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SHORT COMMUNICATIONS

1-Benzoyl-2-phenylacetylene and 1-Methyldithiobiuret as Key Compounds in the Synthesis of *N*-Methyl-*N′*-(4,6-diphenyl-1,3-thiazin-2-ylidene)thiourea

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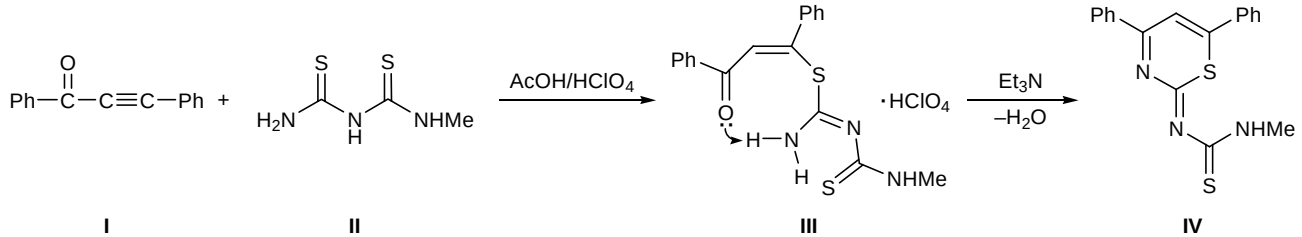
Various N,S-containing heterocycles were synthesized using dithiobiurets as building blocks via reactions with aldehydes, ketones, and α-halo ketones [1–4]. We previously showed that reactions of terminal α,β-acetylenic ketones with dithiobiuret and its 1-mono- and 1,5-disubstituted derivatives lead to formation of new 1,3,5-dithiazines, 1,3,5-thiadiazines, and 1,3,5-triazines, depending on the conditions [5, 6]. 1-Benzoyl-2-phenylacetylene reacts with 1,5-diphenyldithiobiuret in glacial acetic acid in the presence of an equimolar amount of perchloric acid to give the corresponding 1,3,5-dithiazinium perchlorate [7].

We have found that the reaction of 1-benzoyl-2-phenylacetylene (**I**) with 1-methyldithiobiuret (**II**) in glacial acetic acid in the presence of an equimolar amount of perchloric acid at 20°C leads to *S*-(1,3-diphenyl-3-oxo-1-propenyl)-*N*-(methylaminocarbonothioyl)isothiuronium perchlorate (**III**) which undergoes intramolecular ring closure to *N*-(4,6-diphenyl-1,3-thiazin-2-ylidene)-*N′*-methylthiourea (**IV**) on treatment with triethylamine in ethanol.

***S*-(1,3-Diphenyl-3-oxo-1-propenyl)-*N*-(methylaminocarbonothioyl)isothiuronium perchlorate (III).** A solution of 1.03 g (5 mmol) of 1-benzoyl-2-phenylacetylene (**I**) and 0.34 ml of 58% $HClO_4$ in 10 ml of glacial acetic acid was slowly added under vigorous stirring to a suspension of 0.75 g (5 mmol) of 1-methyldithiobiuret (**II**) in 20 ml of glacial acetic acid. The mixture was stirred for 1 h at 20°C, and the precipitate was filtered off, washed with diethyl ether, and dried under reduced pressure. Yield 1.43 g (68%), orange crystals, mp 138–142°C (decomp.). IR spectrum, ν, cm^{-1}: 3075, 3219, 3288 (NH); 1477, 1564, 1586 (C=C, C=N, C=O); 1041–1097 (ClO_4^-). ^1H NMR spectrum, δ, ppm: 2.94 d (3H, CH_3N), 7.02 s (1H, CH=), 7.40–8.24 m (10H, C_6H_5), 9.81 q (1H, N**H**CH_3), 11.52 s (1H, NH), 12.34 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.11 (CH_3); 119.77 (CH=); 126.94, 127.55, 128.46, 128.73, 130.50, 131.66, 137.51, 148.05 (C_{arom}); 151.78 (C=**C**–S); 153.92 (N=C–S); 180.04 (C=S); 221.43 (C=O). Found, %: C 47.47; H 4.11; Cl 7.70; N 9.27; S 13.97. $C_{18}H_{18}ClN_3O_5S_2$. Calculated, %: C 47.42; H 3.98; Cl 7.78; N 9.22; S 14.06.

***N*-(4,6-Diphenyl-1,3-thiazin-2-ylidene)-*N′*-methylthiourea (IV).** A solution of 3.12 g (30 mmol) of triethylamine in 10 ml of ethanol was added under stirring to a suspension of 1.45 g (3 mmol) of compound **III** in 60 ml of ethanol. The mixture was stirred for 3 h at 20°C, and the precipitate was filtered off, washed with ethanol, and dried under reduced pres-



I **II** **III** **IV**

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sure. Yield 0.96 g (86%), dark red crystals, mp 168–170°C (from EtOH). IR spectrum, ν, cm^{-1}: 1463–1596 (C=C, C=N), 3173 (NH). ^1H NMR spectrum, δ, ppm: 3.01 d (3H, CH_3N); 7.85 s (1H, CH=); 7.59 m, 7.90 m, 8.28 m (10H, C_6H_5); 9.61 q (1H, N**H**CH_3). ^{13}C NMR spectrum, δ_C, ppm: 31.20 (CH_3); 110.23 (C^5); 127.01, 128.36, 128.50, 128.87, 131.83, 132.54, 135.36, 136.78 (C_{arom}); 157.30, 157.69 (C^4, C^6); 167.75 (C^2); 189.01 (C=S). Found, %: C 64.13; H 4.61; N 12.15; S 19.15. $C_{18}H_{15}N_3S_2$. Calculated, %: C 64.06; H 4.48; N 12.45; S 19.00.

The IR spectra were recorded in KBr on a Specord IR75 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker-DPX 400 instrument at 400.13 and 100.61 MHz, respectively, using DMSO-d_6 as solvent.

REFERENCES

1. Chande, M.S. and Shetgiri, N.P., *J. Indian Chem. Soc*., 1990, vol. 67, p. 849.
2. Chande, M.S., Bhandari, J.D., and Karyekar, A.S., *Indian J. Chem., Sect. B*, 1995, vol. 34, p. 990.
3. Davidson, J.S., Retting, S.J., and Trotter, J., *Acta Crystallogr., Sect. C*, 1999, vol. 55, no. 3, p. 434.
4. Joshua, C.P, Prasannan, E., and Thomas, S.K., *Aust. J. Chem*., 1981, vol. 34, no. 4, p. 917.
5. Glotova, T.E., Protsuk, N.I., Albanov, A.I., Lopyrev, V.A., and Dolgushin, G.V., *Cent. Europ. J. Chem*., 2003, vol. 3, p. 222.
6. Glotova, T. E., Protsuk, N.I., Albanov, A.I., Nakhmanovich, A.S., and Lopyrev, V.A., *Russ. J. Gen. Chem*., 2003, vol. 73, p. 789.
7. Glotova, T.E., Protsuk, N.I., Dvorko, M.Yu., and Albanov, A.I., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1222.