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SHORT COMMUNICATIONS

5′,5′,6,6-Tetramethyl-6,7-dihydro-3′*H*-spiro[1,3-benzodithiole-2,1′-cyclohexane]-3′,4(5*H*)-dione

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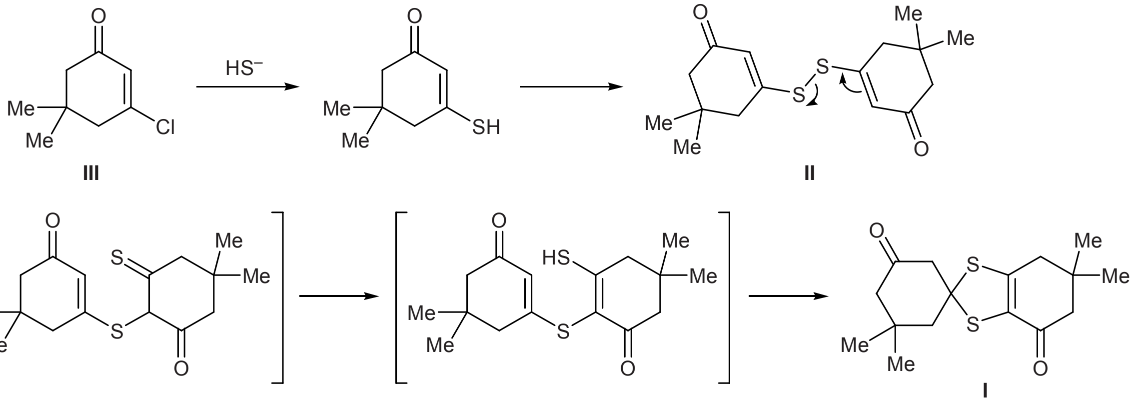
Dalgaard and Lawesson reported [1] on the formation of 5′,5′,6,6-tetramethyl-6,7-dihydro-3′*H*-spiro[1,3-benzodithiole-2,1′-cyclohexane]-3′,4(5*H*)-dione (**I**) from 3,3′-dithiobis(5,5-dimethylcyclohex-2-en-1-one) (**II**) in 79% yield when a solution of the latter in ethanol was irradiated with monochromatic light (λ 254 and 300 nm). Unexpectedly, we isolated spiro compound **I** in the reaction of 3-chloro-5,5-dimethylcyclohex-2-en-1-one (**III**) with sodium sulfide. We tried to synthesize 3,3′-thiobis(5,5-dimethylcyclohex-2-en-1-one) (**IV**) according to the procedure reported previously, which involved no photolysis [1]. The IR, UV, and ^{1}H and ^{13}C NMR spectra of the isolated compound were identical to those given in [1] but considerably differed from the spectra of **IV** [1, 2].

Presumably, spirocyclic compound **I** is formed as a result of transformation sequence shown in Scheme 1 (some steps in this scheme were proposed in [1]), but we showed that these transformations can be performed in one-pot mode without photochemical initiation. It was also surprising that the reaction of compound **I** with 2-aminoethanol in acetonitrile at 50°C resulted in the formation of 3,3,8,8-tetramethyl-3,4,8,9-tetrahydrothianthrene-1,6(2*H*,7*H*)-dione (**V**) which was isolated as an orange crystalline substance (Scheme 2). Compound **V** was not formed on heating in the absence of 2-aminoethanol. Like 2-aminoethanol, triethylamine also initiated transformation of **I** into thianthrenedione **V**.

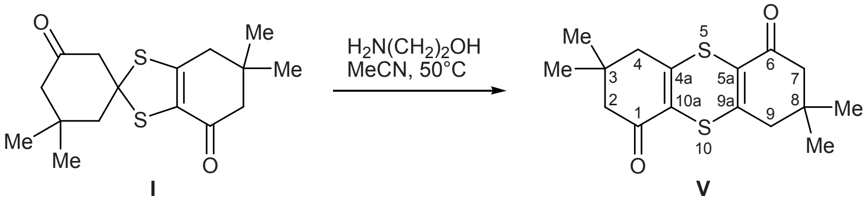
The structure of compound **V** was determined on the basis of its IR, UV, ^{1}H and ^{13}C NMR, and mass spectra. In the ^{1}H NMR spectrum of **V**, the intensity ratio of the methyl proton signals and signals from methylene protons was equal to 1.5, as might be expected for the assumed structure. A structurally related compound, 3,4,8,9-tetrahydrothianthrene-1,6(2*H*,7*H*)-dione [3], was reported previously as orange substance with mp 222–224°C; ^{1}H NMR spectrum, δ, ppm: 2.00 m (4H, CH_2), 2.49 t (8H, CH_2).

5′,5′,6,6-Tetramethyl-6,7-dihydro-3′*H*-spiro[1,3-benzodithiole-2,1′-cyclohexane]-3′,4(5*H*)-dione (I). Chloro ketone **III**, 73.85 g (0.47 mol), was added

Scheme 1.



Scheme 2.



I **V**

dropwise under stirring over a period of 3 h to a solution of 114.5 g (0.48 mol) of sodium sulfide nonahydrate in 115 ml of distilled water. The mixture was stirred for 10 h at 60–62°C until the initial compound disappeared (TLC). The product was extracted into diethyl ether, the extract was washed with water to pH 4–5 and dried over Na_2SO_4, the solvent was removed, and the residue was washed with hexane and dried under reduced pressure. Yield 10.5 g (14%), colorless finely crystalline powder, mp 174–176°C; published data [1]: mp 167–169°C. IR spectrum, ν, cm^{-1}: in KBr: 1554, 1640, 1717; in $CHCl_3$: 1565, 1653, 1718; published data [1]: IR spectrum ($CHCl_3$), ν, cm^{-1}: 1560, 1660, 1710. UV spectrum ($CHCl_3$), λ_{max}, nm (logε): 248 (3.71), 350 (3.73) {250 (3.71), 350 (3.71) [1]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.47, 28.66, 29.40, and 30.42 (CH_3); 35.46 and 36.01 (C^6, $C^{5'}$); 40.56 (C^7); 49.38 (C^5); 50.70 ($C^{4'}$); 53.43 ($C^{6'}$); 57.57 ($C^{2'}$); 67.08 (C^2, $C^{1'}$); 128.65 (C^{3a}); 152.26 (C^{7a}); 189.97 (C^4); 205.19 ($C^{3'}$); published data [1]: ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.4, 28.6, 29.4, and 30.2 (CH_3); 35.3 and 35.9 (C^6, $C^{5'}$); 40.5 (C^7); 49.3 (C^5); 50.5 ($C^{4'}$); 53.2 ($C^{6'}$); 57.4 ($C^{2'}$); 66.9 (C^2, $C^{1'}$); 128.9 (C^{3a}); 152.5 (C^{7a}); 190.0 (C^4); 204.0 ($C^{3'}$). Found, %: C 61.93; H 7.30; S 19.89. $C_{16}H_{22}O_2S_2$. Calculated, %: C 61.94; H 7.10; S 20.65.

3,3,8,8-Tetramethyl-3,4,8,9-tetrahydrothianthrene-1,6(2*H*,7*H*)-dione (V). *a*. A solution of 0.5 g (1.6 mmol) of compound **I** in 20 ml of anhydrous acetonitrile was heated to 50°C, a solution of 0.2 g (3.2 mmol) of 2-aminoethanol in 6 ml of acetonitrile was added dropwise under stirring in an argon atmosphere, and the mixture was stirred for 2 h at 45–50°C. The originally colorless mixture turned violet. It was cooled and filtered, and the filtrate was poured into 50 g of a mixture of ice with water. The precipitate was filtered off, washed with ice water, dried under reduced pressure over $CaCl_2$, and dissolved in chloroform. The solution was passed through a column charged with silica gel L (100–250 μm) using chloroform–ethyl acetate (3 : 1) as eluent. Yield 0.22 g (45%), orange crystals, mp 199–202°C. IR spectrum (KBr), ν, cm^{-1}: 1558 (C=C), 1651 (C=O). UV spectrum ($CHCl_3$), λ_{max}, nm (logε): 238 (4.21), 330 (4.05). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 s (12H, CH_3), 2.52 s (4H, 4-H, 9-H), 2.55 s (4H, 2-H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.50 (C^3, C^8), 45.30 (C^4, C^9), 54.70 (C^2, C^7), 121.80 (C^{4a}, C^{9a}), 154.33 (C^{5a}, C^{10a}), 189.36 (C^1, C^6). Mass spectrum, *m*/*z* (I_{rel}, %): 308 (19) $[M]^+$, 253 (31), 83 (100), 57 (24), 55 (51), 43 (39), 41 (54), 39 (32). Found, %: C 63.09; H 6.81; S 19.87. $C_{16}H_{20}O_2S_2$. Calculated, %: C 62.34; G 6.49; S 20.78.

b. Triethylamine, 0.05 ml, was added dropwise to a solution of 0.1 g (0.32 mmol) of compound **I** in 4 ml of anhydrous acetonitrile. The mixture was kept for 4 h at room temperature, and compound **V** was identified in the mixture by thin-layer chromatography using an authentic sample.

The IR spectra were recorded on an IFS 25 spectrometer. The UV spectra were measured on a Specord UV-Vis spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 instrument at 400.1 and 100.4 MHz, respectively. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer with direct sample admission into the ion source. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform–ethyl acetate (3 : 1) as eluent.

3-Chloro-5,5-dimethylcyclohex-2-en-1-one (**III**) was synthesized as described in [4].

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