Notes

An Alternate Synthesis of Tetraselenafulvalene

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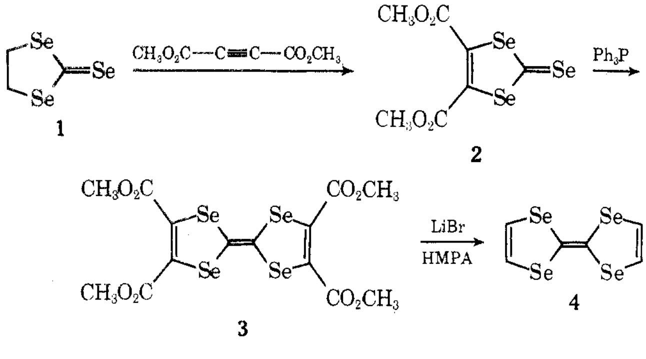
There has been much interest recently in the synthesis of tetraselenafulvalene (**4**, TSeF)[1] and its alkyl derivatives,[2] in view of the fact that these compounds are superior π donors in the preparation of highly conducting charge-transfer complexes. Only one synthesis of the parent TSeF has been reported to date.[1] We now report a convenient alternate synthesis of this compound, employing its previously unknown tetracarbomethoxy derivative **3** as an intermediate.

Ethylene triselenocarbonate (**1**)[3] reacted rapidly (10 min) with dimethyl acetylenedicarboxylate in toluene at 100°C to give (86%) deep red needles of the selone diester **2**, mp 127°C. Triphenylphosphine coupling of **2** (10 min) in refluxing benzene, gave (75%) dark brown needles of tetracarbomethoxy TSeF (**3**), mp 145°C. Direct decarbomethoxylation of ester **3** was effected by lithium bromide in hot hexamethylphosphoramide (10 min, 150°C) to give (35%) tetraselenafulvalene (**4**) as pink plates, mp 133–134°C, identical in properties (melting point, uv, mass spectrum) with the previously reported material.

Several aspects of this new synthesis are worthy of note. The first of these is the greatly accelerated rate of reaction of dimethyl acetylenedicarboxylate with triselenocarbonate **1** as compared with that of ethylene trithiocarbonate, the latter compound requiring a 6-h reaction time at 110°C.[4] The second of these is the fact that a one-step lithium halide decarbomethoxylation has been reported previously only in the case of β-keto esters.[5] The conversion of **3** to **4** by this procedure suggests that it should be applicable to the decarbomethoxylation of related sulfur-containing esters. We are currently exploring the scope of the method with such esters.



Experimental Section

Melting points were determined using a Thomas-Hoover apparatus and are uncorrected. Ultraviolet spectra (cyclohexane solutions) were recorded with a Perkin-Elmer Model 202 spectrometer. NMR spectra were run in $CDCl_3$ solution containing Me_4Si as internal standard, using a JEOL 100-MHz instrument. Mass spectra were obtained using a Perkin-Elmer Model 270 instrument. Molecular ions are based on ^{80}Se.

1,3-Diselenolane-2-selone (1). 1,3-Diselenolane-2-selone was prepared by the method of Henriksen.[3] Carbon diselenide (2 g) was treated with ethylene dibromide (2.2 g) in 10% aqueous dimethyl sulfoxide (120 ml) in the presence of 3 g of potassium carbonate under nitrogen to yield 1.1 g of **1**, mp 100°C (lit.[3] mp 99–101°C), mass spectrum M^+ *m/e* 280 (85%).

4,5-Dicarbomethoxy-1,3-diselenole-2-selone (2). A mixture of **1** (0.772 g) and dimethyl acetylenedicarboxylate (0.4 ml) in toluene (3 ml) was heated on the steam bath for 10 min. Removal of solvent followed by crystallization of the residue from methanol afforded **2** (0.93 g, 86%): mp 127–128°C; mass spectrum M^+ *m/e* 394 (86%); NMR δ 3.88 s; λ_{max} (log ϵ) 217 nm (4.02), 235 (3.97), 252 sh (3.90), 405 (4.02), 562 (2.17).

Anal. Calcd for $C_7H_6O_4Se_3$: C, 21.50; H, 1.54. Found: C, 21.59; H, 1.72.

Tetracarbomethoxytetraselenafulvalene (3). To a boiling solution of **2** (0.120 g) in dry benzene (3 ml) under nitrogen was added a solution of triphenylphosphine (0.080 g) in benzene (3 ml) in portions, in the course of 10 min. The reaction mixture was concentrated and subjected to chromatography on silica, eluting with benzene. The initial colorless band yielded triphenylphosphine selenide (0.100 g) admixed with a small amount of triphenylphosphine. A pale red band led to recovery of **2** (0.009 g). The subsequent dark band upon evaporation yielded a residue (0.079 g) which was crystallized from methanol–benzene to give dark brown **3** (0.069 g, 75%): mp 144–145°C; mass spectrum M^+ 628 (100%); NMR δ 3.83 s; λ_{max} (log ϵ) 212 nm (4.16), 260 (4.39), 285 (4.43), 328 sh (3.70), 422 (4.00).

Anal. Calcd for $C_{14}H_{12}O_8Se_4$: C, 26.94; H, 1.94. Found: C, 27.36; H, 2.01.

Tetraselenafulvalene (4). A mixture of **3** (0.100 g) and lithium bromide (0.216 g) in hexamethylphosphoramide (5 ml) was heated gradually to 80°C. There was gas evolution and considerable lightening of color. When the gas evolution ceased, the temperature was raised to 155–160° for 10 min by which time TLC indicated one spot corresponding to **4**. The cooled mixture was diluted with water and extracted with cyclohexane containing 5% benzene. The orange organic extract was washed, dried (Na_2SO_4), and evaporated to yield salmon-pink plates (0.045 g), which were recrystallized from hot hexane to give pink plates (0.025 g, 35%) of TSeF (**4**), mp 134°C, identical in all respects (melting point, mass spectrum, uv spectrum, and TLC) with an authentic specimen of **4**.[1] Low-temperature crystallization of **4** sometimes affords a labile crystalline modification (pale yellow needles) which reverts to the pink form on standing at room temperature in a hexane suspension.

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Registry No.—**1**, 17107-01-4; **2**, 57653-12-0; **3**, 57653-13-1; **4**, 54489-01-9; dimethyl acetylenidicarboxylate, 762-42-5.

References and Notes

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