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SYNTHESIS OF TETRATHIAFULVALENE DERIVATIVES: THIOCARBONYL TO SELENOCARBONYL CONVERSION IN THE 1,3-DICHALCOGENOLE RING SYSTEM

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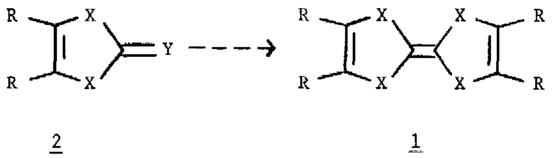
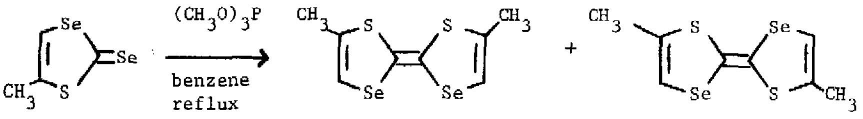
Charge transfer salts of tetrathiafulvalene,[1] its selenium analogs[2] and its substituted derivatives[3] (1) are the most electrically conducting organic solids presently known. The key synthetic step in preparing these organic donors involves the coupling of the 1,3-dichalogenole ring system 2. While a variety of synthetic procedures are available for reacting 2, most of these methods depend very much on the nature of the heteroatom (X and Y) and the R substituent.[4] The most general method appears to be the use of phosphorus bases. In fact, this procedure is the only means capable of preparing selenium derivatives of 1 (X = Se).[2,3b,c] Furthermore, for unsubstituted systems (R = H) when Y = S (2), the use of phosphorus bases does not work.[2a,b] Only when Y = Se does the coupling reaction succeed. The reason for this behavior is most likely due to the weaker C = Se bond which can be more easily broken, under milder reaction conditions, than the C = S bond. This quality of the C=Se bond, also, typically leads to better yields and more easily isolated products for the substituted derivatives of 1 when Y = Se than



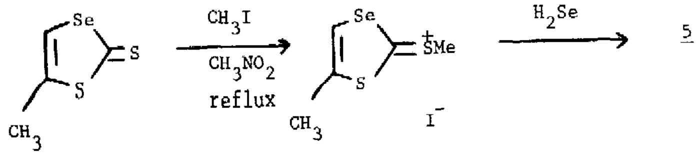
when Y = S.[5]

We report here a simple, convenient scheme for converting derivatives of 2 with Y = S to Y = Se. In order to illustrate the procedure, the preparation of cis/trans-2,2'-bis(5-methyl-1,3-thiaselenole), (DMDSeDTF, 3 and 4)[6] has been chosen, since this synthesis requires the coupling of 5-methyl-1,3-thiaselenole-2-selone (5), a compound which could not be prepared by *existing experimental procedures.*[4]



5 3 4

5-Methyl-1,3-dithiaselenole-2-thione (6) has been previously synthesized by the addition of Se and CS_2 to sodium methylacetylide.[7] Treatment of 6 with an excess of methyl iodide[8] in refluxing nitromethane for several hours, precipitated the yellow iodide salt (7)[9] in quantitative yield. This salt was dissolved in $MeOH-H_2O$ solvent[10] and cooled to 0°C. An excess of hydrogen selenide[11,12] in a nitrogen stream was bubbled through the stirred solution which turned bright red with some precipitate formation. Work up consisted of ether extraction, drying ($MgSO_4$), and evaporation of the ether, to give 5 which was crystallized from hexane as red needles in $\sim$70% yield; mp: 65-66°C; nmr ($CDCl_3$, δ rel TMS): *2.33(3H), 7.38(1H), J(allylic)* $\sim$ 1.5Hz; ir(CCl_4, cm^{-1}): 940 (C=Se); uv-vis(hexane), $\lambda(\varepsilon)$: 540(300), 420(14,800), 300(1,000), 255(6,100); m/e=244 (based on ^{80}Se).



6 7

Treatment of 5 with a 2 molar excess of trimethylphosphite in refluxing benzene for 5 hrs. gave DMDSeDTF in 60% yield as an orange-red solid after column chromatography (silica gel, hexane) and crystallization from hexane; mp: 123-125°C; nmr ($CDCl_3$, δrel. TMS); 2.00(3H), 6.37(1H); uv-vis(hexane), λ(ε):490(200), 370(2,500), 295(21,000), 240(6,200); m/e=328 (based on ^{80}Se).

NMR indicated that the coupling reaction produced both cis and trans isomers (3 and 4), as seen for the unsubstituted system.[2b] The methyl group is a doublet as expected due to allylic coupling with the vinyl proton. However, the vinyl proton appears as an apparent sextet as a result of the similar magnitude of the allylic coupling constant (∿1.5Hz) and the chemical shift difference between cis and trans vinylic protons (∿3Hz).[2b]

Reaction of equal molar amounts of cis/trans-DMDSeDTF with TCNQ in acetonitrile instantly precipated the black 1:1 charge transfer salt. This material is of interest, since it is the first example in which both electronic and steric disorder have been incorporated into the organic conductor, TTF-TCNQ.[13] The room temperature compaction conductivity for cis/trans-DMDSeDTF-TCNQ of ∿10$(ohm\text{-}cm)^{-1}$ is among the higher values reported for organic charge transfer salts.[14] The solid state properties of cis/trans-DMDSeDTF are currently being explored, and will be reported forthwith.

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5. For example, alkyl substituted derivatives of **2** (E. M. Engler, unpublished results.)
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8. Alternately, Meerweins reagent ($Et_3O^+BF_4^-$) can be employed when methyl iodide is unsuitable.
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10. The reaction works fine in anhydrous MeOH when it is desired to exclude water.
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12. For a similar conversion in the γ-pyrone ring system see: G. Traverso, *Ann. Chim.* (Rome), *47*, 3, 1244 (1957).
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14. E. M. Engler, *Chemical Technology*, in press.