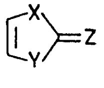
Organic Metals: Synthesis of Benzotetrathiafulvalene

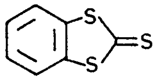
By H. KENNETH SPENCER, MICHAEL P. CAVA,* and ANTHONY F. GARITO*†

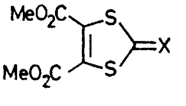
(*Department of Chemistry and* †*Department of Physics, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania* 19174)

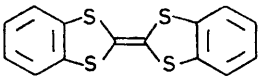
Summary The first synthesis of an unsymmetrical tetrathiafulvalene derivative by a mixed coupling reaction has been achieved; the resulting diester (**7**) has been demethoxycarbonylated to the highly unsymmetrical benzotetrathiafulvalene (**8**).

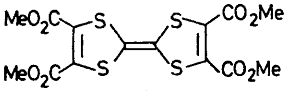
Tetrathiafulvalenes and their selenium analogues are heterocycles of much current interest in view of their ability to act as π-donors in the preparation of organic charge-transfer salts having metallic properties.[1] Almost all these compounds have been obtained either by the base treatment of a 1,3-dithiolium salt,[2] or by a phosphine or phosphite coupling of a thione or selone of the general structure (**1**);[3] these reactions produce only symmetrical products. We now report the first synthesis of an unsymmetrical tetrathiafulvalene by a mixed phosphite coupling, the key to success being the use of one diester component and one unfunctionalized component to allow chromatographic separation of products of widely varying polarity.

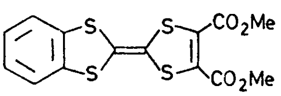

(1), X,Y, and Z = S and/or Se

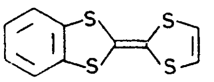

(2)


(3), X = S
(4), X = Se


(5)


(6)


(7)


(8)

Reaction of an equimolar mixture of the thione (**2**)[4] and the thione diester (**3**)[3b] with triethyl phosphite in benzene at 80 °C gave a mixture of the yellow dibenzotetrathiafulvalene (**5**) (38%),[4] the black tetraester (**6**) (18%),[5] and the desired red diester (**7**) (3%), m.p. 173—174 °C; λ_{max} (dichloroethane) 255 (log ϵ 4·28), 313 (4·24), and 416 (2·00) nm. A similar mixed coupling of the thione (**2**) with the selone diester (**4**)[6] afforded a far more favourable yield of the diester (**7**), the products (**5**), (**6**), and (**7**) being produced in yields of 11, 30, and 31%, respectively.

Direct demethoxycarbonylation[7] of (**7**) by lithium bromide in warm moist hexamethylphosphoramide gave 68% of the yellow benzotetrathiafulvalene (**8**), m.p. 138·5—140 °C; λ_{max} (cyclohexane) 215 (log ϵ 4·50), 294 (4·20), 313 (4·21), and 444 (2·00) nm.†

Measurements of the polarographic half-wave potentials of (**8**) showed that two reversible oxidations occur at +0·085 and +0·436 V. These values fall between those for tetrathiafulvalene (TTF) (+0·006 and +0·385 V) and (**5**) (+0·228 V reversible and +0·528 V irreversible).

Reaction of (**8**) with tetracyanoquinodimethane (TCNQ) in acetonitrile gave instantaneously a black crystalline 1 : 1 charge-transfer salt in contrast to (**5**) which has no charge-transfer properties in the solid state. The room-temperature compaction conductivity of (**8**)-TCNQ is 3×10^{-6} Ω^{-1} cm^{-1} which is much lower than that for TTF·TCNQ (20 Ω^{-1} cm^{-1}).

This work was supported by grants from the National Science Foundation and Advanced Research Projects Agency. We thank Mr. P. J. Nigrey for technical assistance.

(*Received*, 20*th July* 1976; *Com.* 821.)

---

† Satisfactory elemental analyses were obtained for compounds (**7**), (**8**), and (**8**)·TCNQ.

[1] A. F. Garito and A. J. Heeger, *Accounts Chem. Res.*, 1974, **33**, 232; E. M. Engler, *Chem. Tech.* (*Berlin*), 1976, 274.

[2] (a) H. Prinzbach, H. Berger, and A. Luttringhaus, *Angew. Chem. Internat. Edn.*, 1965, **4**, 435; F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Comm.*, 1970, 1453; D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Amer. Chem. Soc.*, 1971, **93**, 2258; (b) L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456.

[3] For some examples see: E. M. Engler and V. V. Patel, *J. Amer. Chem. Soc.*, 1974, **96**, 7376; K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J.C.S. Chem. Comm.*, 1974, 937; M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *ibid.*, 1975, 383; H. K. Spencer, M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *ibid.*, p. 867.

[4] S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Annalen*, 1973, 310.

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

[6] M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 879.

[7] M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 882.