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FORMYLATION AND ESTERIFICATION OF *N*-DIACETYLGLYCOLURIL

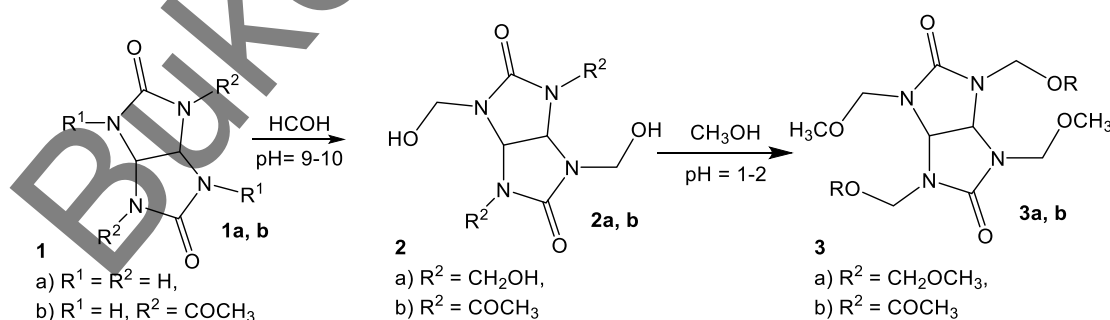
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N-Acetylated glycoluril derivatives are used as effective bleach activators in detergents [1]. Tetra(hydroxymethyl)glycoluril **2a** and *N*-alkoxyderivatives based on it **2a** are currently widely used as cross-linking agents in the production of glycoluril-formaldehyde resins and high-quality thermoset polymer coatings [2, 3]; in the synthesis of macromolecular objects [4], and also as a bactericidal agent for aqueous compositions [5, 6].

Taking into account the relevance of the above derivatives of glycoluril, the purpose of this work was to obtain an ester based on *N*-diacetylglycoluril **1b** via the formylation step (Scheme 1).



Scheme 1

Substance **2a** is synthesized by a typical *N*-formylation reaction of glycoluril **1a** in an alkaline medium [7]. For further synthesis of ester **3a**, the isolated product **2a** was placed in methyl alcohol, which is both a solvent and a reagent at pH = 1–2.

Thus, the highest yields of alkoxyglycolurils are formed using nitric acid as a catalyst [7]. The reaction mass was stirred for 2 hours at 50°C. These conditions were first used to obtain an ester based on of *N*-diacetylglycoluril **1b** via a formylation step. In the formylation reaction of *N*-diacetylglycoluril **1b**, a white crystalline product **2b** was isolated.

It is known [1] that *N*-acetylglycolurils are prone to hydrolysis, which proceeds under the action of various basic and nucleophilic reagents. The hydrolysis process proceeds stepwise with the predominant formation of *anti*-substituted *N*-diacetylglycoluril **1b** [1]. Thus, *N*-diacetylglycoluril **1b** is stable under the above formylation conditions and does not undergo further deacetylation.

N-diacetyl-*N*-dihydroxymethylglycoluril **2b** was placed in methyl alcohol at pH = 1–2, and the reaction mixture was stirred at 50°C for an 1 hour. As a result of the reaction, *N*-diacetyl-*N*-dimethoxymethyl-glycoluril **3b**, colorless product was isolated. The resulting substances **2b**, **3b** were identified and described by IR and NMR spectroscopy (Table 1)

Table 1 – Chemical shifts in the NMR spectra of substances **2a,b**, **3a,b**

№	¹ H NMR (DMSO-d ₆), δ ppm, Hz:			¹³ C NMR (DMSO-d ₆), δ ppm:			
	CH-CH	N-CH ₂	R	C=O	CH-CH	N-CH ₂	R
2a	5.51	4.70 (d, 2H, J = 11.2) 4.80 (d, 2H, J = 11.2)	5.97 (br. s, 4H, OH)	157.5	87.0	65.1	–
2b	5.55	4.71 (d, 1H, J = 11.0) 4.75 (d, 1H, J = 11.0)	2.23 (s, 6H, COCH ₃) 6.75 (br. s, 2H, OH)	157.9	82.4	66.1	175.7, 25.6 (COCH ₃)
3a	5.52	4.67 (d, 2H, J = 10.8) 4.71 (d, 2H, J = 11.2)	3.17 (s, 12H, OCH ₃)	158.5	74.9	67.2	56.0 (OCH ₃)
3b	5.35	4.67 (d, 1H, J = 11.2) 4.60 (d, 1H, J = 10.5)	2.54 (s, 6H, COCH ₃) 3.15 (s, 6H, OCH ₃)	160.2	79.2	69.1	171.9, 25.8 (COCH ₃) 55.5 (OCH ₃)

A distinctive feature for the spectra of compounds **2a,b**, **3a,b** is that in the region of δ 4.60–4.80 ppm there is a doublet of doublets with a constant J = 10.8–11.2 Hz, which indicates the nonequivalence of the protons of the methylene group. Characteristically, minimization of the DFT method for the conformation of compound **2a** showed that the fragments O=C–N–CH₂–OR are almost planar six-membered pseudocycles. The folding angle between the planes of the rings ranges from 123° to 128° for the four most stable conformers of compound **2a** [8]. This angle is estimated as the torsion angle, including the central carbon atoms of the CH groups and the carbons of the C=O groups as terminal centers. It should be noted that the deviation of the angle in the molecule from tetrahedral is due to the fact that the CH₂-methylene group is part of a rigid pseudocycle, which causes limited rotation of the CH₂-groups, as a result of which the protons of the methylene groups become nonequivalent.

Thus, for the first time *N*-diacetyl-*N*-dihydroxymethylglycoluril **2b** and *N*-diacetyl-*N*-dimethoxymethylglycoluril **3b** were obtained. Substances **2b**, **3b** described by IR and NMR spectroscopy.

Experimental part.

NMR spectra were recorded on a Bruker AVANCE III HD spectrometer (Bruker Corporation, Germany) with an operating frequency of 400 and 100 MHz for ^1H and ^{13}C nuclei respectively, in a solutions of DMSO- d_6 with concentration: 0.0001 mol of substance in 0.5 ml of solvent. Tetramethylsilane was used as internal standards for ^1H and ^{13}C nuclei. Chemical shifts of substances are shown in table 1.

IR spectra were recorded on a Nicolet 6700 IR spectrometer, Thermo Fisher Scientific. The samples were studied by the method of disturbed total internal reflection in the spectral range from 400 to 4000 cm^{-1} .

Synthesis of 2,6-diacetyl-4,8-dihydroxymethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (2b). A 20% sodium hydroxide solution is added to a suspension of 2.26 g of N-diacetylglycoluril **1b** and 10 g (0.33 mol) of a 40% formaldehyde solution until pH 9–10 is reached. Then the reaction mixture was stirred at a temperature of 50°C for 2 hours. After the solution is neutralized and evaporated to 1/3 of the volume, 50 ml of methyl alcohol is added, the precipitate is filtered off, washed with 20 ml of methyl alcohol. Yield **2b** 1.28 g (45%), m.p. 158 °C. IR spectrum, ν , cm^{-1} : 1750 (C=O), 1679 (C=O), 3330 (OH).

Synthesis of 2,6-diacetyl-4,8-methoxymethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (3b). 50 ml of methyl alcohol (0.125 mol), 1.5 ml of 70% nitric acid, and 1.5 g of **2b** (0.004 mol) are placed into a flask equipped with a stirrer, thermometer, and reflux condenser. The mixture is heated until complete dissolution, then stirred at a temperature of 55°C for an 1 hour. Then the reaction mixture is cooled to 22°C and neutralized with 20% sodium hydroxide solution to pH=7–8. Residues of methyl alcohol are removed under reduced pressure. The precipitated crystals are filtered off and recrystallized from acetone. Yield **3b**: 0.88 g (70%), m.p. 320°C. IR spectrum, ν , cm^{-1} : 1170, 1213 (C–O–C), 1760 (C=O), 1700 (C=O), 2978 (CH_3).

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СИНТЕЗ И МОЛЕКУЛЯРНЫЙ ДОКИНГ НОВЫХ ПРОИЗВОДНЫХ 1,3,4-ТИАДИАЗОЛА НА ОСНОВЕ 3-АМИНОПИРИДОНА

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В продолжении нашего научного исследования, связанного с химической модификацией монотиоксамидных производных на основе 3-аминопиридин-2(1H)-она 1a-c, которые в первичных биологических испытаниях *invitro* показали высокую противодиабетическую активность [1], мы провели синтез аналогичных производных 1,3,4-тиадиазола, используя ангидриды одноосновных и двухосновных кислот (Схема 1).

Схема 1

