

SHORT
COMMUNICATIONS

Synthesis of New 1,3,5-Dithiazine Derivatives

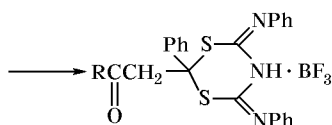
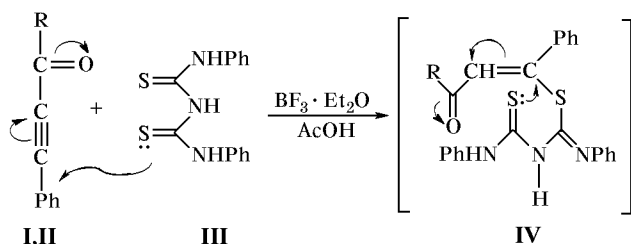
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2,4-Dithiobiurets are known to be used as synthons in preparation of various derivatives of 1,3,5-dithiazine and 1,3,5-triazine, potential biologically active substances [1–5]. In extension of our previous research on reactions of activated acetylenes with polyfunctional nucleophiles containing sulfur and nitrogen [6–8] we report here on reactions between 1-aryloxy-2-phenylacetylenes **I**, **II** with 1,5-diphenyl-2,4-dithiobiuret (**III**).

It was established that 1-benzoyl- and 1-(2-thenoyl)-phenylacetylenes (**I**, **II**) reacted with 1,5-diphenyl-2,4-dithiobiuret (**III**) in glacial acetic acid at 20°C in the presence of equimolar amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ affording in good yield 2-arylmethyl-2-phenyl-4,6-bis(phenylimino)-5H-1,3,5-dithiazinium trifluoroborates **V**, **VI**.



V,VI

R = Ph (**I**, **V**), 2-thienyl (**II**, **VI**).

The reaction apparently proceeded via intermediate formation of ketovinyl sulfide **IV**, and the attack of the second sulfur atom on the conjugated C=C bond of the intermediate **IV** led to the closure of 1,3,5-dithiazine ring.

2-Benzoylmethyl-2-phenyl-4,6-bis(phenylimino)-5H-1,3,5-dithiazinium trifluoroborate (V). To a mixture of 1.43 g (5 mmol) of 1,5-diphenyl-2,4-dithiobiuret (**III**) and 0.71 g (5 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in 20 ml of glacial acetic acid was added dropwise slowly at vigorous stirring a solution of 1.03 g (5 mmol) of 1-benzoyl-2-phenylacetylene (**I**) in 10 ml of glacial acetic acid. The reaction mixture was stirred at 20°C for 2 h, the separated precipitate was filtered off, washed with 10 ml of glacial acetic acid, then with 30 ml of anhydrous ether, and dried in a vacuum. Yield 1.93 g, colorless crystals, mp 119–121°C. IR spectrum, cm^{-1} : 3240 (NH), 1685 (C=O), 1430–1590 (C=C, C=N), 1000–1070 (BF_3^-). ^1H NMR spectrum, δ , ppm: 4.73 s (2H, CH_2), 7.29–8.01 m (20H_{arom}), 12.36 br.s (1H, NH). ^{13}C NMR spectrum, δ , ppm: 48.70 (CH_2), 58.81 (C_2), 124.15, 126.17, 127.09, 127.53, 128.49, 128.82, 129.04, 129.96, 134.12, 135.79, 136.41, 138.43 (C_6H_5), 165.65 (C_4 , C_6), 194.52 (C=O). Found, %: C 62.15; H 4.35; F 10.38; N 7.28; S 11.47. $\text{C}_{29}\text{H}_{23}\text{N}_3\text{OS}_2 \cdot \text{BF}_3$. Calculated, %: C 62.03; H 4.10; F 10.16; N 7.49; S 11.41.

2-(2-Thenoyl)methyl-2-phenyl-4,6-bis(phenylimino)-5H-1,3,5-dithiazinium trifluoroborate (VI) was prepared similarly to compound **V** from 1.43 g (5 mmol) of reagent **III**, 0.71 g (5 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and 1.06 g of acetylene **II**. Yield 1.88 g (66%), light-yellow crystals mp 122–124°C. IR spectrum, cm^{-1} : 3260 (NH), 1655 (C=O), 1410–1600 (C=C, C=N), 1000–1100 (BF_3^-). ^1H NMR spectrum, δ , ppm: 4.59 s (2H, CH_2), 7.20–8.17 m (18H, $3\text{C}_6\text{H}_5$, $\text{C}_4\text{H}_3\text{S}$), 12.37 br.s (1H, NH). ^{13}C NMR spectrum, δ , ppm: 48.87 (CH_2), 59.05 (C_2), 143.19, 136.72, 136.37, 130.11 ($\text{C}_4\text{H}_3\text{S}$), 123.50, 124.24, 126.27, 127.17, 127.69, 129.14, 135.53, 138.42 ($3\text{C}_6\text{H}_5$), 165.70 (C_4 , C_6), 187.45 (C=O). Found, %: C 57.39; H 3.88; F 10.47; N 7.22; S 16.45. $\text{C}_{27}\text{H}_{21}\text{N}_3\text{OS}_3 \cdot \text{BF}_3$. Calculated, %: C 57.14; H 3.70; F 10.05; N 7.41; S 16.93.

IR spectra were recorded on spectrophotometer Specord 75IR from KBr pellets. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 at operating frequencies 400.13 and 100.61 MHz respectively from solutions in $\text{DMSO}-d_6$.

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