (DMSO-d_6): δ_P 29.2 ppm.

Tertiary phosphine oxides VIII and IX *(general procedure).* *N*-glycoside **VI** or **VII**, 5 mmol, was dissolved in a mixture of 5 ml of chloroform and 1 ml of pyridine, 5 mmol of compound **III** was added, and the mixture was stirred for 24 h at 80–85°C. The solvents were evaporated, and the syrup-like residue was subjected to chromatography on silica gel in benzene–acetonitrile–hexane (4 : 2 : 1).

1,2;4,5-Di-*O*-isopropylidene-6-(diphenylphosphinoyl)-6-(phenylamino)hexane-1,2(*R*),3(*R*),4(*S*),5(*S*)-pentaol (VIII). Yield 70%. Product **VIII** (as a mixture of two isomers) is a yellow syrup. R_f 0.46. ^{13}C NMR spectrum of **VIIIa** (DMSO, δ_C, ppm): isopropylidene fragment: 25.3–27.3 (H_3CCCH_3); 108.5 (O^4*C*(CH$_3$)$_2$O^5); 108.6 (O^1*C*(CH$_3$)$_2$O^2); hexane fragment: 50.6 d (C6, $^1J_{CP}$ 81.7 Hz); 66.9 (C^1); 68.9 (C^3); 75.2 (C^4); 75.9 (C^2); 77.3 d (C^5, $^2J_{CP}$ 11.6 Hz); aniline fragment: 112.9 (C^2, C^6); 117.1 (C^4); 128.9 (C^3, C^5); 147.6 d (C^1, $^3J_{CP}$ 5.5 Hz); diphenylphosphinoyl fragment: 127.6–128.2 m (2C^3, 2C^5); 130.6–133.7 m (2C^1, 2C^4, 2C^2, 2C^6). ^{13}C NMR spectrum of **VIIIb** (DMSO-d_6, δ, ppm): isopropylidene fragment: 25.3–27.3 (H_3CCCH_3); 108.2 (O^4*C*(CH$_3$)$_2$O^5); 108.8 (O^1*C*(CH$_3$)$_2$O^2); hexane fragment: 54.7 d (C^6, $^1J_{CP}$ 77.8 Hz); 66.4 (C^1); 69.6 (C^3); 74.9 d (C^4, $^3J_{CP}$ 5.4 Hz); 76.0 (C^2); 80.2 d (C^5, $^2J_{CP}$ 8.6 Hz); aniline fragment: 112.8 (C^2, C^6); 116.5 (C^4); 128.6 (C^3, C^5); 147.3 d (C^1, $^3J_{CP}$ 3.5 Hz); diphenylphosphinoyl fragment: 127.6–128.2 m (2C^3, 2C^5); 130.6–133.7 m (2C^1, 2C^4, 2C^2, 2C^6). ^{31}P NMR spectrum (DMSO-d_6, δ_P, ppm): 29.5 (31.3%, **VIIIa**); 31.0 (68.7%, **VIIIb**).

1,2;4,5-Di-*O*-cyclohexylidene-6-(diphenylphosphinoyl)-6-(phenylamino)hexane-1,2(*R*),3(*R*),4(*S*),5(*S*)-pentaol (IX). Yield 75%, light yellow syrup, slowly crystallizes on standing. R_f 0.58. ^{13}C NMR spectrum of isomer **IXa** (DMSO, δ_C, ppm): cyclohexylidene fragment: 21.2–24.4, 34.2–36.1 (H_2C); 108.4 (O^4*C*(CH$_2$)$_2$O^5); 108.7 (O^1*C*(CH$_2$)$_2$O^2); hexane fragment: 50.7 d (C^6, $^1J_{CP}$ 83.4 Hz); 66.1 (C^1); 68.9 (C^3); 74.4 (C^4); 75.3 (C^2); 76.6 d (C^5, $^2J_{CP}$ 11.5 Hz); aniline fragment: 112.6 (C^2, C^6); 117.1 (C^4); 127.5 (C^3, C^5); 146.9 d (C^1, $^3J_{CP}$ 6.0 Hz); diphenylphosphinoyl fragment: 127.5–128.7 m (2C^3, 2C^5); 130.4–133.5 m (2C^1, 2C^4, 2C^2, 2C^6). ^{13}C NMR spectrum of isomer **IXb** (DMSO-d_6, δ, ppm): cyclohexylidene fragment: 21.2–24.4, 34.2–36.1 (H_2C); 108.3 (O^4*C*·(CH$_2$)$_2$O^5); 108.6 (O^1*C*(CH$_2$)$_2$O^2); hexane fragment: 54.2 d (C6, $^1J_{CP}$ 77.6 Hz); 65.7 (C^1); 69.0 (C^3); 73.4 d (C^4, $^3J_{CP}$ 3.4 Hz); 78.9 (C^2); 79.8 d (C^5, $^2J_{CP}$ 9.6 Hz); aniline fragment: 112.2 (C^2, C^6); 116.0 (C^4); 128.2 (C^3, C^5); 146.7 d (C^1, $^3J_{CP}$ 3.1 Hz); diphenylphosphinoyl fragment: 127.5–128.7 m (2C^3, 2C^5); 130.4–133.5 m (2C^1, 2C^4, 2C^2, 2C^6). ^{31}P NMR spectrum (DMSO-d_6, δ_P, ppm): 28.4 (40.65%, isomer **IXa**); 30.9 (59.35%, isomer **IXb**).

ACKNOWLEDMENTS

The authors are grateful to A.A. Borisenko for help in recording the NMR spectra.

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