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2-METHYLENE-1,3-DISELENOLE:A PRECURSOR OF TETRASELENAFULVALENE (TSeF)

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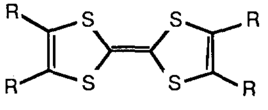
Abstract: The preparation of methylene-1,3-diselenole and its ready conversion to TSeF are discussed.

The quasi-metallic conductivity of charge-transfer salts of tetrathiafulvalenes (1) and tetraselenafulvalenes (2) with acceptor molecules (e.g. tetracyanoquinodimethane, TCNQ) has led to widespread research into the synthesis and chemistry of tetrachalcogenafulvalenes. Synthetic methods have been reviewed by Narita and Pittman[1] and by Krief.[2]



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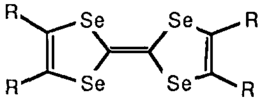

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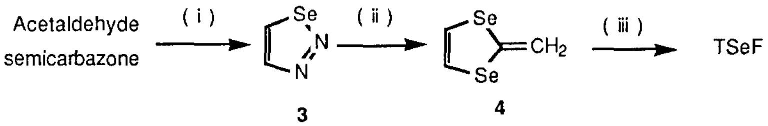
Tetrasubsituted analogs (e.g. R = alkyl, carbomethoxy or cyano) have been well studied and synthetic methods established.[1,2] Some salts of tetramethyltetraselenafulvalene and bis(ethylene- dithio) tetrathiafulvane have shown superconductivity.

The parent selena-system (2, R=H) however, although known since 1974, has been the subject of much less study in view of its limited synthetic accessibility. Of the three methods of synthesis reported to date[3] the first two involve the use of the noxious reagent CSe_2 which is not easily obtained; the third is a rather involved, multi-step preparation.

We now describe a short, simple and economical synthesis starting with the readily available acetaldehyde semicarbazone which is converted in three steps to TSeF via methylene-1,3-diselenole (4).



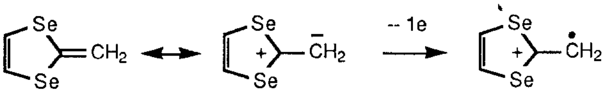
Scheme 1

Reagents (i) SeO_2, HOAc; (ii) *t*-BuOK/*t*-BuOH/DMF; (iii) I_2/morpholine/DMF

No chemistry of compound (4) has been described to date, though a number of substituted 1,3-diselenafulvenes have been prepared and their chemistry extensively reviewed.[4] The synthesis of compound (4) was mentioned briefly by us, without experimental detail, in a symposium report.[4] We now describe the preparation of 4 and its ready conversion to TSeF.

1,2,3-Selenadiazole (3) (formed by reaction of acetaldehyde semicarbazone with selenium dioxide)[5,6] reacts quickly with potassium *tert*-butoxide in DMF/*tert*-BuOH to give fulvene 4. In a typical procedure 1,2,3-selenadiazole (10.0 g, 47.2 mmol) in DMF/*t*-BuOH (200 ml:32 ml) was chilled in ice and to this was added, under nitrogen, potassium *tert*-butoxide (6.47 g, 57.7 mmol) in small portions over a 40-min. period, care being taken to keep the reaction temperature at 15-20°C. The reaction was done under nitrogen. The mixture was then stirred at room temperature for 30 mins., diluted to 1 L with cold water and the resultant precipitate collected by suction filtration. The mother-liquor was extracted with cyclohexane:hexane - 1:1 (3 x 150 ml), and the organic layer dried (Na_2SO_4) and concentrated. The solid obtained was combined with the above precipitate and recrystallized from hexane to give shiny plates (6.42 g, 81%): mp 58-60°C; ^1H NMR ($CDCl_3$) δ 5.67 (dd, 2H, J=1.0, 1.5 Hz), 6.99 (dd, 2H, J=1.0, 1.5 Hz); $\lambda^{cyclohex}$ (log ε) 208 nm (3.63), 282 (3.63), 307 sh (3.17), 360 br (2.47); M^+ 212 (100%). The freshly crystallized material is stable for several weeks at -20°C, but undergoes noticeable decomposition on standing for a few hours at room temperature. It is photosensitive and immediately decomposes on exposure to acids.

The chemistry of methylene-1,3-diselenole would seemingly be dominated by the dipolar form (5) and also by the cation radical (6) which can be formed from (5) by loss of one electron.



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Earlier work in our laboratory with substituted selena- and thiafulvenes led us to believe that they underwent electron transfer reactions more readily than electrophilic substitutions.[4,7] We therefore explored the reaction of compound 4 with iodine, and discovered that on reaction with iodine in the presence of pyridine, a black powder was produced which could readily be reduced to TSeF. This reaction always produced TSeF but the yields varied dramatically with slight variations in reaction conditions. Further experimentation led to the use of iodine in the presence of morpholine with DMF as solvent, giving rise to TSeF with consistent yields of about 30%.

Iodine (2.50 g, 9.8 mmol) was added to a mixture of morpholine (2.70 g, 31 mmol) and DMF (40 ml). This solution, *freshly prepared*, was poured into a solution of 2-methylene-1,3-diselenole (1.0 g, 4.7 mmol) in DMF (25 ml) while stirring at room temperature. [There was a mildly exothermic reaction. The mixture was brought to room temperature with the use of a water-bath.] The reaction mixture was stirred at room temperature for 25 mins., diluted with water, and extracted with cyclohexane:benzene - 1:1 (4 x 35 ml). The organic extract was washed with sodium thiosulfate, then water, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (silica gel, hexane:benzene - 3:1) to produce red crystals of TSeF (308 mg, 33%) mp 132-3°, identical in all respects (TLC,UV, NMR) with an authentic sample.

The mechanism of this reaction is still under investigation, and further chemistry of methylene-1,3-diselenole is being pursued in our laboratory.

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