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LETTERS TO THE EDITOR

NOVEL ROUTE TO 2,6-DIPHENYL-1,4-DITHIINE

L. G. Shagun, L. P. Ermolyuk, I. A. Dorofeev, L. N. Il'icheva, and M. G. Voronkov

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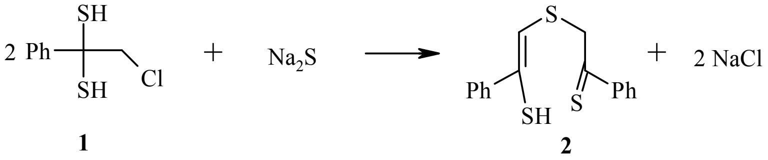
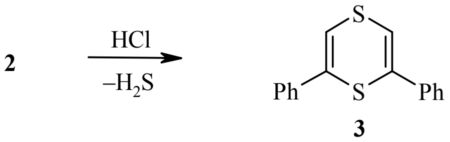
1,4-Dithiine and its derivatives have not been well studied [1]. We synthesized 2,6-diphenyl-1,4-dithiine for the first time [2] by hydrothiolysis of diphenacyl sulfide at -20°C. The reaction occurs through a step of formation of thiophenacyl (2-mercapto-2-phenylvinyl) sulfide [3].

Continuing a study of the chemical properties of α-halo-*gem*-dithiols [4], we observed that the reaction of an ether solution of 1-phenyl-2-chloroethane-1,1-dithiol (**1**) with an aqueous solution of sodium sulfide at -5°C leads to formation of thiophenacyl (2-mercapto-2-phenylvinyl) sulfide (**2**).



The latter, when treated with hydrogen chloride in methanol solution at -10°C, readily eliminates hydrogen sulfide and undergoes ring closure to form 2,6-diphenyl-1,4-dithiine (**3**) in 80% yield.



Thus we have found a novel approach to synthesis of difficultly accessible 2,6-substituted derivatives of 1,4-dithiine, starting from highly reactive α-halo-*gem*-dithiols.

Thiophenacyl (2-Mercapto-2-phenylvinyl) Sulfide (2). Na_2S (0.4 g, 0.16 mmol) in water (3 ml) was added with stirring to a solution (cooled down to -5°C) of *gem*-dithiol **1** (0.4 g, 2 mmol) in ether (20 ml). The reaction mixture was stirred for 2 h until the starting dithiol **1** disappeared. The ether layer was removed and dried above Na_2SO_4. After removal of ether, we obtained 0.25 g (85%) of sulfide **2** in the form of a thick

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A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk 664033; e-mail: tim@irioch.irk.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1400-1401, September, 2004. Original article submitted April 8, 2004.

yellow-orange oil, identical to the product described previously in [3]. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, HMDS), δ, ppm: 45.3 (CH_2); 128-135 (C_{Ph}); 147 (C-SH); 194 (C=S). IR spectrum (thin film), ν, cm^{-1}: 2550 (SH). Found, %: C 63.10; H 4.80; S 31.28. $C_{16}H_{14}S_3$. Calculated, %: C 63.56; H 4.63; S 31.78.

2,6-Diphenyl-1,4-dithiine (3). Dry HCl was passed into solution of sulfide **2** (0.25 g) in anhydrous methanol (20 ml) for 2 h at -10°C. The reaction mixture was poured over finely crushed ice. The precipitate formed was filtered off, washed with water, and dried under vacuum. We obtained 0.19 g (86%) of dithiine **3** as yellow crystals; mp 78-79°C. The physicochemical characteristics of dithiine **3** were identical to those obtained in [2].

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