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Synthesis and photochromic properties of 1,2-dihetarylethenes with 1,3-dioxole- and 1,3-oxazole-2-thione bridges*

S. N. Ivanov, M. M. Krayushkin,* B. V. Lichitsky, A. A. Dudinov, and A. Yu. Martynkin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 6939. E-mail: mkray@ioc.ac.ru

Methods for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)ethenes with 1,3-dioxole- and 1,3-oxazole-2-thione fragments as ethene bridges were developed. These compounds exhibit photochromic properties.

Key words: 1,2-dithienylethenes, 4,5-dithienyl-1,3-dioxole-2-thione, 4,5-dithienyl-1,3-oxazole-2-thione, thenoine, photochromes.

Earlier,[1] in the study of reactions of 1,2-dithienyl-2-hydroxyethanones **1** with 1,1´-thiocarbonyldiimidazole, we discovered an unexpected reaction pathway: instead of the expected 4,5-dihetaryl-1,3-dioxole-2-thiones (**2**), 4,5-dihetaryl-1,3-oxathiol-2-ones (**3**) formed (Scheme 1).

In the present communication, we describe the synthesis of compound **2** and its close analog oxazolethione **4**; the photochromic properties of products **2**, **3a**,**b**, and **4** were also examined.

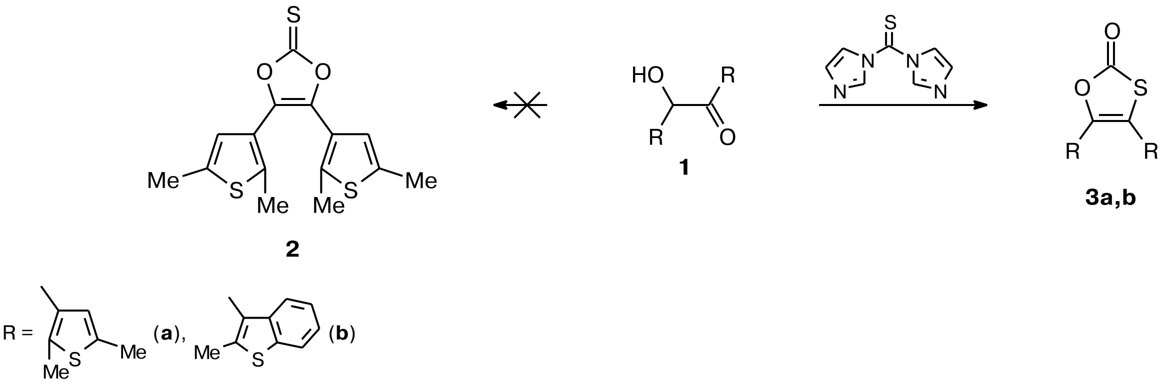
4,5-Bis(2,5-dimethyl-3-thienyl)-1,3-dioxole-2-thione (**2**), which is a thio analog of carbonate **5**,[2] was obtained in 68% yield by treatment of the latter with P_2S_5. 4,5-Bis(2,5-dimethyl-3-thienyl)-3-methyl-1,3-oxazole-2-thione (**4**) was synthesized from compound **2** according to a procedure analogous to that used earlier[2] for 1,3-dioxol-2-one **5** without isolating the 4-hydroxy intermediate (Scheme 2).

The structures of thiones **2** and **4** were confirmed by data from ^{1}H NMR spectroscopy (note that the replacement of the carbonyl group by the thiocarbonyl one virtually does not affect the chemical shifts of the protons of the thiophene rings), mass spectrometry, and elemental analysis. Product **4** was also obtained by an independent synthesis from *N*-methyl-1,3-oxazol-2-one (**6**)[2] and P_2S_5.

The spectroscopic data suggest that products **2**, **3a**,**b**, and **4** are photochromes. The absorption bands of their open forms appear at 284 (**2**), 286 (**3a**), 300 (**3b**), and 297 nm (**4**), while the spectra of the cyclic photochromes (Scheme 3) show peaks at 473 (**2**), 467 (**3a**), 460 (**3b**), and 489 nm (**4**).

Thus, we developed the methods for the synthesis of photochromic 1,2-dihetarylethenes with the 1,3-dioxole- and 1,3-oxazole-2-thione bridges.

Scheme 1



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* Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

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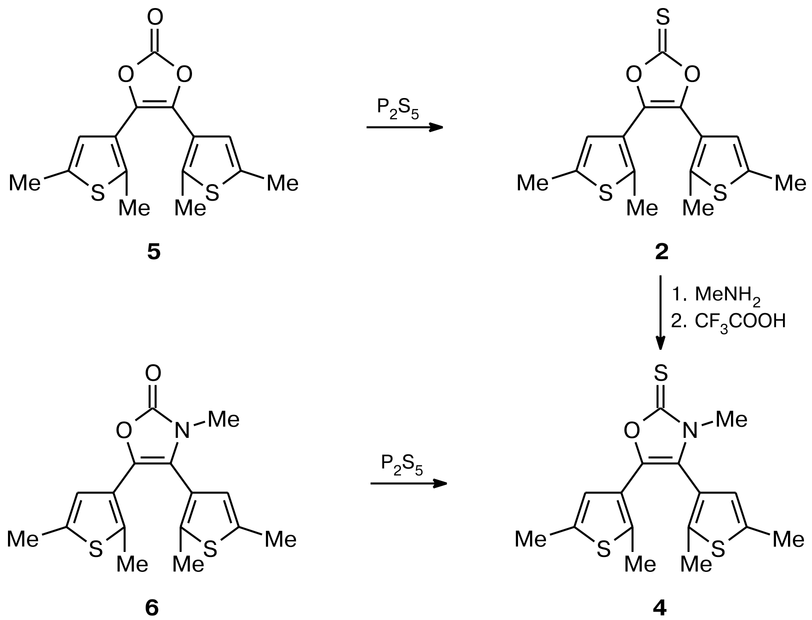
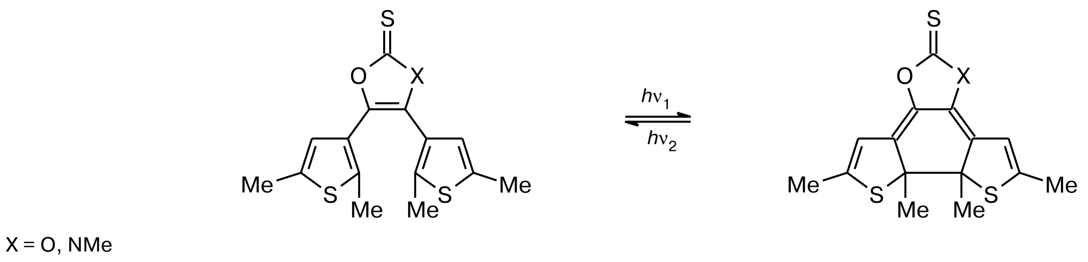
Scheme 2



Scheme 3



Experimental

^{1}H NMR spectra were recorded on Bruker AM-300 and Bruker WM-250 instruments (300.13 and 250.13 MHz, respectively) in DMSO-d$_6$ and CDCl$_3$. Melting points were determined on a Boetius microscope stage and are given uncorrected. Mass spectra were recorded on a Kratos MS-30 instrument (70 eV, direct inlet probe). The course of the reactions was monitored and the purity of the products isolated was checked by TLC on Silica gel 60 F$_{254}$ plates (Merck) with AcOEt—hexane as an eluent.

The photochromic characteristics of compounds **2**, **3a,b**, and **4** were examined in acetonitrile solutions. High-purity acetonitrile was used. Cyclic forms of the photochromes were obtained by irradiation of samples with a DRSh-500 mercury lamp through light filters for the wavelengths $\lambda = 313$, 546, and 578 nm and identified from λ_{max} in the UV spectra. The radiation intensity of the mercury lamp was measured with an F4 photocell calibrated with a ferrioxalate actinometer[3] for $\lambda = 313$ nm and a Reinecke salt actinometer[4] for $\lambda = 546$ and 578 nm. Electronic absorption spectra were recorded on a Shimadzu UV—3100 spectrophotometer.

4,5-Bis(2,5-dimethyl-3-thienyl)-1,3-dioxole-2-thione (2). A stirred mixture of compound **5** [2] (0.100 g, 0.33 mmol) and P$_2$S$_5$ (0.328 g, 2.00 mmol) in xylene (5 mL) was refluxed for 8 h, cooled, and filtered. The solvent was removed *in vacuo* and the residue was crystallized from ethanol to give product **2** (0.071 g, 68%), m.p. 163—164 °C. Found (%): C, 55.95; H, 4.31; S, 29.67. $C_{15}H_{14}O_2S_3$. Calculated (%): C, 55.87; H, 4.38; S, 29.83. ^{1}H NMR (CDCl$_3$), δ: 2.21, 2.39 (both s, 6 H each, 2 Me); 6.64 (s, 2 H, H$_{Het}$). MS (EI), *m/z* (I_{rel} (%)): 322 [M$^+$] (95).

4,5-Bis(2,5-dimethyl-3-thienyl)-3-methyl-1,3-oxazole-2(3*H*)-thione (4). A 2 *M* solution of methylamine (Aldrich) (3 mL) in methanol was added to a solution of 1,3-dioxole-2-thione **2** (0.322 g, 1 mmol) in methanol (5 mL). The reaction mixture was kept at ~25 °C for 6 h and concentrated *in vacuo* and CF$_3$COOH (5 mL) was added. The resulting solution was kept at room temperature for 3 h and concentrated. The residue was crystallized from ethanol to give product **4** (0.245 g, 73%), m.p. 149—150 °C. Treatment of oxazol-2-one **6** [2] with P_2S_5 as described above for thione **2** also gave oxazole-2-thione **4** in 62% yield. Found (%): C, 57.36; H, 5.06; N, 3.95, S, 28.81. $C_{16}H_{17}NOS_3$. Calculated (%): C, 57.28; H, 5.11; N, 4.17, S, 28.67. ^{1}H NMR ($CDCl_3$), δ: 2.09, 2.30, 2.35, 2.48 (all s, 3 H each, Me); 3.38 (s, 3 H, NMe); 6.34, 6.55 (both s, 1 H each, CH_{Het}). MS (EI), m/z (I_{rel} (%)): 335 [M^+] (90).

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