

Tetrathiodilactones

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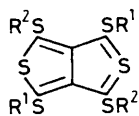
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Novel tetrathiodilactone derivatives [thienothiophenedithiones (**2**)] have been obtained by the reaction of tetrakis(alkylthio)thienothiophenes (**1b** and **c**) with thionyl chloride (as an electron-deficient reagent), along with the corresponding thiophene-3,4-bisthiocarboxylic thioanhydride derivatives (**3**).

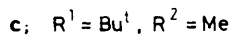
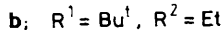
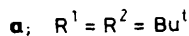
We have reported previously the synthesis of 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]thiophenes (**1a—c**) by dimerization of 2,3-bis(alkylthio)cyclopropenethiones.¹ During investigation of the interaction between (**1a—c**) and electron-deficient reagents, we found that the 3,6-bis(alkylthio)thieno[3,4-*c*]thiophene-1,4-dithiones (**2**) were formed by the reactions of 1,4-bis(*t*-butylthio)-3,6-bis(ethylthio)- and 1,4-bis(*t*-butylthio)-3,6-bis(methylthio)-thieno[3,4-*c*]thiophenes (**1b** and **c**)

with thionyl chloride. Compounds (**2**) are representatives of a new π -system containing a tetrathiodilactone skeleton.

A typical procedure for the reaction of (**1b**) with thionyl chloride is as follows. A degassed benzene solution of (**1b**) and thionyl chloride (10 equiv.) was stirred for 1 h at room temperature under nitrogen. The solvent was evaporated off and the residue was reprecipitated with degassed dichloromethane-hexane. The resulting solid was reprecipitated with



(1)

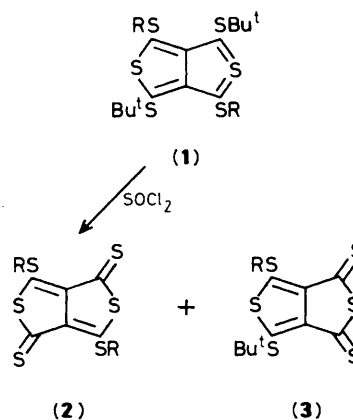


degassed benzene-hexane to give the tetrathiodilactone (**2b**)† as fine black-violet needles in 34% yield. Chromatography of the filtrate on silica gel afforded 2-t-butylthio-5-(ethylthio)-thiophene-3,4-bisthiocarboxylic thioanhydride (**3b**) in 9% yield. Similarly, the reaction of (**1c**) with thionyl chloride afforded the tetrathiodilactone derivative (**2c**)† in 30% yield, along with 4% yield of the corresponding thioanhydride (**3c**).

It seemed to us that this reaction must proceed by reversible generation of a charge-transfer-type intermediate, followed by elimination of two t-butyl groups.

In the reaction of 1,3,4,6-tetrakis(t-butylthio)thieno[3,4-c]thiophene (**1a**) with thionyl chloride, the corresponding tetrathiodilactone derivative was not obtained; only the thioanhydride (**3a**) formed was recently synthesized by a similar reaction of (**1a**) with electron acceptors.²

The tetrathiodilactone derivatives (**2b** and **c**), rapidly decomposed in non-degassed solution, but were stable in the crystalline state for long periods. Compound (**2b**) is sparingly soluble in benzene, chloroform, and dichloromethane, and



(**2c**) slightly soluble in benzene and dichloromethane. Both compounds are insoluble in other polar or nonpolar organic solvents.

In its ¹H n.m.r. spectrum, (**2b**) showed an interesting shift of about 0.9 p.p.m. to higher field in C₆D₆ than in CDCl₃. This might be explained by contact interaction of the electron deficient π-system in (**2**) with a π-electron donating solvent.

In their u.v. spectra, (**2b** and **c**) show characteristic absorption bands at 531sh (log ε 3.73) and 565 nm (4.07) [for (**2b**)] and 535sh (3.52) and 568 nm (3.80) [for (**2c**)]. These may be regarded as 'intramolecular charge-transfer absorptions,' due to transitions between energy levels produced by the interaction of the highest occupied levels of the two alkylthio groups with the lowest vacant levels of the two thioketone groups.

† (**2b**), M.p. >300°C; i.r. (KBr) 1470, 1300, 1280, and 923 cm⁻¹; ¹H n.m.r. (degassed CDCl₃) δ 1.52 (t, 6H) and 3.12 (q, 4H); ¹H n.m.r. (degassed C₆D₆) δ 0.73 (t, 6H) and 2.14 (q, 4H); u.v. (degassed CH₂Cl₂) λ_{max} 345sh (log ε 3.69), 382 (3.98), 442sh (3.29), 531sh (3.73), and 565 nm (4.07); *m/z* 322 (*M*⁺); (**2c**), m.p. >300°C; i.r. (KBr) 1455, 1410, 1300, 1280, and 915 cm⁻¹; ¹H n.m.r. (degassed CD₂Cl₂) δ 2.67 (s); u.v. (degassed CH₂Cl₂) λ_{max} 341sh (log ε 3.70), 382 (3.87), 432sh (3.29), 535sh (3.52), and 568 nm (3.80); *m/z* 294 (*M*⁺); satisfactory elemental (C and H) analyses were obtained in both cases.

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References

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- 2 S. Yoneda, K. Ozaki, K. Yanagi, and M. Minobe, *J. Chem. Soc., Chem. Commun.*, 1986, 19.