4-DIETHOXYPHOSPHORYL-5-ETHOXY-4-PHENYL-3,4,5,6-TETRAHYDRO-DIAZINO[2,3-*c*]FURAZANE

F. I. Guseinov, Kh. A. Asadov, R. N. Burangulova, and V. V. Moskva

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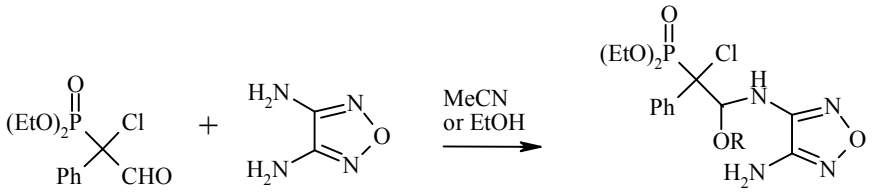
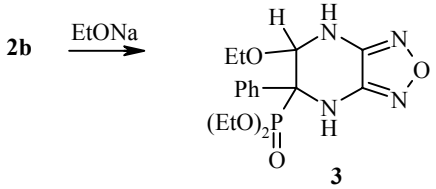
In a study of the synthesis of C-phosphorylated heterocyclic compounds [1, 2] using the reactions of phosphorylated acetaldehydes with polyfunctional nucleophilic reagents, we investigated the reaction of acetaldehyde **1** with 3,4-diaminofurazane. Carrying out this reaction in acetonitrile leads to hydroxy compound **2a**. In ethanol, this reaction gives ethoxy derivative **2b**, which is a hemiaminal.



1 **2a**,**b**

a R = H, **b** R = Et

The reaction of **2b** with sodium ethylate in ethanol gives in good yield a condensed heterocyclic product, namely, **3**, which is the first phosphorylated diazino[2,3-*c*]furazane reported [3].



3

The structure of **3** was proven by IR, ^{1}H NMR, and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **3** has signals at 20.83 and 20.91 ppm, indicating the existence of two diastereomers.

Diethyl Ester of 2-(4-Amino-3-furazanyl)amino-2-chloro-2-hydroxy-1-phenylethylphosphonic Acid (2a). A mixture of aldehyde **1** (5.81 g, 20 mmol) and furazane (2 g, 20 mmol) in acetonitrile (30 ml) was heated at reflux for 12 h. The solvent was evaporated and 10 ml 1:1 ether–ethanol was added to the reaction

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Kazan State Technological University, 420015 Kazan, Russia, e-mail: eltos@Kai.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1140-1142, August, 2001. Original article submitted February 27, 2001.

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mixture. The precipitate formed was filtered off and recrystallized from ethanol to give 6.48 g (83%) **2a**; mp 152-153°C. IR spectrum, ν, cm^{-1}: 1280, 1650, 3100, 3250, 3340. ^{31}P NMR spectrum, δ, ppm: 15.0. ^{1}H NMR spectrum ($(CD_3)_2CO$), δ, ppm, *J* (Hz): 1.10 (6H, dt, $2CH_3$); 3.90 (4H, m, $2OCH_2$); 5.50 (1H, d, $^{3}J_{PH}$ = 5, OCH); 6.00 (2H, br. s, NH_2); 7.25 (3H, m, Ph); 7.60 (2H, m, Ph); 10.30 (1H, br. s, OH); 11.50 (1H, br. s, NH). Found, %: Cl 9.18; N 14.47; P 7.98. $C_{14}H_{20}ClN_4O_5P$. Calculated, %: Cl 9.09; N 14.34; P 7.94.

Diethyl Ester of 2-(4-Amino-3-furazanyl)amino-1-chloro-2-ethoxy-1-phenylethylphosphonic Acid (2b) was obtained analogously. The reaction of aldehyde **1** (5.81 g, 20 mmol) and 3,4-diaminofurazane (2 g, 20 mmol) gave 6.7 g (80%) **2b**; mp 158-159°C. IR spectrum, ν, cm^{-1}: 1285, 1640, 3100, 3250. ^{31}P NMR spectrum, δ, ppm: 15.15, 15.20. ^{1}H NMR ($(CD_3)_2CO$), δ, ppm, *J* (Hz): 1.00 (9H, dt, $3CH_3$); 3.75 (4H, m, $2OCH_2$); 4.00 (2H, q, OCH_2); 5.75 (1H, d, $^{3}J_{PH}$ = 5, OCH); 6.10 (2H, br. s, NH_2); 7.30 (3H, m, Ph); 7.80 (2H, m, Ph); 11.70 (1H, br. s, NH). Found, %: Cl 8.57; N 13.44; P 7.55. $C_{16}H_{24}ClN_4O_5P$. Calculated, %: Cl 8.48; N 13.38; P 7.41.

4-Diethoxyphosphoryl-5-ethoxy-4-phenyl-3,4,5,6-tetrahydrodiazino[2,3-*c*]furazane (3). A sample of metallic sodium (0.23 g, 10 mmol) was dissolved in ethanol (20 ml) and a solution of **2b** (4.19 g, 10 mmol) in ethanol (10 ml) was added dropwise to the sodium methoxide solution at 50°C. The reaction mixture was then heated at reflux for 8 h. The solvent was evaporated and 15 ml ether was added to the residue. The precipitate of NaCl was filtered off and the filtrate was evaporated in vacuum. The precipitate formed was recrystallized from acetone to give 2.9 g (76%) **3**; mp 150-151°C. IR spectrum, ν, cm^{-1}: 1280, 1620, 3250. ^{31}P NMR spectrum: 20.83, 20.91. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15 (9H, dt, $3CH_3$); 3.80 (4H, m, $2OCH_2$); 4.10 (2H, q, OCH_2); 5.00 (1H, dt, OCH); 7.35 (3H, m, Ph); 7.50 (2H, m, Ph); 12.38 (2H, br. s, 2NH). Found, %: N 14.34; P 8.22. $C_{16}H_{23}N_4O_5P$. Calculated, %: N 14.66; P 8.12.

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