

3,3'-Bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine and 6,6'-dibromo-3,3'-bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine

Danuta Branowska*, Beata Iwańska and Andrzej Rykowski

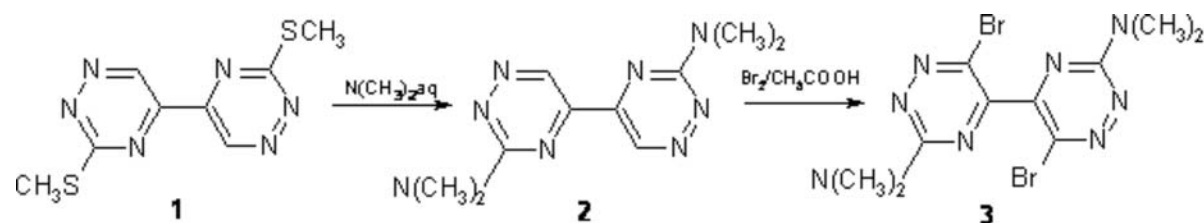
Institute of Chemistry, University of Podlasie, ul. 3 Maja 54, PL-08-110 Siedlce, Poland

E-mail: dankab@ap.siedlce.pl

Received: 18 November 2003 / Accepted: 18 February 2004 / Published: 24 February 2004

Keywords: 5,5'-bi-1,2,4-triazine, nucleophilic substitution, bromination

Continuing our study on the application of 1,2,4-triazines in organic synthesis [1] we prepared the title compounds as valuable intermediates for metalation reactions leading to functionalized 5,5'-bi-1,2,4-triazines [2].



The mixture of 3,3'-bis(methylsulfanyl)-5,5'-bi-1,2,4-triazine (**1**) [3] (756 mg, 3.0 mmol) and dimethylamine, 40 wt. % solution in water (40 g), was stirred at room temperature for 20 hrs, and then was heated at 70 ° C during a period of 30 min. The precipitate was filtered off and it was purified by column chromatography on silica gel (Merck type 60, 230-400 mesh) using a mixture of chloroform/acetone (100:1) as eluent to give 709 mg (96 %) of 3,3'-bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine of (**2**) as a yellow solid.

To a solution **2** (246 mg, 1.0 mmol) in acetic acid (8 mL) the bromine (1.6 g, 10 mmol) was added. The reaction mixture was refluxed for 2 hrs. After that time the reaction mixture was cooled to 20 ° C, diluted with water (50 mL) and extracted with chloroform (5 x 25 mL). The organic extract was washed with water (125 mL) and dried over $MgSO_4$. Removal of the solvent in vacuum and purification of the residue by column chromatography on silica gel (Merck type 60, 230-400 mesh) using a mixture of chloroform/acetone (100:1) as eluent gave 222 mg (55 %) of 6,6'-dibromo-3,3'-bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine (**3**) as a yellow solid.

3,3'-Bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine (**2**)

M.p. 223-224 ° C

1H NMR ($CDCl_3$, 200 MHz): 3.37 (s, 12H, 4 x CH_3), 9.44 (s, 2H, H –triazine).

Anal Calcd. for $C_{10}H_{14}N_8$: C, 48.78; H, 5.69; N, 45.53. Found: C, 48.88; H, 5.57; N, 45.40

6,6'-Dibromo-3,3'-bis(*N,N*-dimethylamino)-5,5'-bi-1,2,4-triazine (**3**)

M.p. 122-123 ° C

^1H NMR(CCl_4 , 60 MHz): 3.85 (s, 12H, 4 x CH_3).

Anal Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_8\text{Br}_2$: C, 29.73; H, 2.99; N, 27.73. Found: C, 29.84; H, 2.83; N, 27.63

References:

1. For previous paper in this series, see: Branowska, D., Rykowski, A., *Synlett*, **2002**, 1892-1895.
2. Hundsdorf, T., Neunhoeffer, H., *Synthesis*, **2002**, 1800-1805.
3. Krass, K.D., Chen, T.-K., Paudler, W.W., *J. Heterocycl. Chem.* **1973**, *10*, 343-345.

© 2004 [MDPI](http://mdpi.org). All rights reserved