

SHORT  
COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences  
B.A. Trofimov on the 65th Anniversary of His Birth

## Synthesis of 4,5-Substituted 1,3,4-Thiadiazolidin-2-iminium Perchlorate

T. N. Komarova, T. V. Nizovtseva, A. S. Nakhmanovich, L. I. Larina,  
and V. A. Lopyrev

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,  
ul. Favorskogo 1, Irkutsk, 664033 Russia  
e-mail: ktn@irioc.irk.ru

Received June 23, 2003

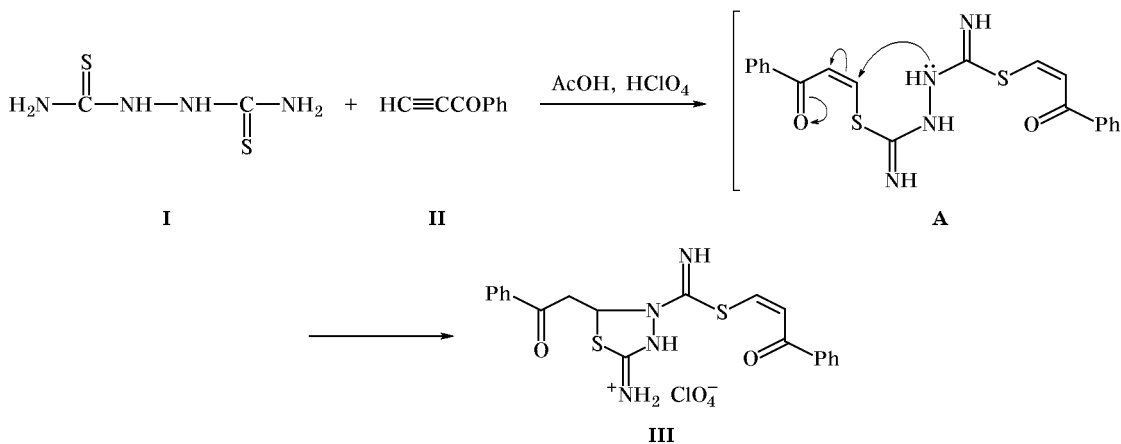
Oxidative cyclization of dithiobiuret is known to afford 1,2,4-dithiazolidines [1–3] and 1,3,5-triazine-4-thiones [4]. The reaction of 1,5-diphenyldithiobiuret with an equimolar amount of benzoylacetylene in acetic acid in the presence of perchloric acid gives 2-benzoyl-4,6-bis(phenylimino)-1,3,5-dithiazinium perchlorate [5].

We examined the reaction of 1,2-hydrazinedicarbothioamide (**I**) with benzoylacetylene (**II**) under analogous conditions. Unlike dithiobiuret, compound **I** takes up two benzoylacetylene molecules. The reaction is likely to involve intermediate formation of *S,S'*-bis(2-benzoylvinyl) derivative **A** and its subsequent intramolecular cyclization at the hydrazine nitrogen atom to form substituted 1,3,4-thiadiazolidin-2-iminium perchlorate (**III**) (Scheme 1). The observed pattern may be interpreted in terms of increased

nucleophilicity of the internal nitrogen atom in initial compound **I** due to  $\alpha$ -effect of the neighboring nitrogen atom having a lone electron pair [6, 7].

**4-[2-Benzoylvinylsulfanyl(imino)methyl]-5-phenacyl-1,3,4-thiadiazolidin-2-iminium perchlorate (**III**)**. Perchloric acid, 0.5 ml (4 mmol), was added to a solution of 0.6 g (4 mmol) of 1,2-hydrazinedicarbothioamide (**I**) in 20 ml of glacial acetic acid, and a solution of 0.5 g (4 mmol) of benzoylacetylene (**II**) in 10 ml of glacial acetic acid was slowly added (dropwise) under vigorous stirring. The mixture was stirred for 8 h at 20°C, and the precipitate was filtered off and washed first with ether and then with acetone. The undissolved material (0.16 g) was unreacted compound **I**. The acetone solution was evaporated, and the residue was heated in boiling methanol. The undissolved material was compound **III**. Yield 0.5 g

Scheme 1.



(33%), dark red crystals, mp 200–202°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1000–1100 ( $\text{ClO}_4^-$ ), 1430–1620 ( $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ ), 1680 ( $\text{C}=\text{O}$ ), 3050–3300 ( $\text{NH}$ ,  $\text{NH}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 4.32 d.d (2H,  $\text{CH}_2$ ), 6.99 s (1H, 5-H), 7.53–8.81 m (15H,  $\text{C}_6\text{H}_5$ ,  $\text{NH}$ ,  $\text{NH}_2$ ,  $=\text{CHCO}$ ), 8.84 d (1H,  $\text{SCH}=\text{}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 44.36 ( $\text{CH}_2$ ), 67.61 ( $\text{C}^5$ ), 115.30 ( $=\text{CHCO}$ ), 128.27–135.49 ( $\text{C}_6\text{H}_5$ ), 148.82 ( $\text{SCH}=\text{}$ ), 164.53 ( $\text{C}^2$ ), 166.50 ( $\text{SC}=\text{NH}$ ), 182.56 and 196.96 ( $\text{C}=\text{O}$ ). Found, %: C 47.22; H 3.30; Cl 7.49; N 11.41; S 11.95.  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2 \cdot \text{HClO}_4$ . Calculated, %: C 47.01; H 3.75; Cl 6.94; N 10.96; S 12.55.

The IR spectrum was recorded on a Specord 75IR instrument in KBr. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz, respectively, using  $\text{DMSO}-d_6$  as solvent.

## REFERENCES

1. All, M.R., Singh, R., and Verna, V.K., *J. Chem. Eng. Data*, 1983, vol. 28, p. 276.
2. Dixit, S.N., *J. Indian Chem. Soc.*, 1961, vol. 38, p. 44.
3. Joshua, C.P. and Varghese, A., *Indian J. Chem., Sect. B*, 1990, vol. 29, p. 937.
4. Pathe, P.P. and Paranjpe, M.G., *Indian J. Chem., Sect. B*, 1981, vol. 20, p. 824.
5. Glotova, T.E., Nakhmanovich, A.S., Albanov, A.I., Protsuk, N.I., Nizovtseva, T.V., and Lopyrev, V.A., *Khim. Geterotsikl. Soedin.*, 2002, no. 1, p. 81.
6. Jencks, W.P. and Carriuolo, J., *J. Am. Chem. Soc.*, 1960, vol. 82, p. 1778.
7. Edwards, J.O. and Pearson, R.G., *J. Am. Chem. Soc.*, 1962, vol. 84, p. 16.