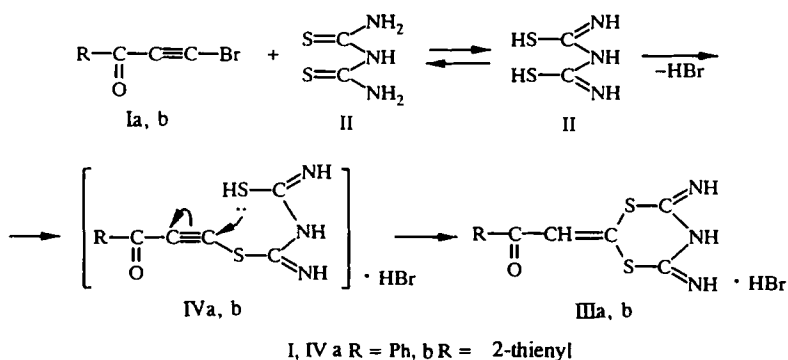


# NEW ROUTE FOR THE SYNTHESIS OF HYDROBROMIDES OF SUBSTITUTED 5,6-DIHYDRO-1,3,5-DITHIAZINES BY THE REACTION OF 1-ACYL-2-BROMOACETYLENES WITH DITHIOBIURET

A. S. Nakhmanovich, T. E. Glotova, T. N. Komarova,  
and V. A. Lopyrev

The 2,4,6-trisubstituted 5,6-dihydro-1,3,5-dithiazines are obtained by the reaction of aliphatic and aromatic aldehydes with ammonia and hydrogen sulfide in alcohol at 0°C [1]. The N-substituted 5,6-dihydro-1,3,5-dithiazines are obtained together with thioamides by the reaction of 2-substituted 1,3-dithietane with ethylamine in acetonitrile at 20°C [2].

We showed that 1-benzoyl- and 1-(2-thenoyl)-2-bromoacetylenes (Ia, b) react with dithiobiuret (II) in glacial acetic acid or benzene at 20°C with the formation of hydrobromides of 2-acylmethylene-4,6-diimino-5,6-dihydro-1,3,5-dithiazines (IIIa, b).



It can be assumed that the reaction includes the formation of the intermediates (IVa, b), which further undergo intramolecular cyclization with the formation of the hydrobromides (IIIa, b). The structure of the compounds (IIIa, b) were confirmed by the data of the elemental analysis, IR, and NMR spectroscopy. The IR spectra were obtained on the UR-20 instrument (KBr tablets). The  $^1\text{H}$  NMR spectra of solutions in DMSO- $\text{D}_6$  were obtained on the DS-487 spectrometer (80 MHz), and the internal standard was HMDS. The  $^{13}\text{C}$  NMR spectra were obtained on the FX-90 Q spectrometer (22.49 MHz,  $\text{CDCl}_3$ ), and the internal standard was HMDS.

**2-Benzoylmethylene-4,6-diimino-5,6-dihydro-1,3,5-dithiazine Hydrobromide (IIIa).** To the solution of 1.0 g (5 mmole) of the ketone (Ia) in 20 ml of glacial acetic acid is added, with intensive stirring, 0.68 g (5 mmole) of dithiobiuret (II), and the mixture is stirred at 20°C for 5 h. The mixture is cooled to 0°C, and the precipitated residue is filtered off, washed with cold ether, and dried *in vacuo*. The yield of compound (IIIa) is 1.48 g (86%), and the mp is 240-242°C. When the reaction is conducted in benzene, the yield of compound (IIIa) is 64%. The IR spectrum ( $\nu$ ) is as follows: 1630  $\text{cm}^{-1}$  1645  $\text{cm}^{-1}$  (C=O, C=N), 1680  $\text{cm}^{-1}$  (C=C), 3280  $\text{cm}^{-1}$ , and 3340  $\text{cm}^{-1}$  (NH). The spectrum lacks the absorption band of the disubstituted  $\text{C}\equiv\text{C}$  bond at 2200-2265  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum is as follows: 7.63 ppm (1H, s, CO-CH=), 7.8-8.2 ppm (5H, m, Ph), 10.11 ppm (1H, s, NH), and 10.35 ppm (1H, s, NH). The  $^{13}\text{C}$  NMR spectrum is as follows: 187.03 ppm (C=O), 140.01 ppm (CO-CH=), 121.08 ppm ( $\text{C}_{(2)}$ ), 165.57 ppm ( $\text{C}_{(4)}$ ), 167.78 ppm ( $\text{C}_{(6)}$ ), 136.17 ppm, 133.96 ppm, 129.02 ppm, and 128.63 ppm (Ph). Found, %: C 38.42, H 2.91, Br 23.08, N 12.29, and S 18.42.  $\text{C}_{11}\text{H}_{10}\text{BrN}_3\text{OS}_2$ . Calculated, %: C 38.37, H 2.91, Br 23.26, N 12.21, and S 18.60.

Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033, Russia. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 3, pp. 417-418, March, 1998. Original article submitted February 2, 1998.

**2-(2-Thenoyl)methylene-4,6-diimino-5,6-dihydro-1,3,5-dithiazine Hydrobromide (IIIb).** This compound is synthesized by analogy with compound (IIIa) from 1.08 g (5 mmole) of the ketone (Ib) and 0.68 g (5 mmole) of dithiobiuret. The yield is 1.54 g (88%), and the mp is 234-236°C. When the reaction is conducted in benzene, the yield of compound (IVb) is 61%. The IR spectrum ( $\nu$ ) is as follows: 1630  $\text{cm}^{-1}$ , 1648  $\text{cm}^{-1}$  (C=O, C=N), 1685  $\text{cm}^{-1}$  (C=C), 3285  $\text{cm}^{-1}$ , and 3350  $\text{cm}^{-1}$  (NH). The spectrum lacks the absorption band of the disubstituted C $\equiv$ C bond at 2200-2265  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum is as follows: 7.61 ppm (1H, s, CO-CH=), 7.45-8.31 ppm (3H, m, C<sub>4</sub>H<sub>3</sub>S), 10.15 ppm (1H, s, NH), and 10.38 ppm (1H, s, NH). The  $^{13}\text{C}$  NMR spectrum is as follows: 187.11 ppm (C=O), 140.08 ppm (CO-CH=), 121.05 ppm (C<sub>(2)</sub>), 165.44 ppm (C<sub>(4)</sub>), 167.80 ppm (C<sub>(6)</sub>), 136.50 ppm, 132.24 ppm, 130.87 ppm, and 129.40 ppm (C<sub>4</sub>H<sub>3</sub>S). Found, %: C 30.69, H 2.31, Br 22.69, N 11.88, and S 27.50. C<sub>9</sub>H<sub>8</sub>BrN<sub>3</sub>OS<sub>3</sub>. Calculated, %: C 30.86, H 2.29, Br 22.86, N 12.00, and S 27.43.

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