4,5-Ethylendithio-1-selenole-3-thiole-2-one as Starting Material for the Preparation of New Tetrachalcogenafulvalenes

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Tetrachalcogenafulvalenes, π-Donors, Organic Conductors

Starting from 3-chloro-2-oxo-1,4-dithiane the title compound was prepared and characterized analytically and spectroscopically. It was used then for the preparation of some new tetrachalcogenafulvalenes (π-donor molecules).

The title compound has been prepared in a low yield from 1,3-thiaselenole-2-thione by a five-step sequence: lithiation with lithium diisopropylamide, sulfurization with powdered sulfur, treatment with mercuric acetate, sodium borohydride, tetramethylthiourea, all Fluka, as well as some reagents, solvents and apparatus described in [1, 2, 7, 8] were used.

Preparation of 7

To a solution of 3-chloro-2-oxo-1,4-dithiane (1) (4.0 g, 24.2 mmol) and tetramethylthiourea (2) (3.2 g, 24.2 mmol) in ethanol (35 ml), HClO₄ 70% (5 ml) was added with stirring. The stirring was continued for 3 h and the resulting mixture was cooled to 0 °C. The resulting yellowish precipitate was filtered, washed with a small volume of cooled ethanol and air dried to give 6.0 g (67.5%) of 3. A suspension of 3 (6.0 g, 16.5 mmol) in water (150 ml) was kept under argon and treated with a fourfold excess of H₂Se with stirring. The stirring was continued for 2 h. The excess of H₂Se was removed by a stream of argon and the precipitate was filtered, washed with water and air dried to give 3.5 g (71%) of 4. It is a redish crystalline solid, m.p. = 123–125 °C. Compound 4 (3.5 g, 11.7 mmol) was added in small portions to conc. H₂SO₄ (25 ml) at 0 °C with stirring. The resulting

Also, we report analytical and spectroscopic data of 7 as well as the preparation and characterization of some tetrachalcogenafulvalenes (8, 11, 13, 16) based on 7. The latter compounds were prepared by reactions outlined in Scheme 2.

Experimental

Reagents, solvents and apparatus

Chloroacetyl chloride, 1,2-ethanediethiol, N-chlorosuccinimide, selenium powder, mercuric acetate, sodium borohydride, tetramethylthiourea, vinylenethiocarbonate, all Fluka, as well as some reagents, solvents and apparatus described in [1, 2, 7, 8] were used.

Scheme 2
mixture was warmed to ambient temperature and stirred for 2 h. EtOAc (~500 ml) was added cautiously to cause precipitation of the hydrosulfate. The solution was then filtered into a mixture of HClO₄ 70% (12 ml) and ethanol (200 ml), and ether (11) was added. The resulting white precipitate was filtered, washed with ether and dried in air to give 3.1 g (68.5%) of 5. Compound 5 (3.1 g, 8.1 mmol) was dissolved in a mixture of methanol (175 ml) and water (75 ml) and cooled to −5 °C. The solution was kept under argon and treated with a sixfold excess of H₂Se, with stirring [9]. An orange-red solid was slowly formed and the mixture was allowed to warm to 0 °C over 1 h and then at room temperature over 2 h. The excess of H₂Se was removed by a stream of argon and then water (100 ml) was added. The precipitate was filtered, washed with water and dried in air. The red solid was extracted with CH₂Cl₂ and chromatographed on silica gel column to give 1.0 g (37.5%) of 6. This is a red crystalline solid, m. p. = 142 °C. To a solution of 6 (1.0 g, 3.1 mmol) in a mixture of CH₂Cl₂ (400 ml) and CH₃COOH (250 ml), Hg(CH₂COO)₂ (2.5 g) was added and the mixture was stirred for 10 min at room temperature. The resulting white mixture was filtered, the filtrate was washed with water, and the organic layer was dried over MgSO₄. A yellowish solid was obtained after evaporation of the solvent. It was recrystallized from methanol to give 6 (0.6 g, 76%) as a white crystalline solid, m. p. = 110 °C; UV (CH₂CN): 209, 220 (sh), 281 nm; IR (KBr): 1635–1619 cm⁻¹ (C=O); ¹H-NMR (CDCl₃–CS₂): δ = 3.4 ppm; MS: m/z = 256 (strongest M⁺, 80%Se).

C₇H₅OS₂Se (255)
Calcd C 23.53 H 1.57 S 37.65.
Found C 23.43 H 1.62 S 37.52.

Preparation of 8 (cis- and/or trans-form)
A solution of 7 (50 mg) in triethyl phosphate (2 ml) was heated to ~150 °C for 30 min with stirring under argon. The precipitate was filtered, washed with acetone and dried in air to give 8 as a brown crystalline solid (m. p. = 250 °C) in a yield of 5 mg (5.2%); UV/visible (CH₂CN): 217 (vs), 310 (s), 336 (sh), 440 (br).

C₁₀H₆SeS₂ (478)
Calcd C 25.10 H 1.67 S 40.18.
Found C 25.45 H 1.78 S 40.15.

Preparation of 11
A solution of 7 (200 mg, 0.78 mmol) and 9 (200 mg, 1.49 mmol) in triethyl phosphate (5 ml) was heated to ~150 °C for 3.5 h with stirring under argon. The resulting mixture was concentrated to dryness, extracted with CS₂ and chromatographed on a silica gel column using CS₂ as eluent. The second fraction was concentrated to give 11 in a yield of 12 mg (4.5% based on 7). It is an orange crystalline solid, m. p. = 195 °C; UV (CH₃CN): 218 (sh), 298 (s), 330 (sh), 360 (sh).

C₈H₇S₅Se (341)
Calcd C 28.08 H 1.76 S 46.92.

Preparation of 13
It was prepared by the same method as 11 except that 12 [1] was used instead of 9. Compound 13 was obtained in a yield of 4.5%. It is a red crystalline solid, m. p. = 196 °C; UV/visible (CH₃CN): 260 (sh), 313 (s), 480 (br).

C₁₀H₆O₂S₃Se (399)
Calcd C 30.08 H 2.01 S 40.10.
Found C 30.15 H 1.96 S 40.00.

Preparation of 16
It was prepared by the same method as 11, except that 15 [8] was used instead of 9, and CH₂Cl₂ instead of CS₂. Compound 16 was obtained as an orange-red crystalline solid, in a yield of 8.1%, m. p. = 233 °C; UV (CH₃CN): 213 (s), 224 (sh), 292 (s), 384 (br).

C₁₀H₆N₂S₃Se (487)
Calcd C 24.64 H 1.23 N 5.75 S 19.71.

Results and Discussion
Starting from 3-chloro-2-oxo-1,4-dithiane (1), 4,5-ethylenedithio-1-selenole-3-thiole-2-one (7) was prepared by a five-step sequence in a 10% overall yield. This compound is a precursor for the preparation of new tetrachalcogenafulvalenes (for example 8, 11, 13, 16) which are π-donor molecules. It was found that these donors give a number of conducting cation radical salts by chemical or electrochemical procedures. Electrocrystallization of 8, for example, in the presence of CuSCN and KSCN, in 1,1,2-trichloroethane containing 18-crown-6, gave black conducting crystals.

However, details on the physical properties as well as on the crystal structures of new materials, especially those related to cis- and/or trans-form of 8 will be reported elsewhere. Results similar to those obtained from 4,5-ethylenedithio-1,3-dithiole-2-one are expected, because the substitution of one or two sulfur atoms in the tetrathiafulvalene core by selenium atoms, in some cases, does not affect the properties of the resulting tetrachalcogenafulvalenes and their conducting salts [10].
[9] A mixture of CH₃COOH and NaHSe can be used instead of H₂Se: see D. L. Klayman and T. S. Griffin, J. Am. Chem. Soc. 95, 197 (1973) and ref. [6] herein.