Triselenathiafulvalenes: a Novel Sulphur–Selenium Interchange on Trimethyl Phosphite Coupling of Substituted 1,3-Diselenole-2-thiones

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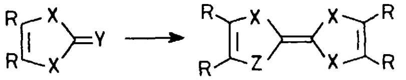
Summary Coupling using trimethyl phosphite of 4,5-dimethoxycarbonyl- and 4,5-ditrifluoromethyl-1,3-diselenole-2-thiones unexpectedly gave only tetramethoxycarbonyl- and tetratrifluoromethyl-triselenathiafulvalene respectively, while self-coupling of 4,5-dimethyl-1,3-diselenole-2-thione provided a mixture (85:15) of tetramethyltetraselenafulvalene and tetramethyltriselenathiafulvalene.

Coupling of compounds of type (**1**) using trialkyl phosphites is one of the most general methods available for preparing tetrathiafulvalene, its selenium analogues, and their substituted derivatives (**2**).[1] For the parent systems (R=H), the coupling reaction requires that Y should be Se in (**1**).[2] For the substituted dithioles (**1**, X=S) coupling occurs when Y = Se or S, but lower yields are obtained in the latter case.[3]† In a study of the cross-coupling reactions of dichalcogenole derivatives to 1,3,4,6-tetrathiapentalene-2,5-dione,[4] we discovered an unexpected sulphur–selenium interchange when substituted 1,3-diselenole-2-thiones are treated with trimethyl phosphite.



(1) (2)

a; R=CO$_2$Me, X=Y=Se
b; R=CF$_3$, X=Y=Se
c; R=CO$_2$Me, X=Se, Y=S
d; R=CF$_3$, X=Se, Y=S
e; R=CH$_3$, X=Se, Y=S

a; R=CO$_2$Me, X=Z=Se
b; R=CF$_3$, X=Z=Se
c; R=CO$_2$Me, X=Se, Z=S
d; R=CF$_3$, X=Se, Z=S
e; R=CH$_3$, X=Z=Se
f; R=CH$_3$, X=Se, Z=S

Treatment of the diselenolethiones (**1c**)‡ or (**1d**)§ with trimethyl phosphite in refluxing benzene for 4 h under nitrogen did not provide the expected tetraselenafulvalene derivatives¶ (**2a**) and (**2b**), respectively, but instead the triselenathiafulvalene derivatives (**2c**) and (**2d**) were obtained [(**2c**): purple-red crystals (from benzene–MeOH); m.p. 140—141 °C; i.r. (KBr) cm^{-1} 2960 w, 1750, 1730, 1710, 1700s, 1570s, 1440s, 1275s,br, and 1235s,br; ^{1}H n.m.r. (CDCl$_3$) δ 3·74 and 3·78 (two unequal singlets); *m/e* 460 (for ^{80}Se); (**2d**): red needles (from hexane); m.p. 103·5—104 °C; i.r. (KBr) 1595s, 1250s,br, and 1165s,br cm^{-1}; ^{19}F n.m.r. (CHCl$_3$, relative to CCl$_3$F) 47·0 (3F) and 49·2 p.p.m. (1F); *m/e* 620 (for ^{80}Se)]. Unscrambled products (**2a**) or (**2d**) were not detected by mass spectroscopy. Interestingly, both the ^{1}H and the ^{19}F n.m.r. spectra of (**2c**) and (**2d**), respectively show the inequivalence due to the sulphur in the ring.

In order to study the effect of electron-donating substituents on this S–Se scrambling reaction, the 4,5-dimethyl compound (**1e**) was prepared.[5] Reaction of (**1e**) with trimethyl phosphite required refluxing in toluene for 4 days to effect self-coupling. The product [purple needles (from iso-octane); m.p. 253—254 °C (decomp.)] was analysed by mass spectroscopy, and found to contain *m/e* clusters at 452 and 404 (for ^{80}Se) with relative intensities of 85 and 15%, respectively. These *m/e* values correspond to the unscrambled (**2e**) and scrambled (**2f**) products.

Apparently, only one ring is scrambled in the coupling of substituted 1,3-diselenole-2-thiones as judged by mass spectroscopy. This suggests a step-wise mechanism, involving initial attack of the phosphorus base on the thione derivative to give an intermediate which can scramble the ring selenium atoms with the carbonyl sulphur. This intermediate then attacks unchanged thione to yield coupled product.

Coupling with phosphorus bases of substituted 1,3-thiaselenole-[3,6] and 1,3-diselenole-2-thiones[7] has been employed for the preparation of diselenadithiafulvalene and tetraselenafulvalene derivatives, respectively. In view of this problem of S–Se scrambling, selone coupling is *required* if uncontaminated donors are to be prepared with confidence. This has important consequences concerning the solid-state properties of conducting charge-transfer salts of selenium heterofulvalene donors prepared from thione coupling, since small amounts of donor[8] and acceptor[9] doping are known to produce important changes in intrinsic solid-state properties.[10]

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† Alkyl 1,3-dithiole-2-thiones require more strenuous conditions for self-coupling and give considerably lower yields than the corresponding selones (E. M. Engler and V. V. Patel, unpublished work). For a convenient procedure for converting these thiones into selones see: E. M. Engler and V. V. Patel, *Tetrahedron Letters*, 1976, 423.

‡ Prepared from the corresponding selone (**1a**) (M. V. Lakshmikanthan and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 882) using phosphorus pentasulphide in refluxing toluene.

§ Prepared by the reaction of ethylene triselenocarbonate with hexafluorobut-2-yne which gives the selone (**1b**), which is converted into the thione on treatment with phosphorus pentasulphide in refluxing toluene.

¶ Self-coupling of (**1a**) gives the tetramethoxycarbonyltetraselenafulvalene (**2a**). Self-coupling of (**1b**) gives the tetratrifluoromethyltetraselenafulvalene (**2b**) [dark-red needles; m.p. 111—112 °C, ^{19}F n.m.r. (CHCl$_3$, relative to CCl$_3$F) 47·0 p.p.m.; *M*: 665·648 (calc.), 665·647 (found)].

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[10] See for example: Y. Tomkiewicz, E. M. Engler, and T. D. Schultz, *Phys. Rev. Letters*, 1975, **34**, 741.