

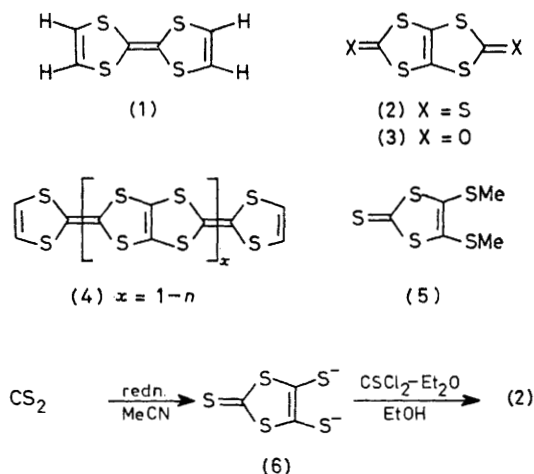
Electrochemical Synthesis of 1,3,4,6-Tetrathiapentalene-2,5-dithione

By WILLIAM P. KRUG, AARON N. BLOCH, and DWAIN 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 derivatives² with suitable acceptors such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has prompted us to continue our systematic³ 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

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. $240.5-242^\circ\text{C}$ (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 ($M^+ - \text{CS}_2$, 5), 120 ($M^+ / 2$, 7), 100 (C_2S_2 , 6), 88 ($M^+ - 2\text{CS}_2$, 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. $179-181^\circ\text{C}$; 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 ($M^+ - \text{CO}$, 43), 152 ($M^+ - 2\text{CO}$, 20), 120 (C_2S_2 , 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.

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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 $207-210^\circ\text{C}$ (decomp.) for (**2**) and 150°C for (**3**).

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