

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-dithiin derivative, is demonstrated spectroscopically and a mechanism for its formation suggested.

In connection with studies concerned with the consequences of α lone pair—lone pair interactions,¹ we were attracted to the novel 1,2-dithiins (e.g. 3). It has been reported² 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 Ochs² (Fig. 1). Although no definite evidence for

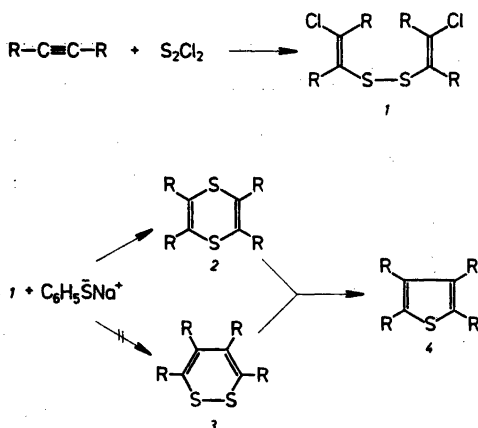


Fig. 1. $R = COOCH_3$.

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 reported² 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.³⁻⁶

An important clue to the constitution of the yellow product lies in its colour. Most known 1,2-dithiins are red with $\lambda_{max} > 450$ nm,³ while the 1,4-isomers are generally white or yellow unless embedded in a planar, highly conjugated system.^{4,5a} Indeed the UV spectrum of the yellow dithiin (longest $\lambda_{max} = 356$ nm) is superimposable with that of the 1,4 derivative 2 prepared independently.^{4,7} 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 ¹³C 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

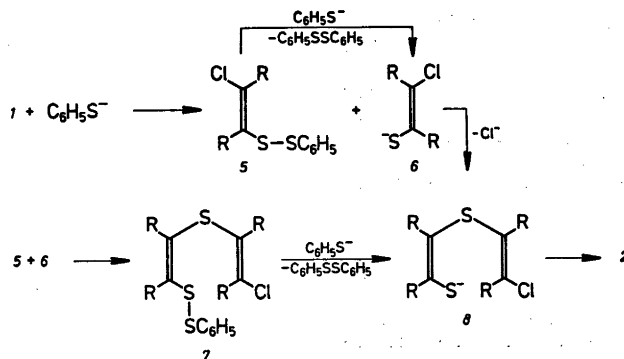


Fig. 2. $\text{R} = \text{COOCH}_3$.

latter was likewise observed by Ried and Ochs, **5** went undetected. Structure **5** rests on spectroscopic data (see Experimental), and it indicates the possible mechanistic course of the reaction. Fig. 2 depicts the formation of compound **5** from nucleophilic attack of benzenethiolate on the disulfide linkage of **1**, a very well-known transformation.⁸ The enethiolate intermediate **6** might dimerize head-to-tail⁹ with loss of chloride ion to give a second enethiolate **8**. Ring closure produces **2**. Alternatively the anion **6** may displace chlorine in **5** leading to intermediate **7**. Subsequent attack by benzenethiolate 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 methoxycarbonyl 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-dithiin **3**.² The identification of **2** and the isolation of **5** renders the radical pathway unlikely.

The reevaluation of structure for the tetrakis(methoxycarbonyl)dithiin **2** invites speculation concerning the constitution of other 1,2-dithiins reported to be yellow in colour.^{8,10}

EXPERIMENTAL

¹H NMR spectra (60 MHz) were obtained on a Varian T-60 A instrument, and ¹³C 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'-dithiofumurate (**1**). Compound **1** was prepared as described by Ried and Ochs;² m.p. 151–152°C (lit.² 152°C); ¹H NMR (CDCl_3): δ 3.96 (6 H, s), 3.87 (6 H, s) (lit.² ($\text{CDCl}_3/\text{HMDS}$) 3.78, 3.71); ¹³C 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 benzenethiolate (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°C, dec.;² 126–127°C⁷); ¹H NMR (CDCl_3): δ 3.85 (s) (lit.² ($\text{CDCl}_3/\text{HMDS}$) δ 3.72); ¹³C NMR (CDCl_3): δ 161.8 (>C=O), 134.6 (>C=C) and 53.6 (Me); UV (abs. ethanol) λ_{max} nm (log ϵ): 250 (3.83, sh), 314 (3.82) and 356 (2.47, sh); (lit.² 312 (3.74)). The UV spectrum is identical to that of 1,4-dithiin **2** prepared by an independent route.⁴

Dimethyl 2-chloro-3-(phenyldithio)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.¹¹ 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 **5** as a colourless oil (28 mg, 4 %); $^1\text{H NMR}$ (CCl_4): δ 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, $\text{M}^+ - \text{SPh}$), 109 (51, SPh), 77 (15), 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 $\text{C}_{13}\text{H}_{11}\text{ClO}_4\text{S}_2$ 317.979.

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