ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 2, pp. 338–339. © Pleiades Publishing, Ltd., 2014.
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LETTERS TO THE EDITOR

New Heterocycles Based on Tetramethylol Glycoluril

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Received May 23, 2013

DOI: 10.1134/S1070363214020339

Recently there is a strong tendency for increasing a number of investigations devoted to the synthesis and studying of properties of heterocycles using an available 2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione **I** (tetramethylol glycouril) as a synton [1,2].

In order to expand preparative possibilities of chemical transformation of tetramethylol glycoluril **I** under the action of nitrogen-containing bases, we studied its condensation with 2-amino-4-phenylthiazole **II** as the specimen of polyfunctional organic compounds. Dione **I** and thiazole **II** were prepared and isolated by procedures [3] and [4], respectively (see Scheme 1).

We found that the direction of the reaction between compounds **I** and **II** depends primarily on the amount of reagent **II**.

Thus, the reaction of **I** with twofold excess of thiazole derivative **II** within 4 h afforded predominantly azaheterocyclization product **III** with a yield of 64%, whereas with 4-fold excess of thiazole **II** under similar conditions we isolated the condensation product **IV** with a yield of 58%. Low yields of azaheterocycles **III** and **IV** are mainly due to the fact that under conditions studied the side reactions of the products of autocondensation of **I** and **II** proceed to form a complex mixture of unidentified compounds (the presence of aminothiazole fragment in the structure of these compounds was unambiguously proved by NMR spectra).

Furthermore, we have shown that the condensation product **IV** underwent the azacyclization in 4 h to give **III** with a yield of 84%. This suggests that the synthesis of **III** in the reaction also may occur through the intermediate formation of tetrathiazole derivative **IV**.

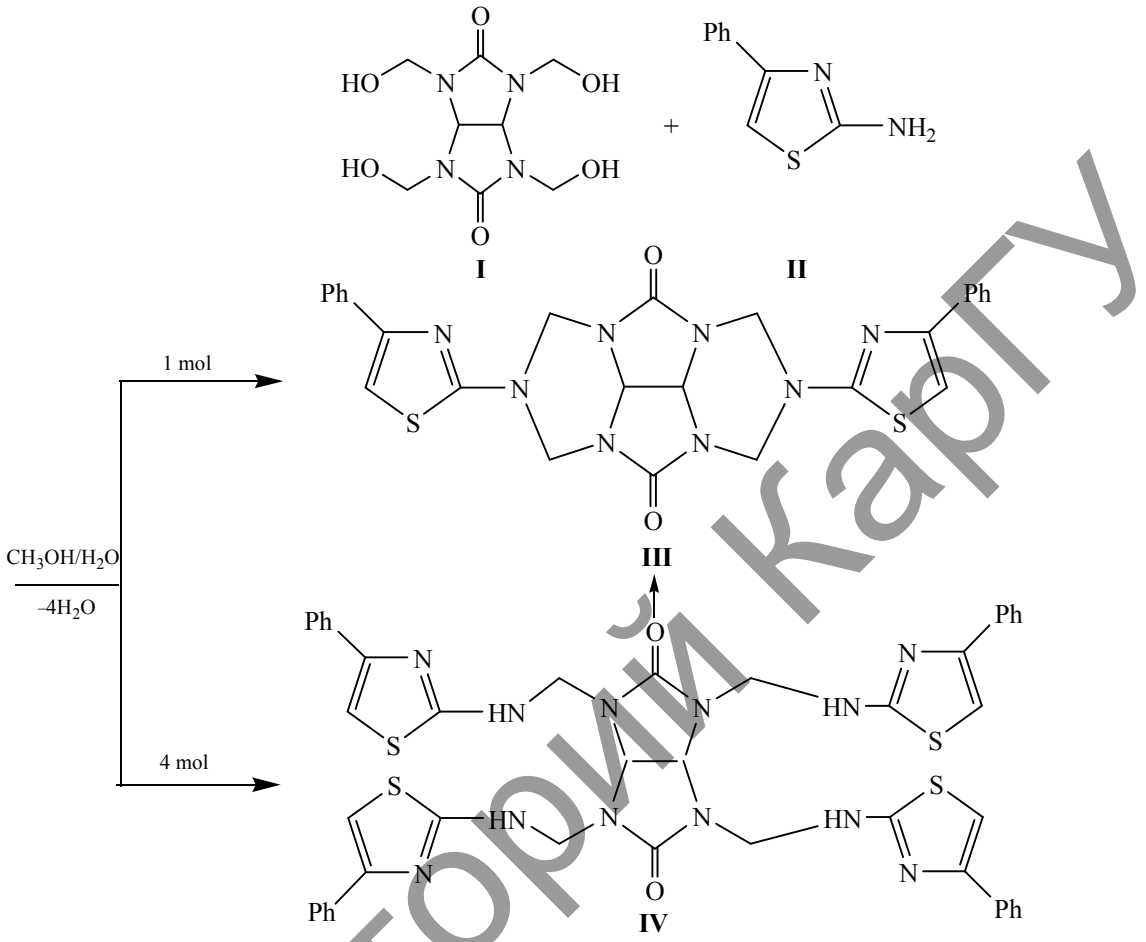
One-step synthesis of azaheterocycle **III** from glycoluril **V** via the Mannich reaction resulted in the desired product in low yield (17%). In this case high molar mass compounds were predominantly obtained.

In summary, the reaction of tetramethylol glycoluril **I** with thiazole **II** afforded new nitrogen-containing heterocycles **III** and **IV**, which are of interest as convenient preparative synthons for further transformations and possess potential useful properties (see Scheme 2).

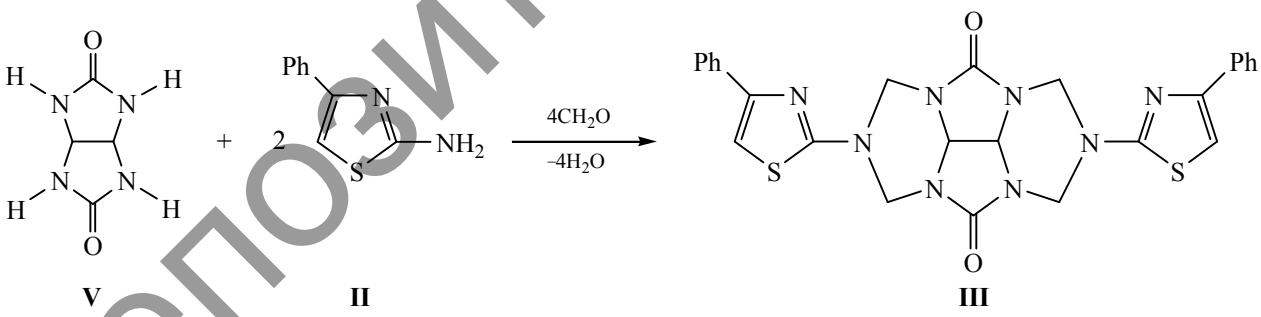
Composition and structure of the obtained azaheterocycles **III** and **IV** were recorded by the data of elemental analysis, NMR spectroscopy and mass spectrometry. NMR spectra were registered on a spectrometer Bruker DRX-300, operating frequency 300 MHz, internal reference TMS.

3,9-Bis[2-(4-phenyl)thiazolyl]-1,3,5,7,9,11-hexaazatetracyclo[5.5.2.$0^{3,14}$.$0^{9,13}$]tetradodeca-6,12-dione (III). Yield 5.2 g (68%), decomp. point 270°C. IR spectrum (KBr), ν, cm^{-1}: 1706 (C=O), 1604 (C=C), 1476 (C=N). ^{1}H NMR (DMSO-d_6), δ, ppm: 3.34 d. d [8H, N<u>CH$_2$</u>NC(O), $^2J_{HH}$ –12.4 Hz], 4.75 s [4H, (O)CN<u>CH</u>NC(O)], 5.58 s (4H, $H^5_{thiazole}$), 7.71–7.25 m (20H, C_6H_5). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 62.98 [N<u>CH$_2$</u>NC(O)], 72.59 [(O)CN<u>CH</u>NC(O)],

Scheme 1.



Scheme 2.



127.67, 128.70, 129.00, 129.98 (C_{Ar}), 116.54 ($C^5_{thiazole}$), 135.67 ($C^2_{thiazole}$), 152.75 ($C^4_{thiazole}$), 167.82 (C=O).

2,4,6,8-Tetramethylamino-{2-(4-phenylthiazolyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione} (IV). Yield 3.4 g (58%), mp 201–203°C. IR spectrum (KBr), ν, cm^{-1}: 3391 (N–H), 1684 (C=O), 1618 (C=C), 1474 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.16 s (8H, HN$\underline{CH_2}$N), 4.71 s [2H, (O)CN$\underline{CH}$NC(O)], 5.52 s (4H, $H^5_{thiazole}$), 7.70–7.26 m (20H, C_6H_5), 8.59 br.s (4H, NH).

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