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LETTERS TO THE EDITOR

SYNTHESIS OF 2-ACYLMETHYLENE-4-AMINO-1,3-DITHIEN-6-IMINIUM PERCHLORATES

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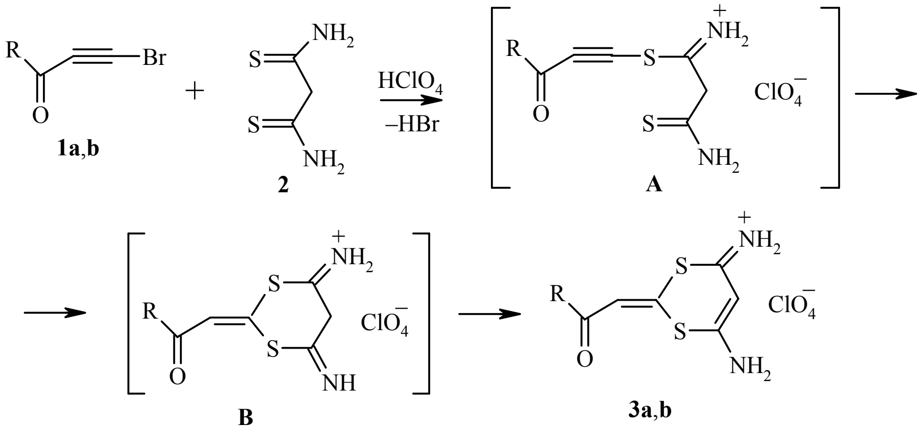
The reaction of thioamides with activated acetylenes usually involves participation of the sulfur and nitrogen atoms and leads to the formation of substituted 1,3-thiazolines [1, 2] and 1,3-thiazines [3, 4]. The reactions of dithioamides with alkynyl halides have not yet been studied extensively.

In a continuation of a study of the reactions of 1-acyl-2-bromoacetylenes with ambifunctional nucleophiles [5, 6], we investigated the reaction of these compounds with dithiomalonamide.

The addition of a solution of 1-bromo-2-benzoyl- (**1a**) and 1-bromo-2-(2-thenoyl)acetylenes (**1b**) in glacial acetic acid and perchloric acid to a solution of dithiomalonamide **2** in glacial acetic acid led to the formation of 4-amino-2-benzoyl- (**3a**) and 4-amino-2-(2-thenoyl)methylene-1,3-dithien-6-iminium perchlorates (**3b**) in 35 and 55% yield, respectively.



a R = Ph; **b** R = 2-thienyl

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This reaction probably involves the loss of HBr to give intermediate perchlorates **A**, which undergo intramolecular cyclization to give intermediates **B**. Under conditions of this synthesis, intermediates **B** convert to substituted 1,3-dithien-6-iminium perchlorates (**3a** and **3b**).

The structures of compounds **3a** and **3b** were supported by ^{1}H NMR, ^{13}C NMR, and IR spectral data.

4-Amino-2-benzoylmethylene-1,3-dithien-6-iminium Perchlorate (3a). Solution of 2-benzoyl-1-bromoacetylene **1a** (0.79 g, 3.8 mmol) in glacial acetic acid (10 ml) and 40% $HClO_4$ (0.29 ml) was added slowly with vigorous stirring to a solution of dithiomalonamide (0.34 g, 2.5 mmol) in glacial acetic acid (20 ml). The mixture was stirred at ~20°C for 4 h. The precipitate formed was filtered off, washed on the filter with ether, and dried in vacuum to give 0.32 g (35%) of compound **3a**; mp 193-195°C. IR spectrum (KBr pellets), ν, cm^{-1}: 624 (C–S), 1122 (ClO_4^-), 1543-1596 (C=C, C=N), 1705 (C=O), 3215 (N^+H_2), 3305 (NH_2). ^{1}H NMR spectrum (400 MHz), δ, ppm: 6.10 (1H, s, =CH); 8.01 (1H, s, =CHCO); 9.30-9.35 (4H, two s, NH_2, N^+H_2); 7.55-8.08 (5H, m, Ph). ^{13}C NMR spectrum (100 MHz, DMSO-d$_6$), δ, ppm: 88.3 (=CH); 121.9 (=$\underline{C}$HCO); 129.3, 129.8, 134.6, 137.0 (Ph); 140.9 (C–S); 165.5 (C–NH_2); 167.4 (C=N^+H_2); 200.8 (C=O). Found, %: C 40.09; H 2.92; Cl 9.28; N 7.30; S 17.92. $C_{12}H_{11}ClN_2O_5S_2$. Calculated, %: C 39.73; H 3.06; Cl 9.77; N 7.72; S 17.68.

4-Amino-2-(2-thenoyl)methylene-1,3-dithien-6-iminium Perchlorate (3b) was obtained analogously to compound **3a** from amide **2** (0.34 g, 2.5 mmol), ketone **1b** (0.82 g, 3.8 mmol), and $HClO_4$ (0.3 ml). Yield of compound **3b** 0.51 g (55%); mp 258-260°C. IR spectrum (KBr pellets): 628 (C–S), 1120 (ClO_4^-), 1550-1594 (C=C, C=N), 1708 (C=O), 3159 (N^+H_2), 3314 (NH_2). ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$), δ, ppm: 6.12 (1H, s, =CH); 7.89 (1H, s, =CHCO); 9.49-9.60 (4H, two s, NH_2, N^+H_2); 7.28-8.21 (3H, m, 2-thienyl). Found, %: C 32.12; H 2.88; Cl 9.26; N 7.88; S 26.46. $C_{10}H_9ClN_2O_5S_3$. Calculated, %: 32.56; H 2.46; Cl 9.61; N 7.59; S 26.08.

REFERENCES

1. L. K. Mushkalo and G. Ya. Yangol', *Ukr. Khim. Zh.*, **21**, 732 (1955).
2. J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Am. Chem. Soc.*, **86**, 107 (1964).
3. J. W. Lown and J. C. N. Ma, *Canad. J. Chem.*, **45**, 953 (1967).
4. R. M. Acheson and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 1*, 415 (1981).
5. T. E. Glotova. A. S. Nakhmanovich, T. N. Komarova, and M. V. Sigalov, *Khim. Geterotsikl. Soedin.*, 1142 (1990).
6. T. E. Glotova, T. N. Komarova, A. S. Nakhmanovich, and V. A. Lopyrev, *Izv. Akad. Nauk, Ser. Khim.*, 1947 (2000).