The Formation of Tetramethyl 1,4-Dithiin-2,3,5,6-tetracarboxylate from a Disulfide Precursor. A Structural Reassignment

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The structure of the title compound, previously mistaken for the 1,2-dithin derivative, is demonstrated spectroscopically and a mechanism for its formation suggested.

In connection with studies concerned with the consequences of a lone pair–lone pair interactions, we were attracted to the novel 1,2-dithiins (e.g. 3). It has been reported that treatment of disulfide 1 with sodium benzenethiolate delivers compound 3 in good yield. Reinvestigation of the reaction demonstrates that the product is in fact the 1,4-derivative (2).

DISCUSSION

The disulfide 1 was prepared without complication by the procedure of Ried and Ochs (Fig. 1). Although no definite evidence for a trans addition of disulfur dichloride to the acetylene exists, we depict product 1 as did the previous authors. Its subsequent reactions are independent of configuration. Reaction of 1 with sodium benzenethiolate leads to a yellow solid with physical properties identical with those previously reported for the 1,2-dithiin 3. Presumably the elemental analysis and the observation that sulfur is thermally extruded to give thiophene 4 were motivation for assignment of the structure to a 1,2-dithia isomer. However, both 1,2- and 1,4-dithiins release sulfur upon heating to provide the corresponding thiophene.

An important clue to the constitution of the yellow product lies in its colour. Most known 1,2-dithiins are red with $\lambda_{\text{max}} > 450$ nm, while the 1,4-isomers are generally white or yellow unless embedded in a planar, highly conjugated system. Indeed the UV spectrum of the yellow dithiin (longest $\lambda_{\text{max}} = 356$ nm) is superimposable with that of the 1,4 derivative 2 prepared independently. The proton NMR trace shows a singlet compatible with four equivalent methoxycarbonyl groups in the 1,4 system. Although structure 3 might give rise to accidentally coincident methyl proton shifts, it would not be expected to exhibit pairwise coalescence of its six $^{13}$ C NMR signals. The broad band decoupled spectrum displays peaks from only three different carbon atoms, again in agreement with the 1,4-dithiin species.

Finally, from the combination of disulfide 1 and sodium benzenethiolate, vinyl disulfide 5 tentatively assigned a trans configuration and diphenyl disulfide were isolated. While the
latter was likewise observed by Ried and Ochs, δ went undetected. Structure δ rests on spectroscopic data (see Experimental), and it indicates the possible mechanistic course of the reaction. Fig. 2 depicts the formation of compound δ from nucleophilic attack of benzzenethiolate on the disulfide linkage of 1, a very well-known transformation. The enethiolate intermediate 6 might dimerize head-to-tail with loss of chloride ion to give a second enethiolate 8. Ring closure produces 2. Alternatively the anion δ may displace chlorine in 5 leading to intermediate 7. Subsequent attack by benzzenethiolate with the elimination of diphenyl disulfide provides anion 8, the immediate precursor of 1,4-dithiin 2. Both structures 7 and 8 have for convenience been pictured with cis-disposed methoxy-carbonyl groups. If the reaction proceeds as suggested, the cis and trans isomers should exist in equilibrium. However, the production of 1,4-dithiin 2 requires an ultimate, irreversible shift in the direction of the cis isomer. Ried and Ochs mentioned a possible, unspecified radical process in their postulated formation of the 1,2-dithin 3. The identification of 2 and the isolation of 5 renders the radical pathway unlikely.

The reevaluation of structure for the tetrakis(methoxy carbonyl)dithiin 2 invites speculation concerning the constitution of other 1,2-dithiins reported to be yellow in colour.\(^9\)\(^{10}\)

**EXPERIMENTAL**

\(^1\)H NMR spectra (60 MHz) were obtained on a Varian T-60 A instrument, and \(^13\)C NMR spectra on a Bruker WH 90 instrument. The IR spectra were recorded with a Perkin-Elmer Model 337 grating spectrophotometer. The mass spectra were obtained with an A.E.I. MS 902 mass spectrometer, and the UV spectra on a Pye Unicam SP 1800 UV spectrophotometer.

**Tetramethyl 2,2'-dichloro-3,3'-dithiofumarate (1).** Compound 1 was prepared as described by Ried and Ochs\(^4\) m.p. 151 – 152°C (lit.\(^4\) 152°C); \(^1\)H NMR (CDCl\(_3\)) δ 3.96 (6 H, s), 3.87 (6 H, s) (lit.\(^4\) (CDCl\(_3\)/HMDS) 3.78, 3.71); \(^13\)C NMR (CDCl\(_3\)) δ 162.8 and 162.2 (> C = O), 147.1 and 115.6 (> C = C <), 53.7 and 53.2 (Me).

**Tetramethyl 1,4-dithiin-2,3,5,6-tetracarboxylate (2).** A solution of disulfide 1 (1.05 g, 2.5 mmol) in 1,2-dimethoxyethane (50 ml) was added dropwise to a suspension of sodium benzzenethiolate (0.66 g, 5.0 mmol) in 1,2-dimethoxyethane (25 ml) at 0°C. The solution was stirred for 2 h at room temperature, filtered and evaporated. Purification by preparative layer chromatography with toluene as eluent yielded after recrystallization (MeOH) dithiin 2 (\(R_F\) 0.09) (0.404 g, 46%), m.p. 125 – 126°C (lit.126 – 127°C); \(^1\)H NMR (CDCl\(_3\)) δ 3.85 (s), \(^1\)C NMR (CDCl\(_3\)) δ 161.8 (> C = O), 134.6 (> C = C) and 53.6 (Me); UV (abs. ethanol) \(\lambda_{max}\) nm (log e): 250 (3.83, sh), 314 (3.82) and 356 (2.47, sh); (lit.\(^*\) 312 (3.74)). The UV spectrum is identical to that of 1,4-dithiin 2 prepared by an independent route.\(^4\)

**Dimethyl 2-chloro-3-(phenyl dithio) fumarate (5) and diphenyl disulfide.** Faster moving fractions from the preparative layer chromatographic isolation of 2 yield diphenyl disulfide and vinyl disulfide 5. The most mobile fraction (\(R_F\) 0.55) was identified as diphenyl disulfide (238 mg, 44%), m.p. 58 – 59°C (lit.\(^*\) 60 – 61°C). The next most rapid band (\(R_F\) 0.32) (115 mg) was sublimed twice at 112°C/1.7 mmHg.

yielding the vinyl disulfide \( \delta \) as a colourless oil (28 mg, 4 %); \(^1\)H NMR (CCl\(_4\)): \( \delta \) 7.15 – 7.54 (5 H, m), 3.83 (3 H, s), 3.77 (3 H, s); MS (70 eV/80°C, direct inlet), \( m/e \) (% rel. int.): 318 (33, M\(^+\)), 209 (100, M\(^+\) – SPh), 109 (51, SPh), 77 (10), 65 (26), 59 (40), 39 (16); IR (CCl\(_4\)): 2949 m, 1745 s, 1700 s, 1477 m, 1437 s, 1280 s, 1245 s, 1084 w, 1028 s, 904 w, 834 w and 687 cm\(^{-1}\) w; mol. wt.: found 317.980, calc. for \( \text{C}_{13}\text{H}_{11}\text{ClO}_{2}\text{S}_{4} \) 317.979.

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REFERENCES


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