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SHORT COMMUNICATIONS

Dedicated to the 70th anniversary of O.N.Chupakhin,
Full Member of the Russian Academy of Sciences

Synthesis of Photochromic 4,5-Dithienyl-1,3-oxathiol-2-ones

S.N. Ivanov[1], M.M. Krayushkin[1], B.V. Lichitskii[1], L.G. Vorontsova[1], Z.A. Starikova[2], A.A. Dudinov[1], and A.Yu. Martynkin[1]

[1]*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
e-mail: mkray@ioc.ac.ru
[2]*Nesmeyanov Institute of Organoelemental Chemistry, Russian Academy of Sciences, Moscow, Russia*

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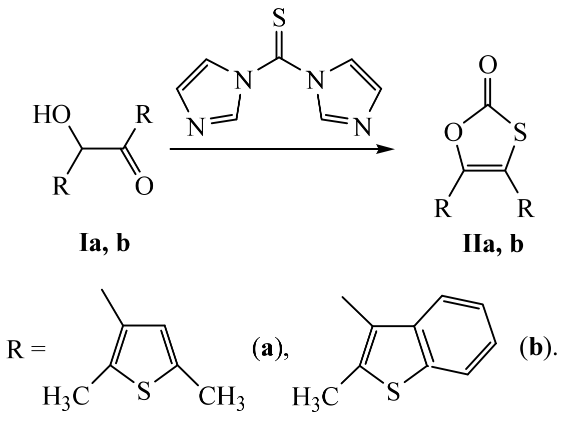
With a goal to find new accessible compounds possessing photochromic activity we formerly synthesized dithienylethenes with various heterocyclic bridges [1, 2]. To this end 1,2-bis(hetaryl)hydroxyethanones **Ia, b** containing thienyl groups are convenient initial compounds. In extension of this research we descried here the reaction of these substances with 1,1'-thiocarbonyldiimidazole (Scheme 1).

Scheme 1.



We revealed a new unexpected direction of the process: Instead of expected 4,5-(dihetaryl)-1,3-dioxol-2-thiones 4,5-bis(2,5-dimethyl-3-thienyl)-1,3-oxathiol-2-one (**IIa**) and 4,5-bis-(2-methyl-3-benzo[*b*]thienyl)-1,3-oxathiol-2-one (**IIb**) were obtained whose structure was established from ^{1}H NMR and mass spectra, X-ray diffraction study (**IIa**), and elemental analysis.

According to X-ray diffraction data the molecule of compound **IIa** exists in antiparallel conformation characteristic of photochromic substances [3]. The distance between the photoreactive centers 2 and 2' of thiophene rings equal to 3.60 Å corresponds to the photoactive form of the [4], and 4,5-dithienyl fragments are asymmetrically turned with respect to the plane of the oxathiol-2-one bridge by 42.2 and 48.6° respectively.

More complete data on the molecular and crystal structure of compound **IIa** will be published elsewhere.

The spectral investigation showed that compounds **IIa, b** are photochromic. The longwave spectral bands of open forms of the oxathiols synthesized are located in the range 286 (**IIa**) and 300 nm (**IIb**). The longwave spectral bands of cyclic forms of the photochromic oxathiols have the respective maxima at 467 (**IIa**) and 460 nm (**IIb**).

The availability of initial hydroxyketones **I** and high yields of compounds **II** (65–80%) show that this simple and convenient method is promising for preparation of compounds with 1,3-oxathiol-2-one structure.

Crystallographic data of compound (IIa). Crystals $C_{15}H_{14}O_2S_3$ monoclinic, space group $P2_1/c$, at 293 K a 9.073(2), b 14.235(3), c 12.298(4) A, β 94.328(3)°, V 1583 (7) A^3, Z 4, d_{calc} 1.352 g/cm^3, mp 92–93°C, M 322.44. Intensities of 4570 independent reflections were measured on a diffractometer Bruker SMART 1000 CCD [λ(MoK_α) 0.71072 Å, ω-scanning, angles range $2.19 \leq \theta \leq 21.75°$]. The structure was solved by the direct method and refined in least-squares full-matrix anisotropic approximation for the nonhydrogen atoms.

Hydrogen atoms were localized from the difference Fourier synthesis and were refined in least-squares full-matrix isotropic approximation. Divergence factor R_1 was 0.060 (wR_2 0.144) for 903 reflections with $I > 2\sigma(I)$; for all reflections R_1 was 0.280 (wR_2 0.207). The structure was solved with the use of software packages Bruker SHELXTL [5] SHELXS-97, SHELXL-97 [6]. The atomic coordinates, temperature factors, and geometric parameters of the molecule are deposited in the Cambridge Crystallographic Data Center (CCDC), register no. 233550.

2-(2-Methyl-3-benzo[*b*]thienyl)-2-oxoacetaldehyde was prepared by a standard procedure from 1-(2-methyl-3-benzo[*b*]thienyl)ethanone [7]. Yield of ketoaldehyde crystal hydrate 69%, mp 95–97°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.78 s (3H, CH_3), 5.62 t (1H, CH, *J* 7.0 Hz), 6.67 d (2H, 2OH, *J* 7.0 Hz), 7.39 m (2H, H arom), 8.16 m (2H, H arom). Found, %: C 59.61; H 4.48; S 14.59. $C_{11}H_{10}O_3S$. Calculated, %: C 59.44; H 4.54; S 14.43.

1,2-Bis(2-methyl-3-benzo[*b*]thienyl)-2-hydroxyethanone (Ib). To a solution of 2.22 g (0.01 mol) of 2-(2-methyl-3-benzo[*b*]thienyl)-2-oxoacetaldehyde crystal hydrate and 1.63 g (0.011 mol) of 2-methylbenzo[*b*]thiophene [8] in 50 ml of benzene was added at stirring a solution of 2.60 g (0.01 mol) of $SnCl_4$ in 20 ml of benzene. The mixture obtained was kept for 3 h at room temperature, then it was poured into 50–60 ml of water, and extracted with ether (3×20 ml). The extract was washed with water, with sodium carbonate, again with water, dried with $MgSO_4$, and evaporated. The residue was crystallized from ethanol to obtain 2.35 g (67%) of hydroxyketone **Ib**, mp 120–121°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s (3H, CH_3), 2.31 s (3H, CH_3), 6.17 s (1H, OH), 6.21 s (1H, OCH), 7.25 m (4H, H arom), 7.74 m (4H, H arom). Found, %: C 68.33; H 4.64; S 17.95. $C_{20}H_{16}O_2S_2$. Calculated, %: C 68.15; H 4.58; S 18.19.

4,5-Bis(hetaryl)-1,3-oxathiol-2-one (IIa, b) (general procedure). A mixture of 1 mmol of an appropriate 1,2-bis(hetaryl)-2-hydroxyethanone and 1.5 mmol of 1,1'-thiocarbonyldiimidazole was boiled in 5 ml of benzene (TLC monitoring). The reaction mixture was cooled, washed with water, with 10% HCl solution, with water, dried with $MgSO_4$, and the solvent was evaporated in a vacuum. The residue was crystallized from ethanol.

4,5-Bis(2,5-dimethyl-3-thienyl)-1,3-oxathiol-2-one (IIa) was obtained from 1,2-bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone [1] (**Ia**) and 1'-thiocarbonyldiimidazole. Yield 85%, mp 92–93°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 s (3H, CH_3), 2.07 s (3H, CH_3), 2.32 s (3H, CH_3), 2.36 s (3H, CH_3), 6.59 s (1H, H hetaryl), 6.65 s (1H, H hetaryl). Mass spectrum (electron impact), *m/z* (I_{rel}, %): 322 $[M]^+$ (70). Found, %: C 55.76; H 4.46; S 30.02. $C_{15}H_{14}O_2S_3$. Calculated, %: C 55.87; H 4.38; S 29.83.

4,5-Bis(2-methyl-3-benzo[*b*]thienyl)-1,3-oxathiol-2-one (IIb) was obtained from hydroxyketone **Ib** and 1,1'- thiocarbonyldiimidazole. Yield 79%, mp 152–153°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 s (3H, CH_3), 2.13 s (3H, CH_3), 7.34 m (4H, H hetaryl), 7.82 m (4H, H hetaryl). Mass spectrum (electron impact), *m/z* (I_{rel}, %): 394 $[M]^+$ (70). Found, %: C 64.05; H 3.66; S 24.25. $C_{21}H_{14}O_2S_3$. Calculated, %: C 63.93; H 3.58; S 24.38.

^{1}H NMR spectra were registered on spectrometers Bruker AM-300 (300.13 MHz) and Bruker WM-250 (250.13 MHz) in DMSO-d_6 and $CDCl_3$. Melting points were measured on a Boëtius heating block and were reported without corrections. Mass spectra were recorded on a Kratos MS-30 instrumentat at ionizing electrons energy 70 eV and direct admission of samples into the ion source. The reaction progress was monitored and the homogeneity of compounds obtained was checked by TLC on Merck Silica gel 60 F_{254} plates, eluent AcOEt–hexane.

Photochromic characteristics of compounds **IIa, b** were investigated in acetonitrile solution. The acetonitrile used for measurements was of “special purity” grade. The cyclic B forms of the photochromic compounds were obtained by samples irradiation with a mercury lamp DRSh-500 using light filters for selection of mercury spectrum lines (313, 546, and 578 nm). The forms obtained were identified by the λ_{max} in the UV spectra. The intensity of the mercury lamp radiation was measured with photodetector F4 calibrated by ferrioxalate actinometer [9] for the λ 313 nm and actinometer based on the Reinecke salt [10] for λ 546 and 578 nm. The absorption spectra were registered on a spectrophotometer Shimadzu UV-3100.

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