Effective Synthesis of 1,3-Diselenole-2-selone-4,5-diselenolate (dsis) and its Utilization for the Synthesis of Selenocycle-fused Tetraselenafulvalene (TSF) Derivatives

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Abstract: A facile and effective synthetic procedure for 1,3-diselenole-2-selone-4,5-diselenolate (dsis, 2) has been established. The utilization of 2 for the synthesis of selenocycle-fused tetraselenafulvalene derivatives is also reported.

Key words: lithiation, diselenolate ligands, protecting groups, ring-closure reaction, selenium-containing heterocycles

In the field of organic conductors, 1,3-dithiole-2-thione-4,5-dithiolate (dmit, 1) is a very important compound both as a key intermediate for the synthesis of thio-substituted tetrathiafulvalene (TTF)-type electron donors and as a ligand for metal complexes of M(dmit)₂ type.¹ Indeed, a great number of organic conductors and superconductors have been produced from the TTF-type donors and the M(dmit)₂ metal complexes.² In such organic conductors and superconductors, intermolecular interactions through sulfur atoms play an important role in the electrical conduction in the solid state. Because the more spatially extended p- and d-orbitals of the selenium atom, compared to those of sulfur atom, lead to more effective intermolecular interactions, the selenium counterpart of 1, 1,3-diselenole-2-selone-4,5-diselenolate (2, dsis), is very interesting.

Although the formation of 2 was first reported in 1976, its chemistry has only been sporadically described in the literature. In the early papers, 2 was synthesized by electro-



Figure 1

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chemical reduction of carbon diselenide (CSe₂),³ and later on, by chemical reduction of CSe₂ with an alkaline metal.⁴ These syntheses are analogous to that of **1** which is usually isolated as the complex of Zn(dmit)₂ type.⁵ In contrast to Zn(dmit)₂, which is now easily synthesized on a large scale of 90 g by chemical reduction of cheap CS₂ with sodium metal,⁶ the analogous synthesis of Zn(dsis)₂ is less effective with a reported yield of ~15%.⁴ In addition, the formation of one mole of **2** requires four moles of CSe₂, and is accompanied with an equimolar amount of byproduct CSe₃²⁻ (**3**), which makes purification of **2** difficult (Scheme 1).



Scheme 1 Suggested reaction path for 2 via reduction of CSe₂

During the course of our synthetic study on selenium containing electron donors, we have established a facile and practical synthetic procedure for $Zn(dsis)_2$. In this paper we would like to describe the synthetic detail of $Zn(dsis)_2$ and its utilization as a key intermediate for the synthesis of selenocycle-fused tetraselenafulvalene (TSF) type electron donors through deprotection/realkylation sequence of protected TSF selenolate intermediates.

Our synthetic procedure for dsis 2 consists of lithiation of 1,3-diselenole-2-selone (4), readily available on a multigram scale,⁷ followed by introduction of selenium atoms. Thus, to a THF solution of 4 was added freshly prepared LDA solution at -78 °C, and then selenium powder was added to the resulting solution. After usual work up with tetrabutylammonium bromide and zinc chloride, 2 was isolated as Zn(dsis)₂·(*n*-Bu₄N)₂ (5) in 82% isolated yield



Scheme 2 Reagents and conditions: i) n-BuLi, Se, CSe₂; ii) LDA, Se; iii) n-Bu₄NBr, ZnCl₂; iv) Br(CH₂)₂CO₂Me; v) P(OMe)₃; vi) P(OMe)₃, 4

(Scheme 2). This method is more advantageous than the previous synthesis of **2** based on the reduction of CSe_2 in terms of isolated yield and reproducibility even on a relatively large scale (7–8 g of **5** can be synthesized in one batch). An additional advantage is that, in contrast to the use of four equivalents of CSe_2 for the previous methods, only one equivalent CSe_2 is required here since the starting material **4** is prepared in a quantitative yield from equimolar reaction of both selenium powder and CSe_2 to lithium trimethylsilylacetylide.⁷

Alkylation of the zincate (5) with methyl 3-bromopropionate gave selone 6 (82% yield), which was then effectively converted into the symmetrical TSF derivative, 2,3,6,7-tetrakis[(2-methoxycarbonyl)ethylseleno]-TSF (7) in 74% yield (Scheme 2). Compound 7 is a stable crystalline solid and was fully characterized not only by spectroscopic analyses but also by X-ray crystallographic analysis.

As shown in Figure 2, the central C_6Se_8 moiety of 7 is essentially planar, and the alkyl substituents stand perpendicular to the central C_6Se_8 plane. Owing to thermal motion, the ellipsoids of the alkyl moieties are relatively larger than those of the core.

Selone **6** is also amenable to a cross-coupling reaction; when **6** was reacted with three-fold excess of **4**, the corresponding unsymmetrical TSF (**8**) was obtained in 48% isolated yield based on **6** (Scheme 2).

These TSF derivatives with (2-methoxycarbonyl)ethylseleno groups (7 and 8) were then utilized for the synthesis of selenocycle-fused TSF derivatives. Treatment of 7 or 8 with caesium hydroxide monohydrate in DMF⁸ generated reactive TSF selenolate intermediates in situ, which were readily alkylated with diiodomethane or 1,2-dibromoethane to give selenocycle-fused TSF derivatives (9–12) in good yields (Scheme 3). Thus, 7 and 8 can be regarded as excellent synthons of the corresponding TSF bis- or tetraselenolate, similarly to the protected TTF thiolates such as tetrakis[(2-cyanoethyl)thio]-TTF.⁸

Since the direct phosphite-mediated coupling of 1,3-diselenole-2-selones having a heterocyclic ring such as **13** and **14** does not proceed smoothly to give the corresponding TSF derivatives,⁹ the present reaction protocol provides a practical synthetic method for such less accessible heterocycle-fused TSF-type electron donors.

In summary, we have established a practical and reliable synthetic method of $Zn(dsis)_2 \cdot (n-Bu_4N)_2$ (5), and also de-



Figure 2 Molecular structure of 7 (stereo view)



Scheme 3 Reagents and conditions: i) CsOH·H₂O; ii) CH₂I₂ or Br(CH₂)₂Br





veloped its utilization as a versatile synthetic intermediate for selenocycle-fused TSF type electron donors. We strongly hope that this method and thereby synthesized new TSF derivatives (9–11) would contribute to the development of superior organic conductors.

All chemicals and solvents were of reagent grade unless otherwise indicated. All reactions were carried out under a N2 atm. THF was purified by distillation from sodium benzophenone ketyl under N2 prior to use. MeOH was distilled from Mg under a N2 atm. Toluene was dried over CaH2 and distilled under a N2 atm. Dry DMF (H2O < 50 ppm) was purchased from Nacalai tesque and used without purification. Column chromatography was carried out with silica gel (Daisogel IR-60, 63-210 µm). Mps are uncorrected. IR spectra were obtained on a Shimadzu FTIR-8100A spectrometer. ¹H and ¹³C NMR spectra were obtained in CDCl₃ on a JEOL Lambda 400 spectrometer operating at 400 MHz (¹H) and 100 MHz (¹³C) with TMS as internal reference; δ are reported in ppm. EI-MS spectra were obtained on a Shimadzu QP-2000 spectrometer using an electron impact ionization procedure (70 eV). FAB-MS spectra were recorded on a JEOL JMS-SX 102A spectrometer using 3-NBA as matrix. The molecular ion peaks of the selenium-containing compounds showed a typical selenium isotopic pattern, and all the seleniumcontaining mass peaks are reported for ⁸⁰Se. Elemental analyses were performed by Mr. Hideaki Iwatani, Microanalytical Laboratory at the Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. Cyclic voltammetry (CV) was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator using benzonitrile as solvent, and containing tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆; 0.1 M) as supporting electrolyte with a sweep rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. The midpoint of a reversible redox wave was determined as a half-wave oxidation potential (E_{1/2}). 1,3-Diselenole-2-selone (**4**) was synthesized according to the reported procedures.⁷

Tetrabutylammonium 4,5-Bis(2-selenoxo-1,3-diselenole-4,5-diselenolate)zincate (5)

To a solution of 1,3-diselenole-2-selone (4, 3.3 g, 12 mmol) in anhyd THF (90 mL) was slowly added a freshly prepared solution of lithium diisopropylamide in THF-hexane (43 mL, 0.55 M, 24 mmol) at -90 °C, and the resulting solution was stirred for 1 h at the same temperature. Selenium powder (1.9 g, 24 mmol) was added in one portion to the solution, and the mixture was allowed to warm to approx. -30 °C over 1.5 h, and kept at the same temperature for 1 h. At this stage, the mixture turned deep blue. Then a solution of tetrabutylammonium bromide (3.87 g, 12 mmol) in anhyd MeOH (15 mL) and anhyd ZnCl₂ (90%, 0.91 g, 6.0 mmol) in anhyd MeOH (15 mL) were successively added, and the mixture was stirred for 1 h at r.t. The solvent was evaporated in vacuo below 40 °C, and the resulting residue was carefully washed with H₂O and MeOH to give a crude solid of 5, which was then dissolved in acetone (200 mL), and the insoluble solid was filtered off. The filtrate was concentrated to give practically pure 5 as reddish purple microcrystals (6.97 g, 82%). An analytically pure sample was obtained by recrystallization from acetone-MeOH (1:10, v/v); mp 172-173 °C.

IR (KBr): v = 891 (C=Se) cm⁻¹.

Anal. Calcd for $C_{38}H_{72}N_2Se_{10}Zn$ (1412.0): C, 32.32; H, 5.14; N, 1.98. Found: C, 32.07; H, 5.16; N, 1.86.

4,5-Bis[(2-methoxycarbonyl)ethylseleno]-1,3-diselenole-2-selone (6)

A mixture of zincate **5** (1.0 g, 0.71 mmol) and methyl 3-bromopropionate (0.39 mL, 3.6 mmol) in MeCN (10 mL) was refluxed for 1 h. The solvent was evaporated, and the residual solid was extracted with CH_2Cl_2 (3 × 100 mL), which was then washed with H_2O (3 × 100 mL) and sat. NaCl (3 × 100 mL), dried (MgSO₄), and concentrated. The crude product was purified with column chromatography on silica gel (CH_2Cl_2) ($R_f = 0.3$) to give pure **6** as red oil (0.71 g, 82%), which solidified in a freezer at -20 °C.

IR (neat): v = 1732 (C=O), 1163 (C-O), 903 (C=Se) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.87 (t, 4 H, *J* = 7.1 Hz), 3.16 (t, 4 H, *J* = 7.1 Hz), 3.73 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 25.55, 35.00, 52.04, 135.91, 171.81, 211.42.

MS (EI): m/z = 610 (M⁺) with an isotopic pattern containing five Se atoms.

Anal. Calcd for $C_{11}H_{14}O_4Se_5$ (609.7): C, 21.84; H, 2.33. Found: C, 21.87; H, 2.34.

2,3,6,7-Tetrakis[(2-methoxycarbonyl)ethylseleno]tetraselenafulvalene (7)

A solution of **6** (0.53 g, 0.88 mmol) in anhyd toluene (15 mL) was refluxed for 1 h. Then trimethyl phosphite (0.6 mL) was added to the solution, and the resulting mixture was further refluxed for 5 h. The reaction mixture was concentrated, and the resulting residue was subjected to column chromatography on silica gel. A fraction containing **7** was eluted with CH₂Cl₂–EtOAc (5:1) (R_f = 0.6) and gave red crystals of pure **7** (0.34 g, 74%) upon concentration. Re-

crystallization from CHCl₃-hexane (1:1, v/v) gave red needles suitable for X-ray analysis; mp 108 °C.

IR (KBr): v = 1732 (C=O), 1169 (C-O) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 2.84$ (t, 8 H, J = 7.2 Hz), 3.10 (t, 8 H, J = 7.2 Hz), 3.72 (s, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ = 24.92, 35.09, 51.82, 110.34, 121.51, 172.00.

MS (FAB): m/z = 1060 (M⁺) with an isotopic pattern containing 8 Se atoms.

Anal. Calcd for $C_{22}H_{28}O_8Se_8$ (1052.1): C, 25.11; H, 2.68. Found: C, 24.92; H, 2.51.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.64 \text{ V}, +0.95 \text{ V}.$

2,3-Bis[(2-methoxycarbonyl)ethylseleno]-tetraselenafulvalene (8)

A mixture of **6** (2.2 g, 3.7 mmol), 1,3-diselenole-2-selone (**4**, 3.0 g, 11.0 mmol) in anhyd toluene (75 mL) was refluxed for 1 h. Then trimethyl phosphite (5.2 mL) was added, and the resulting mixture was refluxed for 3 h. The reaction mixture was concentrated in vacuo, and the resulting residue containing **8** and two homo-coupling products was subjected to column chromatography on silica gel. The first fraction eluted with CH_2Cl_2 was TSF ($R_f = 0.9, 2.14$ g, 80% based on **4**), and the second red band eluted with CH_2Cl_2 ($R_f = 0.5$) gave **8** (1.3 g, 48%) as a red solid upon concentration in vacuo. Recrystallization from $CHCl_3$ -hexane (1:1, v/v) gave analytically pure **8** as orange needles; mp 78 °C. From the third fraction ($R_f = 0.1, CH_2Cl_2$), **7** (0.69 g, 36% based on **6**) was obtained.

IR (KBr): v = 1732 (C=O), 1182 (C-O) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.84 (t, 4 H, *J* = 7.2 Hz), 3.10 (t, 4 H, *J* = 7.2 Hz), 3.71 (s, 6 H), 7.25 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 24.90, 35.16, 51.87, 106.92, 110.58, 121.68, 122.67, 172.10.

MS (EI): m/z = 728 (M⁺) with an isotopic pattern containing 6 Se atoms.

Anal. Calcd for $C_{14}H_{16}O_4Se_6$ (722.0): C, 23.29; H, 2.23. Found: C, 23.31; H, 2.23.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.56$ V, +0.90 V.

Deprotection, Realkylation of 7 and 8

Bis(methylenediseleno)tetraselenafulvalene (9)

To a degassed dry DMF solution (15 mL) of **7** (0.24 g, 0.23 mmol) was added CsOH·H₂O (0.17 g, 1.0 mmol) in MeOH (15 mL) over 10 min with stirring at r.t. After stirring further for 1 h, diiodomethane (37 μ L, 0.46 mmol) in anhyd DMF (10 mL) was slowly added, and the mixture was stirred for an additional 20 h. To the mixture was added H₂O (50 mL), and the resulting brown precipitate was collected by filtration, washed with H₂O, and dried. The solid was then washed successively with hexane and acetone until the washings became clear. Recrystallization from carbon disulfide–hexane (10:1, v/v) gave brown fine needles of **9** (26 mg, 94%); mp 240 °C (dec.).

IR (KBr): v = 2980, 1510 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 4.86$ (s, 4 H).

MS (EI): m/z = 740 (M⁺) with an isotopic pattern containing 8 Se atoms.

Anal. Calcd for $C_8H_4Se_8$ (731.8): C, 13.13; H, 0.55. Found: C, 13.39; H, 0.57.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.59$ V, +0.84 V.

Bis(ethylenediseleno)tetraselenafulvalene (10)

Compound **10** was synthesized as for **9** using 1,2-dibromoethane (86 μ L, 0.91 mmol) in 93% yield. Brown fine needles from carbon disulfide–hexane (10:1, v/v); mp 250 °C (dec.), [Lit.⁹ mp 235–240 °C (dec.)]. Since the reported mp was slightly lower than the present one, a full characterization of **10** including microanalysis was carried out.

IR (KBr): v = 2960, 1509, 1410, 1260 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 3.36$ (s, 8 H).

MS (EI): m/z = 768 (M⁺) with an isotopic pattern containing 8 Se atoms.

Anal. Calcd for $C_{10}H_8Se_8$ (759.9): C, 15.81; H, 1.06. Found: C, 15.65; H, 0.79.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.62$ V, +0.92 V.

Methylenediselenotetraselenafulvalene (11)

To a degassed dry DMF solution (23 mL) of **8** (0.8 g, 1.1 mmol) was added CsOH·H₂O (0.41 g, 2.42 mmol) in MeOH (23 mL) over 5 min with stirring at r.t. After stirring further for 1 h, diiodomethane (89 µL, 1.1 mmol) in DMF (23 mL) was slowly added, and the mixture was stirred for an additional hour. To the mixture was added H₂O (100 mL), and the resulting brown precipitate was collected by filtration, washed with H₂O, and dried. The crude solid was then dissolved in carbon disulfide (200 mL), and the solution was washed with H₂O (3 × 100 mL) and sat. NaCl (100 mL), dried (MgSO₄), and concentrated. Column chromatography of the residue on silica gel (carbon disulfide) gave **11** (R_f = 0.6, 0.47 g, 90%) as red crystals. An analytical sample was obtained by recrystallization from chlorobenzene as red plates; mp 192–194 °C (dec.).

IR (KBr): $v = 3030, 2990, 1541, 718, 634, 625 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): δ = 4.84 (s, 2 H), 7.18 (s, 2 H).

MS (EI): m/z = 568 (M⁺) with an isotopic pattern containing 6 Se atoms.

Anal. Calcd for $C_7H_4Se_6$ (561.9): C, 14.96; H, 0.72. Found: C, 14.90; H, 0.71.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.51$ V, +0.81 V.

Ethylenediselenotetraselenafulvalene (12)

Compound **12** was synthesized as for **11** using 1,2-dibromoethane (190 μ L, 2.19 mmol) in 64% yield. Red needles from carbon disulfide–hexane (1:1, v/v); mp 182–184 °C (dec.).

IR (KBr): $v = 3030, 3010, 2970, 1540, 1510, 1260, 712, 630 \text{ cm}^{-1}$.

¹H NMR (400 MHz, CDCl₃): δ = 3.36 (s, 4 H), 7.19 (s, 2 H).

MS (EI): m/z = 582 (M⁺) with an isotopic pattern containing 6 Se atoms.

Anal. Calcd for $C_8H_6Se_6$ (575.9): C, 16.69; H, 1.05. Found: C, 16.66; H, 1.20.

CV (benzonitrile, versus Ag/AgCl): $E_{1/2} = +0.55$ V, +0.88 V.

Crystallographic Structure Analysis of 7

X-ray crystal structure analysis was made on a Rigaku AFC7R fourcircle diffractometer (MoK α radiation, $\lambda = 0.71069$ Å, graphite monochromator, T = 296 K, $\omega - 2\theta$ scan, $2\theta_{max} = 55.0^{\circ}$). The structure was solved with Patterson methods and refined by full-matrix leastsquares on |F|. All calculations were performed using the crystallographic software package teXsan (Molecular Structure Corporation, 1985 & 1992).

Crystal data for 7: $C_{20}H_{28}O_8Se_8$, $M_r = 1052.14$, Crystal size $0.50 \times 0.10 \times 0.05$ mm, triclinic, a = 8.260(3) Å, b = 19.045(7) Å, c = 5.441(3) Å, $\alpha = 97.93(4)^\circ$, $\beta = 104.32(3)^\circ$, $\gamma = 95.33(3)^\circ$, V = 814.1(6) Å³, space group *P*-1 (no. 2), Z = 1, $\rho_{calcd} = 2.146$ g cm⁻³,

F(000) = 496.00, $\mu = 90.19$ cm⁻¹, R1 = 0.044, wR2 = 0.033, 4002 measured reflections, 2302 observed reflections [I>3.0 σ (I)], 193 refined parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161839. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; email: deposit@chemcrys.cam.ac.uk).

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