'Organic Metals': Synthesis of Dithiolylidenetetrathiapentalenones and their Higher Analogues

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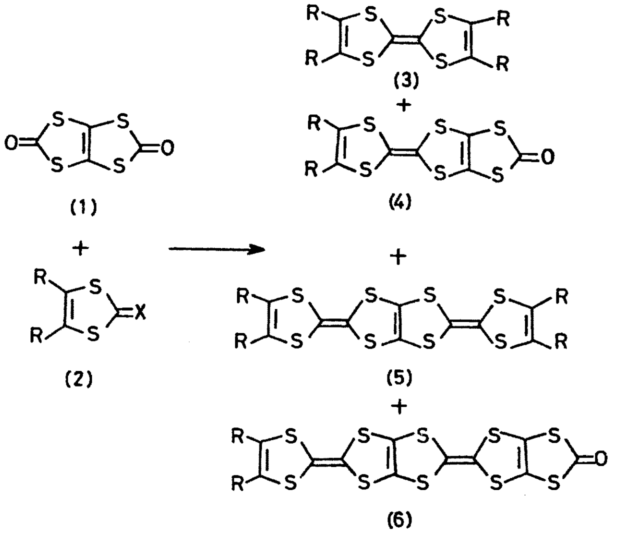
Summary Reaction of the tetrathiapentalene-2,5-dione (**1**) and 4,5-dimethoxycarbonyl-1,3-dithiole-2-thione (**2**) with trimethylphosphite in refluxing benzene provides, along with the expected self-coupled products, the dithiolylidenetetrathiapentalenone (**4**; R = $\mathrm{CO_2Me}$) and its higher analogue (**6**; R = $\mathrm{CO_2Me}$).



Scheme

The chemistry of tetrathiafulvalene (TTF) (**3**; R = H) has attracted considerable attention, since a number of its derivatives have been found to display interesting and unusual properties such as formation of metallic charge-transfer salts[1] and reversible electrochromism.[2] The recent synthesis of the tetrathiapentalene-2,5-dione ring system (**1**)[3] provides a means of elaborating more complex, extended π frame-works based on TTF[4] *via* cross-coupling reactions with 4,5-dimethoxycarbonyl-1,3-dithiole-2-thione (**2**) using alkyl phosphorus bases as shown in the Scheme. The cross-coupling reaction is successful only for strongly electron-withdrawing substituents (R = $\mathrm{CF_3}$ or CN) in (**2**) and for X = O or S, and gives mono- and bis-capped compounds (**3**) and (**5**), respectively.[5] Compound (**5**) is formally the next higher homologue of TTF, and as such the properties of this new π-system are of considerable interest. Unfortunately, the insolubility of these symmetrically substituted compounds has prevented us from evaluating their molecular properties in relation to TTF.

We have discovered that when a less electronegative substituent (*i.e.*, R = $\mathrm{CO_2Me}$) is employed in (**2**), another bis-capped product (**6**) is also formed, corresponding to coupling of (**1**) with itself and with (**2**). The unsymmetrical substitution in (**6**) significantly improves its solubility so as to permit an evaluation of its molecular properties.

Compound (**1**)[3b] and a 5-fold excess of (**2**)[6] were heated at reflux in benzene with an excess of trimethyl phosphite under nitrogen for 8 h. The reaction mixture was filtered hot and the remaining black solid extracted extensively with hot chloroform. Dry column chromatography (silica, $\mathrm{CHCl_3}$–hexane) on these washings provided, in the following order, tetramethoxycarbonyl-TTF (**3**; R = $\mathrm{CO_2Me}$),[7] the mono-capped product, the dithiolylidenetetrathiapentalenone (**4**; R = $\mathrm{CO_2Me}$), brown solid, m.p. 215—220 °C (decomp.), ν(KBr) 3415mbr, 2975, 2960w, 1722, 1705, 1670s, 1575, 1428m, 1280, 1250s, 1092, 1025, 770, and 705m cm^{-1}; 18% yield,† and the bis-capped product (**6**; R = $\mathrm{CO_2Me}$), dark-brown solid, m.p. 265—270 °C (decomp.), ν (KBr)

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† Satisfactory elemental analyses were obtained for these compounds.

3415m br, 2975, 2960w, 1725, 1710, 1680s, 1570, 1430m, 1250br s, 1090, 1022, 765, 750, and 697m cm^{-1}; 3% yield.† Electrochemical and optical data on compounds (**4**) and (**6**) are summarized in the Table.

TABLE. Electrochemical and optical data on compounds (**4**) and (**6**).

Cyclic voltammetry (Volts *vs.* S.C.E. 0·1 N tetraethylammonium perchlorate)	(**4**, R = CO_2Me)	(**6**, R = CO_2Me)
Oxidation peak potentials in MeCN	0·89	0·78
	0·98	0·92
		1·20
Optical spectra λ (log ε) in $CHCl_3$	238 (4·25)	239 (4·22)
	260 (4·11)	280 (4·20)
	295 (4·30)	310 (4·29)
	430 (3·15)	440 (3·14)
In 70% $HClO_4$	225 (4·20)	225 (4·52)
	310 (3·18)	395 (3·84)
	505 (3·76)	440 (3·77)
		545 (3·95)
		1050 (4·00)

Additional chloroform extractions of the black solid removed small amounts of dithiapendione.[3b] The remaining solid appeared to be the symmetrical bis-capped product (**5**; R = CO_2Me) based on the similarity of its i.r. spectrum with that of (**3**), ν (KBr) 3420m br, 2960w, 1730, 1715s, 1575m, 1450, 1430s, 1250s br, 1030, 765m, and 700s cm^{-1}; however we have been unable to obtain satisfactory analysis for this compound.‡

A simple step-wise coupling mechanism for the formation of the bis-capped products (**5**) and (**6**) seems unlikely since treatment of (**4**) and (**2**), or (**4**) and (**1**) with trimethyl phosphite in refluxing benzene failed to produce (**5**) or (**6**), respectively. A possible explanation for this behaviour may lie with the bifunctional character of (**1**). If coupling of (**2**) with (**1**) occurs while the 'uncoupled' carbonyl has formed a phosphorus base adduct,[8] the resulting intermediate may be 'activated' for further reaction with either (**1**) or (**2**). Once (**4**) is formed, however, the carbonyl is apparently unreactive towards coupling.

Both (**4**) and (**6**) display two one-electron redox couples, typical of TTF derivatives,[2a,9] with (**6**) being a slightly better electron-donor. A third, irreversible, oxidation wave is also observed in (**6**). In strong acid media, (**4**) and (**6**) become intensely coloured, probably owing to an internal charge-transfer contribution from the TTF donor portion of the molecule to the protonated dithiocarbonate species. In addition to strong absorptions in the visible region of the spectra for (**4**) and (**6**), (**6**) also displays a strong absorption at unusually low energy.

(*Received*, 16*th January* 1979; *Com.* 044.)

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‡ In the related reaction with R = CN, satisfactory elemental analyses have been obtained for compound (**4**); *cf.* ref. 5.

[1] M. Narita and C. U. Pittman, Jr., *Synthesis*, 1976, 489; J. H. Perlstein, *Angew. Chem. Internat Edn.*, 1977, **16**, 519.

[2] (a) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Annalen*, 1973, 310; (b) E. M. Engler, F. B. Kaufman, and V. V. Patel, *IBM Technical Disclosur: Bulletin*, 1978, **21**, 2084.

[3] (a) R. R. Schumaker and E. M. Engler, *J. Amer. Chem. Soc.*, 1977, **99**, 5519; (b) *ibid.*, p. 5521; (c) W. P. Krug, A. N. Bloch, and D. O. Cowan, *J.C.S. Chem. Comm.*, 1977, 660.

[4] H. Poleschner, W. John, G. Kempe, E. Hoyer, and E. Fanghänel, *Z. Chem.*, 1978, **18**, 346; N. Martinez Rivera, E. M. Engler, and R. R. Schumaker, *J.C.S. Chem. Comm.*, 1979, 180.

[5] R. R. Schumaker and E. M. Engler, *J. Amer. Chem. Soc.*, to be published.

[6] B. R. O'Connor and F. N. Jones, *J. Org. Chem.*, 1970, **35**, 2002.

[7] H. D. Hartzler, *J. Amer. Chem. Soc.*, 1973, **95**, 4379.

[8] E. M. Engler, V. V. Patel, and R. R. Schumaker, *J.C.S. Chem. Comm.*, 1977, 835; S. Yoneda, T. Kawase, M. Inaba, and Z. Yoshida, *J. Org. Chem.*, 1978, **43**, 595.

[9] D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, J. *Amer. Chem. Soc.*, 1971, **93**, 2258.