

SHORT
COMMUNICATIONS

Chlorination of 1,4-Dihydroxythioxanthen-9-one

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Received December 4, 2007

DOI: 10.1134/S1070428008040295

Dihydroxythioxanthen-9-one derivatives are known to exhibit versatile biological activity [1–4]; they are also used as photoinitiators in polymerization processes [5] and analytical reagents [6]. Halogen derivatives of 1,4-dihydroxythioxanthen-9-one (**I**) were not reported; however, these compounds attract interest from the viewpoint of their subsequent functionalization via nucleophilic replacement of the halogen atom.

We examined the chlorination of compound **I** with a solution of molecular chlorine in carbon tetrachloride. When the reaction was performed in chloroform at room temperature, the reaction mixture quickly (within 15–20 min) turned red–violet, and 80% of 2,3-dichlorothioxanthen-1,4,9-trione (**II**) was formed as a result of oxidative chlorination of compound **I**. The ¹H NMR spectrum of **II** lacked signals from hydroxy protons and the neighboring protons in positions 2 and 3, while its IR spectrum contained a strong carbonyl absorption band at 1679 cm⁻¹. The carbonyl groups in **II** can be reduced with sodium dithionite to obtain 2,3-dichloro-1,4-dihydroxythioxanthen-9-one whose UV spectrum was analogous to that of thioxanthen-9-one **I**.

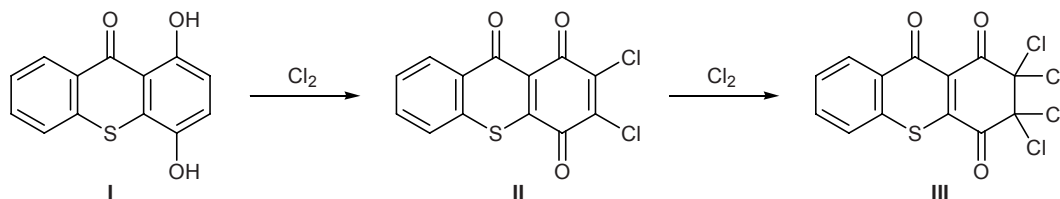
Apart from compound **II**, the reaction mixture contained yellow product **III** which was characterized by a larger *R_f* value on silica gel; therefore, compound **III** can readily be separated from **II** by chromatography. After prolonged keeping (24 h), the reaction mixture changed from red–violet to yellow, and compound **III**

was the only product. It displayed in the IR spectrum two carbonyl absorption bands at 1730 and 1637 cm⁻¹. The presence of the high-frequency band indicates rupture of the conjugated quinoid system. The ¹³C NMR spectrum of **III** contained signals assignable to three carbonyl carbon atoms, eight aromatic carbon atoms, and two *sp*³-hybridized carbon atoms. The analytical and spectral data indicated that compound **III** is the product of addition of two chlorine atoms at one C=C bond in the quinoid ring of molecule **II**; taking into account published data [7–9], this bond may be C²=C³ or C^{4a}=C^{9a}. Insofar as the available published and our experimental data did not allow us to unambiguously choose between two possible structures, 2,2,3,3- and 2,3,4a,9a-tetrachloro derivatives of thioxanthen-1,4,9-trione, the chlorination product was studied by X-ray analysis. The results showed (see figure) that compound **III** has the structure of 2,2,3,3-tetrachloro-1,2,3,4-tetrahydrothioxanthen-1,4,9-trione.

The structure of the isolated compounds was determined on the basis of their analytical and spectral data.

1,4-Dihydroxythioxanthen-9-one (**I**) was synthesized according to the procedure described in [10] by condensation of 2-sulfanylbenzoic acid with benzoquinone, followed by cyclization of 2-[(2,5-dihydroxyphenyl)sulfanyl]benzoic acid thus obtained on heating in polyphosphoric acid.

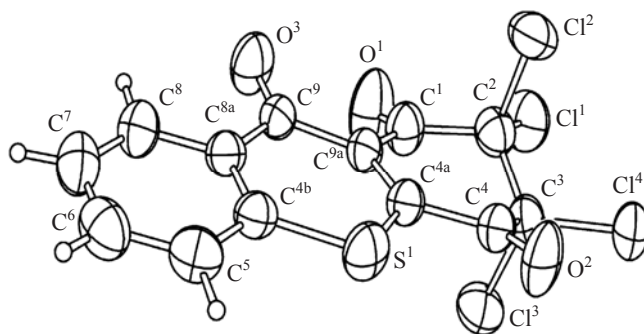
2,3-Dichloro-1,4-dihydro-9H-thioxanthen-1,4,9-trione (II). A solution of ~1 g of chlorine in 5 ml of



carbon tetrachloride was added under stirring at room temperature to a mixture of 0.08 g of compound **I** and 100 ml of chloroform. After 20 min, the mixture was purged with air and subjected to chromatography on a column charged with silica gel using chloroform as eluent. Yield 0.08 g (80%), mp 305–310°C (from toluene). IR spectrum: ν 1679 cm^{-1} (C=O). UV spectrum, λ_{max} , nm (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 246 (27300), 287 (12600), 324 (5000), 483 (3350). ^1H NMR spectrum, δ , ppm: 7.75 br.t and 7.88 br.t (1H each, 6-H, 7-H, $J = 8.0$ Hz), 8.12 d and 8.34 d (1H each, 5-H, 8-H, $J = 8.0$ Hz). Found, %: C 50.34; H 1.34; Cl 22.20; S 9.96. $\text{C}_{13}\text{H}_4\text{Cl}_2\text{O}_3\text{S}$. Calculated, %: C 50.16; H 1.29; Cl 22.83; S 10.29.

2,2,3,3-Tetrachloro-1,2,3,4-tetrahydro-9H-thioxantene-1,4,9-trione (III). A solution of ~1.2 g of chlorine in 6 ml of carbon tetrachloride was added under stirring at room temperature to a mixture of 0.12 g of compound **I** and 100 ml of chloroform. The mixture was stirred until it became homogeneous (30 min) and was left to stand for 24 h. It was then purged with air and evaporated to dryness, and the residue was recrystallized from ethanol. Yield 0.11 g (58%), mp 195–198°C. IR spectrum, ν , cm^{-1} : 1730, 1637 (C=O). UV spectrum, λ_{max} , nm (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 234 (24600), 280 (9100), 322 (40005), 417 (5200). ^1H NMR spectrum, δ , ppm: 7.60–7.80 m (3H, 5-H, 6-H, 7-H), 8.52 d (1H, 8-H, $J = 7.5$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 88.93 and 90.87 (C^2 , C^3), 125.65 (C^{9a}), 127.60 (C^5 , $^1J = 165.0$, $^3J = 8.0$ Hz), 129.67 (C^7 , $^1J = 167.4$, $^3J = 6.7$ Hz), 130.00 (C^6 , $^1J = 165.0$, $^3J = 6.9$ Hz), 132.13 and 133.15 (C^{8a} , C^{10a}), 133.30 (C^8 , $^1J = 165.0$, $^3J = 8.5$ Hz), 149.23 (C^{4a}), 172.91 and 178.38 (C^1 , C^4), 176.17 (C^9 , $^3J = 4.0$ Hz). Found, %: C 41.06; H 1.02; Cl 37.17; S 8.30. $[M]^+$ 379.86380. $\text{C}_{13}\text{H}_4\text{Cl}_4\text{O}_3\text{S}$. Calculated, %: C 40.84; H 1.05; Cl 37.17; S 8.38. M 379.86353.

2,3-Dichloro-1,4-dihydroxy-9H-thioxanthen-9-one. Sodium dithionite, 0.7 g, was added to a solution of 0.11 g of compound **II** in 5 ml of DMSO, the mixture was stirred for 20 min and diluted with 15 ml of water, and the precipitate was filtered off. Yield 0.08 g (72%), mp 279–282°C (from ethanol). IR spectrum: ν 1615 cm^{-1} (C=O). UV spectrum, λ_{max} , nm (ϵ , $1 \times \text{mol}^{-1} \text{ cm}^{-1}$): 203 (24600), 224 (13600), 260 (26900), 277 (24000), 333 (13400), 433 (4400). ^1H NMR spectrum, δ , ppm: 7.60 t and 7.81 t (1H each, 6-H, 7-H, $J = 8.0$ Hz), 7.91 d and 8.42 d (1H each, 5-H, 8-H, $J = 8.0$ Hz), 10.80 br.s (1H, 4-OH), 14.37 s (1H, 1-OH). Found: $[M]^+$ 311.94206. $\text{C}_{13}\text{H}_6\text{Cl}_2\text{O}_3\text{S}$. Calculated: M 311.94147.



Structure of the molecule of 2,2,3,3-tetrachloro-1,2,3,4-tetrahydro-9H-thioxanthen-1,4,9-trione (**III**) according to the X-ray diffraction data (non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%).

The IR spectra were recorded in KBr on a Bruker Vector 22 spectrometer. The ^1H and ^{13}C NMR spectra were measured on Bruker AC-200 and AM-400 spectrometers using $\text{DMSO}-d_6$ as solvent (CDCl_3 for compound **III**); the chemical shifts were determined relative to the residual proton signals of the deuterated solvent. The UV spectra were obtained on a Hewlett-Packard 4853 spectrophotometer from solutions in ethanol (or in chloroform for compound **III**). The high-resolution mass spectra were recorded on a Finnigan MAT-8200 instrument. The molecular weights and elemental compositions were determined from the exact m/z values for the molecular ions. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using chloroform as eluent.

The X-ray diffraction data for a single crystal of compound **III** were acquired on a Bruker P4 diffractometer (graphite monochromator, $\text{MoK}\alpha$ irradiation, $\lambda = 0.71073$ Å, temperature 23°C, $\theta/2\theta$ -scanning). Absorption by the crystal was taken into account by the azimuthal scanning technique ($T_{\text{min}}/T_{\text{max}} = 0.55/0.91$). The structure was solved by the direct method. The positions and temperature parameters of non-hydrogen atoms were refined by the full-matrix least-squares procedure first in isotropic and then in anisotropic approximation. Hydrogen atoms were localized by difference syntheses. All calculations were performed using SHELX-97 software package [11]. Crystallographic data and parameters of X-ray diffraction experiment: $\text{C}_{13}\text{H}_4\text{Cl}_4\text{O}_3\text{S}$; M 382.02; monoclinic crystal system; space group $P2_1/n$; $a = 11.222(2)$, $b = 7.739(1)$, $c = 16.507(3)$ Å; $\beta = 90.57(1)^\circ$; $V = 1433.4(4)$ Å³; $Z = 4$; $d_{\text{calc}} = 1.770 \text{ g/cm}^{-3}$; $\mu = 0.975 \text{ cm}^{-1}$; scan range $2\theta < 54^\circ$; total of 3155 reflections were measured ($R_{\text{int}} =$

0.0206), 2624 of which were with $I \geq 2\sigma(I)$; 206 refined parameters; $R_1 = 0.0528$ [from reflections with $I \geq 2\sigma(I)$], $wR_2 = 0.1628$, $S = 1.011$ (from all 3124 reflections).

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