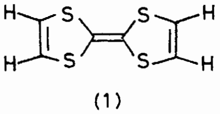
Electrochemical Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-dithione

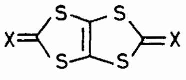
By William P. Krug, Aaron N. Bloch, and Dwaine O. Cowan*
(*Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland* 21218)

Summary 1,3,4,6-Tetrathiapentalene-2,5-dithione (**2**) was prepared in ethanol by the reaction of the electrochemically formed 2-thioxo-1,3-dithiol-4,5-dithiolate (**6**) with thiophosgene.

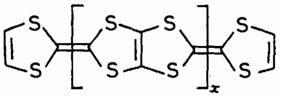
Our interest in the unusually high and anisotropic electrical conductivity of the organic charge-transfer salts of the donor tetrathiafulvalene (TTF)[1] (**1**) and derivatives[2] with suitable acceptors such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has prompted us to continue our systematic[3] investigation of these and related complexes. 1,3,4,6-Tetrathiapentalene-2,5-dithione (**2**) is an important monomeric precursor for the preparation of planar, extended π-electron systems such as those illustrated by formula (**4**).[3–5] Compound (**2**) could possibly be synthesised *via* the electrochemically prepared intermediate dithiolate (**6**) which has previously been trapped and characterized as the methylated product (**5**).[6]



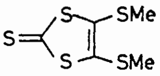
(1)



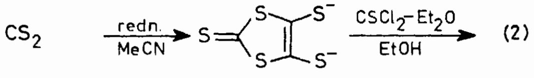
(2) X = S
(3) X = O



(4) x = 1–n



(5)



(6)

We report the synthesis of (**2**) by the reaction of (**6**) in ethanol at room temperature with thiophosgene. The dithiolate (**6**) was obtained by electrochemical reduction of carbon disulphide in acetonitrile at −1·75 V *vs.* S.C.E. Reaction of (**6**) with thiophosgene in ethanol gave (**2**) as an orange solid in 65% yield (based on current passed) after purification, m.p. 240·5—242 °C (decomp.). Surprisingly (**2**) was not obtained by the direct reaction of (**6**) with thiophosgene in acetonitrile.

Compound (**2**) has the following properties: i.r. (KBr) 1058s cm^{-1} (C=S)[6] [*cf.* 1056 cm^{-1} for (**5**)]; Raman (CH_2Cl_2) 1080 (C=S) and 1461 (C=C) cm^{-1} [*cf.* 1069 and 1470 cm^{-1} for (**5**)]; λ_{max} (CH_2Cl_2): 247 (log ϵ 3·98), 281 (3·80), and 407·5 (4·31) nm; *m/e* 239·8326 (calc. 239·8325); *m/e* (low resolution) 240 (M^+, 42%), 164 ($M^+ - CS_2$, 5), 120 ($M^+/2$, 7), 100 (C_3S_2, 6), 88 ($M^+ - 2CS_2$, or C_2S_2, 68), and 76 (CS_2, 100).

Compound (**2**) was converted into the dione (**3**) by reaction with mercury(II) acetate,[7] isolated in 58% yield as pale yellow needles, m.p. 179—181 °C; i.r. (KBr) 1654vs (C=O) cm^{-1}; λ_{max} (CH_2Cl_2) 275 (log ϵ 3·71) nm; *m/e* 208 (M^+, 26), 180 (M^+ −CO, 43), 152 (M^+ −2CO, 20), 120 (C_2S_3, 12), 88 (C_2S_2, 37), and 76 (CS_2, 100).

Satisfactory C and H analyses were obtained for (**2**); S analyses were repeatedly 0·6—3·8% low. However, no concurrent variation in λ_{max} or log ϵ was observed. The dione (**3**) gave satisfactory analyses for C, H, S, and O.

This work was supported by the National Science Foundation and the Materials Science Office, Advanced Research Projects Agency, Department of Defense.

Added in proof. An alternative synthesis of (**2**) and (**3**) has been reported, after submission of this communication; *cf.* R. R. Schumaker and E. M. Engler, *J. Amer. Chem. Soc.*, 1977, **99**, 5521. They report m.p.s of 207—210 °C (decomp.) for (**2**) and 150 °C for (**3**).

(*Received*, 10*th June* 1977; *Com.* 568.)

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