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ORGANIC CONDUCTORS. THE SYNTHESIS OF DI-(2,5-DIHYDROTHIENO)-1,4,5,8-TETRASELENAFULVALENE (DTTSF) AND ITS CHARGE-TRANSFER SALT WITH 7,7',8,8'-TETRACYANO-p-QUINODIMETHANE (TCNQ).

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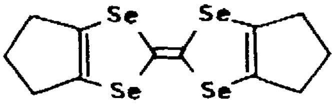
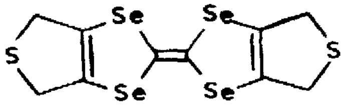
Several charge-transfer salts of sulphur- and selenium-containing heterofulvalenes with 7,7',8,8'-tetracyano-p-quinodimethane (TCNQ) have recently been shown to possess unique solid state properties[3,4,5,6,7]

Of the tetraselenafulvalenes prepared so far, HMTSF (I) has been of particular interest because HMTSF-TCNQ[6] is the first example of an organic compound which retains high electrical conductivity at very low temperatures ($\sigma_{0.03K} \sim 600(\Omega\ cm)^{-1}$)

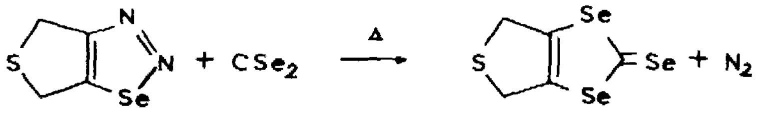

(I)


(II)

Di-(2,5-dihydrethieno)-{3,4-b,3,4-h}-1,4,5,8-tetraselenafulvalene, DTTSF (II), was synthesized in order to investigate the effect of introducing a polarisable heteroatom into the exocyclic rings, while retaining the overall size and symmetry, and thereby probably the packing properties, of the congener (HMTSF)

1,2,3-thiadiazoles are known to react with a 1,3-dipolarophile such as CS_2 to give 1,3-dithiole-2-thiones in low to moderate yields[8]. Recently it was shown that 1,2,3-selenadiazoles can react in an analogous manner to form 1,3-thiaselenole-2-thiones, which in turn were converted to dithiadiselenafulvalenes[9]

We report the reaction of 4,6-dihydro-(3,4-d)-thieno-1,2,3-selenadiazole (III) with CSe_2[10] to yield the 1,3-diselenole-2-selone (IV)


(III) (IV)

(IV) was treated with triethylphosphite to give DTTSF (II).

(III) was prepared from dihydrothiophene-3-one semicarbazone[11] by ring closure with SeO_2 in glacial acetic acid by a procedure analogous to that of Yalpani *et al*[12]. (III) was isolated as colourless needles in 18% yield, m p 85-87°(hexane), and identified as being (III) rather than the other possible isomer, 4,5-dihydro-(2,3-d)-thieno-1,2,3-selenadiazole, by ^{1}H-NMR spectroscopy.

Reaction of (III) with excess CSe_2 in boiling toluene (2h) afforded (IV) in 35% yield, m p 165-166° MS M^+ in accordance with the calculated isotopic cluster for $C_5H_4SSe_3$ NMR($CDCl_3$) 4.07(s) δ relative to TMS

Triethylphosphite coupling of (IV) in toluene (24h, 100°) gave the insoluble (II) in 7-10% yield as black crystals, m p 228-230°(decomp) MS M^+ in accordance with the calculated isotopic cluster for $C_{10}H_8S_2Se_4$ UV(C_6H_5CN), λ_{max} (log ε) 317 (3.92), 438 (2.70) and 495 (2 72) nm

(II) forms a highly conducting 1 1 charge-transfer salt with TCNQ From chlorobenzene black needles of typical dimensions 1 x 0 02 x 0 004 mm were obtained Room-temperature conductivities of at least 600 $(\Omega\ cm)^{-1}$ were measured by 4-probe techniques A detailed account of the temperature-dependent electrical properties will appear elsewhere

References and Notes

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