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> LETTERS TO THE EDITOR

New Heterocycles Based on Tetramethylol Glycoluril

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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-phenyl-thiazole **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), v, cm⁻¹: 1706 (C=O), 1604 (C=C), 1476 (C=N). ¹H NMR (DMSO-*d***₆), \delta, ppm: 3.34 d. d [8H, N<u>CH</u>₂NC(O), ²J_{HH} -12.4 Hz], 4.75 s [4H, (O)CN<u>CH</u>NC(O)], 5.58 s (4H, H⁵_{thiazole}), 7.71–7.25 m (20H, C₆H₅). ¹³C NMR spectrum (DMSO-***d***₆), \delta_C, ppm: 62.98 [N<u>CH</u>₂NC(O)], 72.59 [(O)CN<u>CH</u>NC(O)],**



127.67, 128.70, 129.00, 129.98 (C_{Ar}), 116.54 ($C_{thiazole}^{5}$), 135.67 ($C_{thiazole}^{2}$), 152.75 ($C_{thiazole}^{4}$), 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), v, cm⁻¹: 3391 (N–H), 1684 (C=O), 1618 (C=C), 1474 (C=N). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 3.16 s (8H, HN<u>CH</u>₂N), 4.71 s [2H, (O)CN<u>CH</u>NC(O)], 5.52 s (4H, H⁵_{thiazole}), 7.70–7.26 m (20H, C₆H₅), 8.59 br.s (4H, NH).

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