NOTIZEN

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

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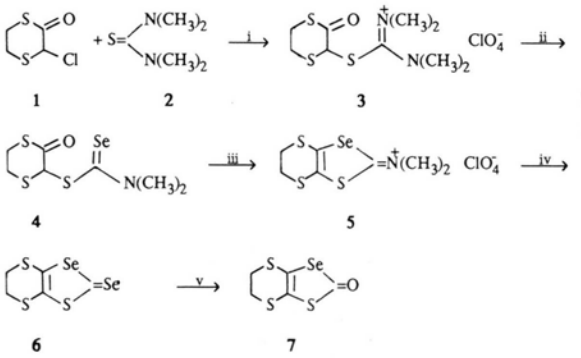
Z. Naturforsch. **47b**, 898–900 (1992); received December 20, 1991

Tetrachalogenafulvalenes, 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).

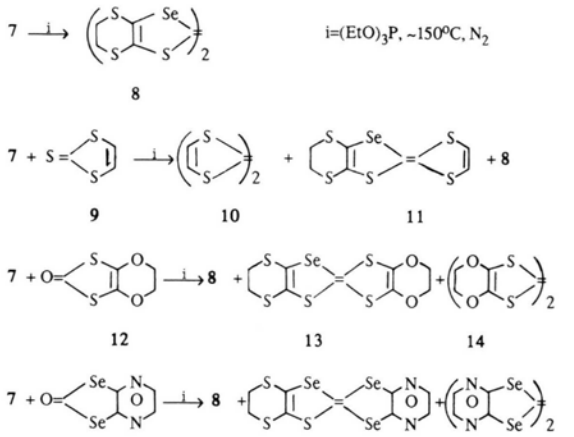
The title compound has been prepared in a low yield from 1,3-thiaselenole-2-thione by a five-step sequence: lithiation with lithium diisopropylamide, sulfurization with powdered sulfur, treatment with zinc chloride in the presence of tetrabutylammonium bromide, treatment with 1,2-dibromoethane, and finally, after chromatographic separation, treatment with mercuric acetate [1, 2]. In this paper we report the preparation of the title compound (**7**) from 3-chloro-2-oxo-1,4-dithiane (**1**) [3] by a five-step sequence [1, 4–6] according to Scheme 1.



i=$HClO_4$ in C_2H_5OH; ii=H_2Se in H_2O; iii=1) H_2SO_4, 2)$HClO_4$; iv=H_2Se in MeOH + H_2O; v=$Hg(OAc)_2$ in $CH_3COOH+CH_2Cl_2$

Scheme 1

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.



i=$(EtO)_3P$, ~150°C, N_2

Scheme 2

Experimental

Reagents, solvents and apparatus

Chloroacetyl chloride, 1,2-ethanedithiol, N-chlorosuccinimide, selenium powder, mercuric acetate, sodium borohydride, tetramethylthiourea, vinylenetrithiocarbonate, 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), $HClO_4$ 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 H_2Se with stirring. The stirring was continued for 2 h. The excess of H_2Se 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. H_2SO_4 (25 ml) at 0 °C with stirring. The resulting

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0932–0776/92/0600–0898/$ 01.00/0

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 $HClO_4$ 70% (12 ml) and ethanol (200 ml), and ether (1 l) 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 H_2Se, 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 H_2Se 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 CH_2Cl_2 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 CH_2Cl_2 (400 ml) and CH_3COOH (250 ml), $Hg(CH_3COO)_2$ (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 $MgSO_4$. 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 (CH_3CN): 209, 220 (sh), 281 nm; IR (KBr): 1635−1619 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3-CS_2$): δ = 3.4 ppm; MS: m/z = 256 (strongest M^+, ^{80}Se).

$C_5H_4OS_3Se$ (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 phosphite (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 (CH_3CN): 217 (vs), 310 (s), 336 (sh), 440 (br).

$C_{10}H_8S_6Se_2$ (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 phosphite (5 ml) was heated to ~150 °C for 3.5 h with stirring under argon. The resulting mixture was concentrated to dryness, extracted with CS_2 and chromatographed on a silica gel column using CS_2 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 (CH_3CN): 218 (sh), 298 (s), 330 (sh), 360 (sh).

$C_8H_6S_5Se$ (341)

Calcd	C 28.08	H 1.76	S 46.92,
Found	C 28.25	H 1.78	S 46.71.

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 (CH_3CN): 260 (sh), 313 (s), 480 (br).

$C_{10}H_8O_2S_5Se$ (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 CH_2Cl_2 instead of CS_2. Compound **16** was obtained as an orange-red crystalline solid, in a yield of 8.1%, m.p. = 233 °C; UV (CH_3CN): 213 (s), 224 (sh), 292 (s), 384 (br).

$C_{10}H_6N_2S_3Se_3$ (487)

Calcd	C 24.64	H 1.23	N 5.75	S 19.71,
Found	C 24.57	H 1.26	N 5.66	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].

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