Organic Metals: Annelated *sym*-Diselenadithiafulvalenes

By H. KENNETH SPENCER, M. V. LAKSHMIKANTHAM, 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)

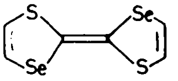
Summary Several annelated derivatives (**12**) and (**13**) of *sym*-diselenadithiafulvalene (**1**) have been synthesized by a novel route employing 1,2,3-selenadiazoles as starting materials; the TCNQ salt of (**13**) shows unusually high compaction conductivity.

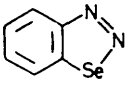
THERE has been much interest recently in the synthesis of selenium-containing analogues of tetrathiafulvalene (TTF).[1–4] Like TTF, such compounds are valuable π-donors in the preparation of organic charge-transfer salts having metallic properties.[5] In this connection, we have described a synthesis of *sym*-diselenadithiafulvalene (DSeDTF, 1).[4]‡ Since the route to the parent heterocycle (**1**) is not applicable to the synthesis of annelated analogues, we have now developed a novel route to such compounds from known and readily prepared 1,2,3-selenadiazole precursors.

Thermolysis of 1,2,3-benzoselenadiazole[6] (**2**) in excess of CS_2 (4·5 h; 160°) afforded the yellow benzo-1,3-selenathiolane-2-thione (**4**), m.p. 130—131° (44·5%). Direct coupling of (**4**) with triethyl phosphite (1 h; 150°)[7] gave, in low yield (4%), *sym*-dibenzodiselenadithiafulvalene (**12**), m.p. 247—248°; λ_{max} (MeCN) 254 (log ε 4·28), 284 (4·18), 315 sh (3·99), and 448 (2·36) nm. A far better yield (39%) of (**12**) was obtained in a similar phosphite coupling of the red selone (**7**), m.p. 195—196°; compound (**7**) was prepared in 52·8% overall yield from (**4**) in the following sequence: (a) methylation of (**4**) by methyl fluorosulphonate to give the sulphonium salt (**5**), m.p. 140°, (b) morpholine treatment of (**5**) to give the immonium salt (**6**), m.p. 105°, and (c) reaction of (**6**) with aqueous H_2Se to give (**7**).[8]

In an analogous manner, thermolysis of cyclopenta-1,2,3-selenadiazole (**3**)[9] in excess of CS_2 (3 h; 160°) afforded the yellow cyclopenta-1,3-selenathiolane-2-thione (**8**), m.p. 109—110° (53%). Methyl fluorosulphonate treatment of (**8**) gave the sulphonium salt (**9**), m.p. *ca.* 160°, converted by morpholine into the immonium salt (**10**), m.p. 175°, which in turn reacted with aqueous H_2Se to give (54% overall yield) the red-orange selone (**11**), m.p. 127°. Triethyl phosphite coupling of (**11**) gave (37%) *sym*-dicyclopentadiselenadithiafulvalene (**13**), m.p. 244° (decomp.); λ_{max} (dichloroethane) 305 (log ε 4·03), 334 (3·77), 347 sh (3·49), 433 (2·31), and 472 (2·41) nm.

The π-donor (**13**) forms highly conducting black crystalline charge-transfer salts with the π-acceptors tetracyanoquinodimethane (TCNQ) and tetracyanonaphthtoquinodimethane (TNAP). For example, the room-temperature four-probe compaction conductivity (σ_c) of *sym*-dicyclopentadiselenadithiafulvalene–TCNQ is 100 Ω^{-1} cm^{-1}, which represents one of the highest values reported to date for an organic metal. The corresponding values for the 1 : 1 TCNQ salts of dicyclopentatetrathiafulvalene,[10] dicyclohexatetrathiafulvalene,[10] and *sym*-dicyclohexadiselenadithiafulvalene[11] are 15, 5×10^{-5}, and 2×10^{-6} Ω^{-1} cm^{-1} respectively. Comparison of these values suggests, firstly, that steric differences between the cyclopenteno and cyclohexeno-substituents play a dominant role in the crystallographic stacking arrangement in the salts;[12] and secondly, that the change in molecular electronic properties accompanying the selenium substitution in (**13**) significantly affects the electronic transport processes in the TCNQ salts.[5] Similar observations are made for the corresponding TNAP salts. With TCNQ and TNAP, (**12**) forms insulating solids; for example, σ_c *ca.* 10^{-8} Ω^{-1} cm^{-1} in the case of TNAP.


(1) ‡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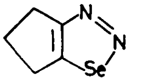
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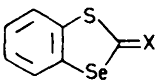
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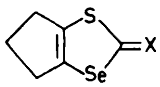
(5) X = +SMe FSO_3^-
(6) X = +N O FSO_3^-
(7) X = Se


(8) X = S
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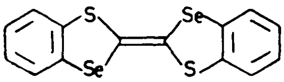
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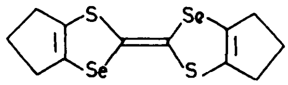
(13)

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‡ It has been found by n.m.r. spectroscopy that DSeDTF (**1**) exists as a 57 : 43 mixture of (*E*) and (*Z*) isomers; δ ($CDCl_3$) 6·84, 6·77, 6·55, and 6·48 (each d, *J* 6·5 Hz), in agreement with E. M. Engler, *Phys. Rev. Letters*, 1975, **34**, 741. In analogy, compounds (**12**) and (**13**), which are homogeneous by analytical and spectral criteria, are assumed to be mixtures of (*E*) and (*Z*) isomers.

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