ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 10, pp. 1554–1555. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © L.K. Papernaya, E.V. Rudyakova, A.I. Albanov, G.G. Levkovskaya, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 10, pp. 1575–1576.

SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on his 70th anniversary

Unexpected Formation of 1,6-Bis[3,5-dimethyl-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazol-1-yl]hexane in the Reaction of 1,1′-(Hexane-1,6-diyl)bis[3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde] with 2-Sulfanylethanol

L. K. Papernaya, E. V. Rudyakova, A. I. Albanov, and G. G. Levkovskaya

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

Received June 2, 2008

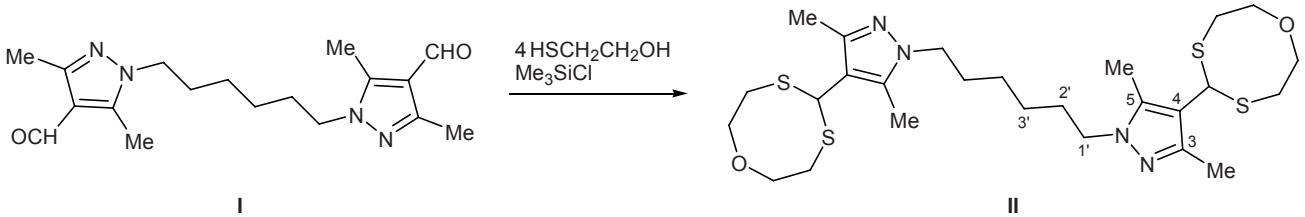
DOI: 10.1134/S1070428008100291

We previously reported that reactions of aldehydes of the thiophene series [1–3] with alkanethiols and dithiols in the presence of chloro(trimethyl)silane Me_3SiCl at reduced temperature provide a simple and convenient synthetic route to acyclic and cyclic dithioacetals possessing thiophene fragments. It is also known that 2-sulfanylethanol and 3-sulfanylpropan-1-ol react with aliphatic and aromatic aldehydes in the presence of scandium trifluoromethanesulfonate [4], boron trifluoride [5], or *p*-toluenesulfonic acid [6] to give the corresponding 1,3-oxathiolane and 1,3-oxathiane derivatives.

In the present work we tried to extend the above approach [1–3] with a view to obtain pyrazoles having an O,S-heterocyclic substituent by reaction of formylpyrazoles with 2-sulfanylethanol in chloro(trimethyl)silane. However, contrary to the expectations, 1,1′-(hexane-1,6-diyl)bis[3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde] reacted with 2-sulfanylethanol at 50–70°C in 10-fold amount of chloro(trimethyl)silane to give previously unknown 1,6-bis[3,5-dimethyl-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazol-1-yl]hexane (**II**) with high selectivity. It should be noted that the expected pyrazolyl-substituted oxathiolane was not formed in excess Me_3SiCl at a **I**-to-$HSCH_2CH_2OH$ ratio of 1:2; in this case, we isolated a mixture of unreacted initial pyrazolecarbaldehyde **I** and compound **II**. No reaction occurred at room temperature.

The structure of compound **II** was determined on the basis of its ^1H and ^{13}C NMR spectra and elemental analysis. The described reaction leading to 1,4,6-oxadithiocane derivative **II** is the first example of synthesis of formylpyrazole precursors. Compound **II** attracts strong interest as a promising biologically active substance, for molecules of many modern drugs, specifically antiphlogistic, antidiabetic, analgesic, etc. [7], as well as of insectoacaricides [8], contain a pyrazole ring.

1,6-Bis[3,5-dimethyl-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazol-1-yl]hexane (II). 2-Sulfanylethanol,



I II

0.66 g (2 mmol), was added dropwise to a hot solution of compound **I** in 2.5 ml of Me_3SiCl, and the mixture was vigorously stirred for 4 h at 50–70°C. The mixture was cooled, and the precipitate was filtered off, washed with cold hexane, and dried under reduced pressure. Yield 1.05 g (92%), white powder, mp 144–146°C. ^{1}H NMR spectrum, δ, ppm: 1.42 m (4H, 3′-H), 1.89 m (4H, 2′-H), 2.55 s and 2.53 s (6H each, CH_3), 2.83 d.t and 2.71 d.t (4H each, SCH_2, ^2J = 13.69, ^3J = 6.36 Hz), 3.76 d.t and 3.73 d.t (4H each, OCH_2, ^2J = 11.37, ^3J = 6.6 Hz), 4.32 t (4H, ^3J = 7.09 Hz), 7.20 s and 5.47 s (1H each, SCHS). ^{13}C NMR spectrum, δ, ppm: 10.74 and 10.38 (CH_3), 26.72 ($C^{3'}$), 30.09 ($C^{2'}$), 36.24 (SCH_2), 43.73 (SCHS), 49.78 (NCH_2), 62.88 (OCH_2), 119.99 (C^4), 145.08 and 144.97 (C^3, C^5). Found, %: C 54.41; H 7.35; N 9.91; S 22.43. $C_{26}H_{42}O_2N_4S_4$. Calculated, %: C 54.92; H 7.04; N 9.85; S 22.69.

The ^{1}H and ^{13}C NMR spectra were recorded on a DPX-400 spectrometer at 400.13 and 101.61 MHz, respectively, using CD_3OD as solvent and hexamethyldisiloxane as internal reference.

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