Synthesis of the Organic Conductor Tetramethyltetraselenofulvalenium 7,7,8,8-Tetracyano-*p*-quinodimethanide (TMTSF–TCNQ) [4,4′,5,5′-Tetramethyl-$\Delta^{2,2'}$-bis-1,3-diselenolium 3,6-Bis-(dicyanomethylene)cyclohexadienide]

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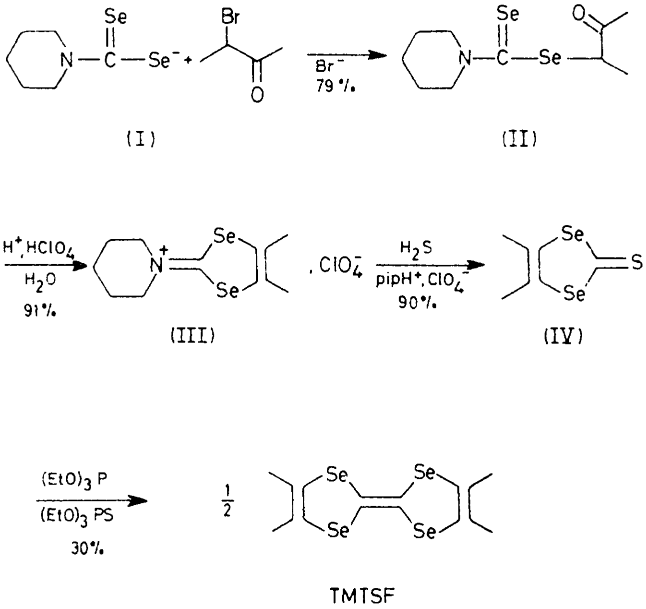
Summary Tetramethyltetraselenofulvalene reacts with tetracyanoquinodimethane to form a highly conducting organic solid.

The synthesis in these laboratories[1] of the salt of tetrathiofulvalene and 7,7,8,8-tetracyanoquinodimethane (TTF–TCNQ) and the discovery of its exceptionally high electrical conductivity[1,2] have encouraged attempts to prepare related organic conductors whose electrical properties are subject to systematic control.[3] Notable successes include the synthesis of the TCNQ salts of the tetramethyl derivative of TTF by Ferraris, *et al.*,[4] and of the selenium analogue of TTF by Engler, *et al.*[5]

Here we report the synthesis of tetramethyltetraselenofulvalene (TMTSF) and its TCNQ salt (TMTSF–TCNQ). Crystals of the latter exist in at least two forms, a coppery red insulator with a room-temperature d.c. conductivity[6] of $10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and a black organic 'metal' with a room-temperature d.c.[6] and microwave[7] conductivity of at least $800\ \Omega^{-1}\ \mathrm{cm}^{-1}$, comparable to the best organic conductors known.[1,2,4,5] A detailed account of the temperature dependent electrical properties will appear elsewhere.



Scheme

The series of reactions leading to TMTSF is outlined in the Scheme. Compound (II) was prepared from the diselenocarbamate (I)[8] and excess of bromobutanone in dry CH_2Cl_2. Ring closure was affected by dissolving (II) in conc. H_2SO_4. Compound (III) was treated with H_2S in neutral or weakly acidic media to form the yellow thione (IV) Treatment of the thione (IV) or the corresponding selone[9] with excess of triethyl phosphite gave TMTSF as violet needles, m.p. $> 250\ ^{\circ}C$ (decomp.); ν_{max} 32,300 and 19,700 cm^{-1} (log ϵ 4·1 and 2·3).† TMTSF is more difficult to oxidize than the corresponding sulphur compound, the difference in halfwave potentials of the first oxidation wave being 0·167 V in CH_2Cl_2. This means that TCNQ cannot oxidize TMTSF to an appreciable extent in CH_2Cl_2 or MeCN from which the dark complexes were grown. TCNQ salts of TMTSF were prepared by dissolving the reactants in hot CH_2Cl_2 or MeCN and cooling, or by diffusion of the reactants in H-shaped tubes.

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† The structure was confirmed by i.r., n.m.r. and mass spectra and elemental analysis.

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