A novel approach to a substituted 1,3-selenazole core as a precursor of electron rich olefins: diselenadiazafulvalene and azino-diselenadiazafulvalene†

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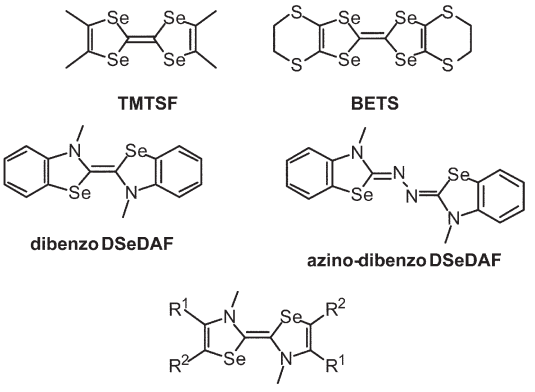
The first approach for the synthesis of 2-alkylthio-4,5-disubstituted-1,3-selenazole cores *via* metallation of dimethyl *N*-(ethoxycarbonylmethyl)iminodithiocarbonate (EMIC) and subsequent reaction with selenothioic acid *S*-ester is described. These selenazoles are easily converted into electron rich olefins such as diselenadiazafulvalenes (DSeDAF) and azino-DSeDAF. Electrochemical investigation demonstrates the excellent reversible donor ability of these novel olefins.

Introduction

Organoselenium compounds have been a matter of considerable interest over the last three decades due to their unique chemical properties and versatility as synthetic reagents in modern organic synthesis.[1] In addition to these applications, organoselenium compounds play important roles in biological systems[2] and molecular-based materials.[3] On the one hand, selenium-containing heterocycles attracted considerable attention, because of their pharmaceutical significance.[4] In particular, Se-N heterocycles have been shown to mimic the activity of glutathione peroxidase (GPx), a key enzyme in the antioxidant defense system, *in vitro*.[5] On the other hand, the first molecular-based superconductor discovered in 1980 was prepared from a tetramethyltetraselenafulvalene (TMTSF) π-donor.[6] Since then, selenium containing fulvalene π-donors have continued to attract interest, and in recent years unique salts were obtained from bis(ethylenedithio)tetraselenafulvalene (BETS) with an interplay of conductivity and magnetism.[7] Quite recently, we reported the first approach to dibenzodiselenadiazafulvalenes (DSeDAF), a novel family of π-donor molecules containing selenium and nitrogen atoms within the fulvalene framework.[8] We developed a synthetic method for benzo-fused DSeDAF donors *via* alkylation of the benzoselenazole-2-thione core. These aza analogues of TSF exhibit excellent electron-donating ability and were found, in consequence, to be oxygen-sensitive in the neutral form.[8a] The next step of development in the area of DSeDAF donors could be anticipated by the modulation of the redox properties of these donors. In this context, two types of modifications can be considered: (i) fused benzo substituents in existing DSeDAFs can be replaced with various groups in the 4,4′ and 5,5′ positions of the DSeDAF framework, (ii) introduction of a conjugated spacer group between the two heterocyclic moieties. Indeed, the latter type of modification such as the introduction of an azino spacer group, first developed by Hünig in the diselenadiazafulvalene series, led to azino-dibenzoDSeDAF which can be easily handled under atmospheric conditions.[9] For this purpose, precursors of DSeDAF, such as nonbenzoannelated 2-alkylthio-1,3-selenazoles, should be prepared. However, the modified Hantzsch method first described by Hofmann[10] more than a century ago, which remained the main approach to the 1,3-selenazole core, as well as some newer methods[11] developed recently did not allow the formation of 2-alkylthio-1,3-selenazoles. Herein, we report the first approach to the 2-alkylthio-4,5-disubstituted-1,3-selenazole ring system and its application to the synthesis of electron rich olefins such as DSeDAF and azino-DSeDAF.



Results and discussion

The approach we chose for the synthesis of the 2-alkylthio-1,3-selenazole skeleton involves the use of dimethyl *N*-(ethoxycarbonylmethyl)iminodithiocarbonate (EMIC) **1**,[12–13] which proved to be a versatile reagent for the formation of β-lactam,[14] 1,3-thiazole,[15] 1,3-oxazole,[16] and pyrimidine[13] heterocyclic systems. It is known that **1** can undergo metallation to afford the corresponding carbanion, which can transfer a C–N=C unit to unsaturated electrophiles like C=X groups (X=O, S) and form heterocyclic systems.[12,15,16] Therefore, we considered the reactivity of metallated **1** towards the selenocarbonyl group in view of the 1,3-selenazole ring formation. Recently, Murai *et al.* reported an extensive study on the

† Electronic supplementary information (ESI) available: cyclic voltammograms of DSeDAF **10** and azino-DSeDAF **12**. See http://www.rsc.org/suppdata/nj/b3/b302942p/

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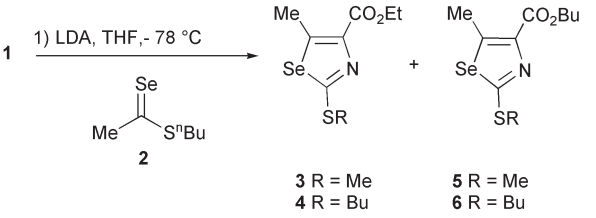
synthesis of selenothioic acid *S*-esters [RC(Se)SR′] and found that aliphatic esters were stable enough to be handled in air.[17] Thus, aliphatic selenothioic acid *S*-esters would be interesting selenium-containing synthons, which could react with metallated **1** to afford the 2-alkylthio-1,3-selenazole core. For our use, we choose ethaneselenothioic acid *S*-butyl ester **2** from Murai's series as the most interesting derivative, since it was prepared in the highest yield.

Our first attempt was realized with a *t*-BuOK–THF system for the deprotonation of **1**. The addition of **1** to a solution of 2.2 equiv. of *t*-BuOK at −78 °C was followed by a dropwise addition of **2** at the same temperature (Scheme 1). We succeeded in isolating selenazoles **3** (15%) and **4** (8%) after hydrolysis of the medium and workup of the ether extract. In addition, the starting materials **1** and **2** (10–15%) were recovered. The formation of the selenazole **3** might be explained as previously described for thiazole derivatives (Scheme 2).[15] Thus, nucleophilic attack of the carbanion derived from **1** at the C=Se group, followed by the elimination of *n*-butyl thiolate would afford intermediary adduct **A**. Subsequent deprotonation of **A**, followed by the intramolecular nucleophilic attack of conjugate base on the imine carbon with the loss of methyl thiolate would result in the selenazole ring formation, compound **3**. However, existence of selenazole **4** suggests that another reaction pathway occurs (pathway b in Scheme 2). **A** might also be attacked by previously released *n*-butyl thiolate, which would afford intermediary adduct **B**. This adduct should react similarly to **A** to afford selenazole **4** as outlined in Scheme 2.

However, the low yield of selenazoles **3** and **4** prompted us to analyze the remaining basic water phase obtained after the extraction with ether. Thus, acidification of the aqueous phase to pH = 1, followed by workup afforded, together with some unidentifiable side products, the carboxylic acid obtained from selenazole **3**, assigned on the basis of the ^{1}H NMR spectrum, which showed two singlets at δ 2.83 and 2.66 and a broad singlet at 8.81 ppm in the ratio 3 : 3 : 1. This, additionally, explains the low yield of isolated selenazoles **3**. Purification of this mixture by chromatography as well as crystallization proved to be troublesome and the pure hydrolysis product of selenazole **3** was not isolated.

Since **2** was not completely consumed when the *t*-BuOK–THF system was used for the deprotonation of **1** and the yield of selenazole was additionally lowered by hydrolysis of the C-4 ester group to produce carboxylic acid, we decided to use a stronger and sterically more hindered base. Using the LDA–THF system for the deprotonation of **1**, we were able to isolate after chromatography on silica gel selenazole **3** in 22% and **4** in 22% yield. In addition, two new, previously unobserved, products were isolated. Analysis by ^{1}H NMR, ^{13}C NMR and HRMS revealed that two new selenazoles **5** (11%) and **6** (11%) were formed in this reaction both containing a butyl chain on the 4-carboxy group instead of the ethyl one (Scheme 3). The mechanism involved in the formation of **5** and **6** is rather doubtful and has not been thoroughly elucidated. Although this reaction afforded four different 2-alkylthio substituted selenazoles, it should be pointed that they differ only in side chains attached to the C-2 and C-4 functional groups. In consequence, they can be all considered as desired, since the 2-alkylthio group is a leaving group on our pathway to DSeDAF (see below) and the C-4 ester group could be transformed to the same functionality. Noteworthy is the fact that this reaction gives approximately twice the yield of selenazoles **3** and **4** (44%) than the one using *t*-BuOK (23%) and relatively high conversion of the starting selenium-containing synthon **1** into the selenazole core (66%).

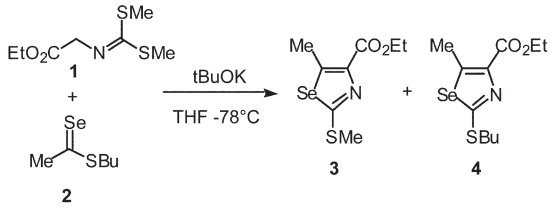


Scheme 3

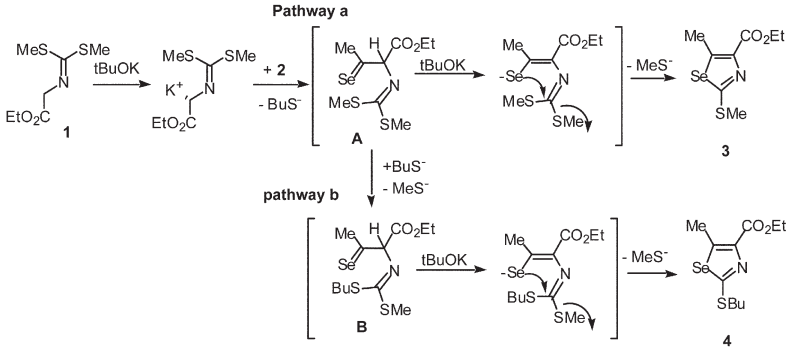
With 2-alkylthio-1,3-selenazoles **3–6** in hand, we moved to the next objective: preparation of selenazole-2-selones, which proved to be suitable precursors for the formation of benzo-fused DSeDAF donors.[8] Thus, the selenazoles **3–6** were readily alkylated on cyclic imine nitrogen using Meerwein salt to produce the corresponding 2-alkylthio-3-methyl-1,3-selenazolium salts **7** and displacement of the alkylthio group in these salts with NaHSe afforded 3-methyl-1,3-selenazole-2-selones **8** and **9**. It is interesting to note that selone **8** was isolated in a higher yield from *S*-methyl selenazole **3** (67%) than from *S*-butyl selenazole **4** (50%). Similarly, selone **9** was obtained in higher yield from *S*-methyl selenazole **5** (50%) than from *S*-butyl selenazole **6** (37%) (Scheme 4).

In order to form the fulvalene framework, coupling of selenazole-2-selone derivatives **8–9** was performed in refluxing toluene in the presence of triethyl phosphite under an inert atmosphere as shown in Scheme 5.[8]

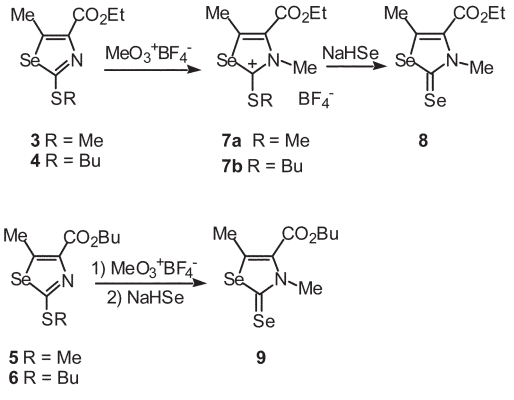
Since it was anticipated that the formed DSeDAFs would be as oxygen sensitive as the benzo-fused derivatives,



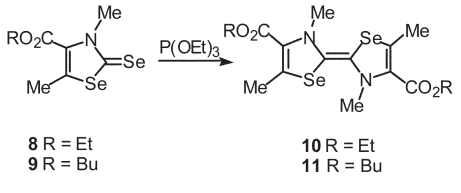
Scheme 1



Scheme 2



Scheme 4

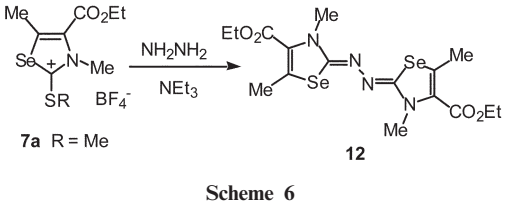


Scheme 5

investigation of their redox properties was carried out directly on the medium where the coupling was realized.[8] Therefore, the reaction mixture was transferred directly into an electrochemical cell under nitrogen containing a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. Only one reversible oxidation wave was observed at the same low potential for DSeDAF **9** and **10** ($E_{pa} = -0.11$ V *vs* SCE) associated with the redox behavior of the donor core and corresponding to the concomitant exchange of two electrons. This behavior is in sharp contrast with what was observed for dibenzo-DSeDAF where two monoelectronic oxidation waves were observed ($E^1_{pa} = -0.07$ $E^1_{pa} = 0.09$ V *vs.* SCE) associated with three distinguishable oxidation states: neutral, cation radical and dication.[8] The redox behavior of **9** and **10** could be due to an electron transfer concerted with conformational changes and, therefore, the second electron is easier to remove than the first one.[18] Indeed, it has been observed with N,N′-dimethyl-DTDAFs, the sulfur analogues of N,N′-dimethyl-DSeDAF, that upon oxidation a marked twist between the thiazole rings occurs.[19] The redox behavior observed here could be influenced by the presence of the electron-withdrawing ester group close to the cyclic nitrogen atom.

Finally, we also investigated the synthesis of the conjugated donor where an azino spacer group is introduced between the two selenazole cores. This was accomplished using thiazolium salt **7a** as the starting material according to the procedure described by Hünig *et al.* for the benzo analogue.[9] In basic medium **7a** reacts with half an equivalent of hydrazine monohydrate to afford diethyl hydrazine-1,2-diylidenebis(3,5-dimethyl-2,3-dihydro-1,3-selenazole-4-carboxylate) **12** in 34% yield (Scheme 6).

The redox properties of this novel azino-DSeDAF were analyzed by cyclic voltammetry. Two reversible monoelectronic oxidation waves are observed. The data collected in Table 1



Scheme 6

Table 1 Oxidation potentials (V) *vs.* SCE, Pt working electrode with n-$Bu_4NPF_6$1 M in (a) CH_2Cl_2 (b) CH_3CN, scanning rate 0.1 V/s

	E^1_{pa}	E^2_{pa}	ΔE/mV
Dibenzo-DSeDAF[8a]	−0.07	0.09	160
10[a]	−0.11	−0.11	
11[a]	−0.11	−0.11	
Azino–dibenzoDSeDAF[20b]	0.61	1.10	490
12[b]	0.44	0.93	490

[a] CH_2Cl_2. [b] CH_3CN, scanning rate 0.1 V s^{-1}.

clearly indicate that for **12**, compared with DSeDAF **10**, the insertion of an azino spacer between the selenazole cores considerably decreases the electron donating ability since E^1_{pa} for **12** is 550 mV higher than for **10**. These redox properties of azino-DSeDAF increase its stability in the neutral form upon exposure to air. Another interesting feature is the large potential difference between the two oxidation waves ($\Delta E = E^2_{pa} - E^1_{pa}$) which indicates that for **12** the cation radical species is stable in a wider potential window.

In summary, we developed the first approach for the synthesis of 2-alkylthio-1,3-selenazole core with alkyl groups at the C-4 and C-5 positions. We showed the first successful transformations of these selenazole cores into new nonbenzoannelated DSeDAF π-donors. Furthermore, the combination of the wide range of selenothioic acid *S*-esters and iminodithiocarbonates available with the synthetic versatility of the C-4 carboxylic functionality could afford a variety of new, previously inaccessible, selenazole derivatives.

Experimental

Materials and methods

The *N*-(ethoxycarbonylmethyl)iminodithiocarbonate (EMIC) **1** was prepared according to the procedure described by Sauter *et al.*[13] Ethaneselenothioic acid *S*-butyl ester **2** was synthesized following the experimental procedure described by Murai *et al.*[17] ^{1}H NMR spectra were recorded at 200 and 300 MHz and ^{13}C NMR spectra at 50 and 75 MHz. Chemical shifts are reported in ppm referenced to TMS. Melting points were measured using a Kofler hot stage apparatus. Elemental analyses were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon) and from the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. Column chromatography was performed on silica gel 60 (0.040–0.063 mm). For the electrochemical determination of the redox potentials, CH_2Cl_2 was dried by refluxing over P_2O_5 followed by distillation.

Syntheses

4-Alkoxycarbonyl-1-alkylthio-5-methyl-1,3-selenazole. *Method a.* In a dried argon-filled round-bottom flask fitted with stirrer and rubber septum, potassium *tert*-butoxide (1.26 g, 10.27 mmol) was dissolved in dry THF (50 mL) and the reaction flask was cooled at −78 °C. A solution of *N*-(ethoxycarbonylmethyl)-iminodithiocarbonate (EMIC) **1** (1.06 g, 5.12 mmol) in dry THF (10 mL) was then added dropwise. The solution was further stirred at −78 °C for 0.5 h and then ethaneselenothioic acid *S*-butyl ester **2** (1.00 g, 5.12 mmol) in dry THF (5 mL) was added slowly. The reaction mixture was stirred at −78 °C for 0.5 h and then was allowed to reach room temperature and stirring was continued for 2 h. The reaction mixture was hydrolyzed with the least amount of water (~100 mL) to get a homogeneous medium. The mixture was extracted with ether (5 × 50 mL). The organic layers were separated, washed with water (50 mL), dried (Na_2SO_4) and combined. The solvent was evaporated and the crude product

was purified by chromatography on silica gel using pentane–AcOEt = 8 : 1 mixture as the eluent to give 1,3-selenazoles **3** and **4**.

Method b. LDA solution was prepared in a dried argon-filled round-bottom flask fitted with rubber septum at −78 °C by slow addition of *n*-BuLi (1.6 M in hexane, 21.1 mL, 33.8 mmol) to a stirred solution of diisopropylamine (3.42 g, 33.8 mmol) in dry THF (150 mL). After 30 min, a solution of *N*-(ethoxycarbonylmethyl)iminodithiocarbonate (EMIC) **1** (3.19 g, 15.37 mmol) in dry THF (20 mL) was added in one portion with continuing stirring at −78 °C for 30 min. To this mixture, a solution of ethaneselenothioic acid *S*-butyl ester **2** (3.00 g, 15.37 mmol) in dry THF (20 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h and then was allowed to reach room temperature and stirring was continued for 2 h. The reaction mixture was hydrolyzed with water (100 mL) and extracted with ether (5 × 50 mL). The organic layers were separated, washed with water (50 mL), dried (Na_2SO_4) and combined. The solvent was evaporated and the crude product was purified by chromatography on silica gel using pentane–AcOEt = 8 : 1 mixture as the eluent to give 1,3-selenazoles **3**, **4**, **5** and **6**.

4-Ethoxycarbonyl-5-methyl-2-methylthio-1,3-selenazole 3. Yield 0.20 g (15%) *by method (a)* or 0.89 g (22%) *by method (b)*, colorless needles, R_f (pentane–AcOEt = 8 : 1) = 0.34, mp 33.5–34.5 °C. ^{1}H NMR ($CDCl_3$): δ 4.33 (2H, q, J = 7.1 Hz), 2.76 (3H, s), 2.62 (3H, s), 1.35 (3H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 166.4, 162.3, 152.1, 142.3, 61.1, 17.6, 15.4, 14.4. HRMS: Calcd for $C_8H_{11}NO_2SSe$: 264.9676. Found: 264.9682. Anal. Calcd. for $C_8H_{11}NO_2SSe$: C, 36.37; H, 4.20; N, 5.30. Found: C, 36.75; H, 4.30; N, 5.30%.

2-Butylthio-4-ethoxycarbonyl-5-methyl-1,3-selenazole 4. Yield 0.13 g (8%) *by method (a)* or 1.04 g (22%) *by method (b)*, pale yellow oil, R_f (pentane–AcOEt = 8 : 1) = 0.57. ^{1}H NMR ($CDCl_3$): δ 4.39 (2H, q, J = 7.1 Hz), 3.18 (2H, t, J = 7.3 Hz), 2.81 (3H, s), 1.78 (2H, m, J = 7.3 Hz), 1.48 (2H, m, J = 7.3 Hz), 1.41 (3H, t, J = 7.1 Hz), 0.96 (3H, t, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 165.4, 162.3, 152.2, 142.2, 61.0, 34.9, 31.0, 21.9, 15.4, 14.3, 13.5. HRMS: Calcd. for $C_{11}H_{17}NO_2SSe$: 307.0145. Found: 307.0149. Anal. Calcd. for $C_{11}H_{17}NO_2SSe$: C, 43.14; H, 5.59; N, 4.57. Found: C, 43.17; H, 5.74; N, 4.73%.

4-Butoxycarbonyl-5-methyl-2-methylthio-1,3-selenazole 5. Yield 0.50 g (11%) *by method (b)*, pale yellow oil, R_f (pentane–AcOEt = 8 : 1) = 0.48. ^{1}H NMR ($CDCl_3$): δ 4.27 (2H, t, J = 6.7 Hz), 2.75 (3H, s), 2.62 (3H, s), 1.72 (2H, m, J = 6.7 Hz), 1.41 (2H, m, J = 6.7 Hz), 0.93 (3H, t, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 166.2, 162.4, 151.8, 142.4, 64.9, 30.7, 19.2, 17.4, 15.4, 13.7. HRMS: Calcd for $C_{10}H_{15}NO_2SSe$: 292.9989. Found: 292.9976. Anal. Calcd. for $C_{10}H_{15}NO_2SSe$: C, 41.10; H, 5.17; N, 4.79. Found: C, 40.57; H, 4.72; N, 5.07%.

4-Butoxycarbonyl-2-butylthio-5-methyl-1,3-selenazole 6. Yield 0.59 g (11%) *by method (b)*, pale yellow oil, R_f (pentane–AcOEt = 8 : 1) = 0.73. ^{1}H NMR ($CDCl_3$): δ 4.31 (2H, t, J = 6.7 Hz), 3.18 (2H, t, J = 7.1 Hz), 2.79 (3H, s), 1.76 (2H, qui, J = 6.8 Hz), 1.75 (2H, m, J = 6.7 Hz), 1.47 (2H, m, J = 7.3 Hz), 1.46 (2H, m, J = 7.3 Hz), 0.97 (3H, t, J = 7.3 Hz). 0.95 (3H, t, J = 7.3 Hz) ^{13}C NMR ($CDCl_3$): δ 165.5, 162.8, 152.3, 142.63, 65.2, 35.1, 31.4, 31.1, 22.3, 19.6, 15.7, 14.1, 13.9. HRMS: Calcd for $C_{13}H_{21}NO_2SSe$: 334.0536. Found: 334.0531. Anal. Calcd. for $C_{13}H_{21}NO_2SSe$: C, 46.70; H, 6.33; N, 4.19. Found: C, 46.60; H, 6.39; N, 4.45%.

4-Ethoxycarbonyl-3,5-dimethyl-1,3-selenazole-2-selone 8. To a stirred solution of 2-alkylthio-4-ethoxycarbonyl-5-methyl-1,3-selenazole (**3**: 0.38 g, 1.44 mmol or **4**: 1.00 g, 3.26 mmol) in CH_2Cl_2 (10 mL) was added a solution of trimethyloxonium tetrafluoroborate (0.21 g, 1.44 mmol for **3** and 0.48 g, 3.26 mmol for **4**) in $MeNO_2$ (10 mL) and the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting salts **7** were washed with ether (3 × 30 mL) and obtained as yellow oils. **7a**: yield quantitative ^{1}H NMR ($CDCl_3$): δ 4.51 (2H, q, J = 7.1 Hz), 4.11 (3H, s), 3.06 (3H, s), 2.87 (3H, s), 1.47 (3H, t, J = 7.1 Hz)^{13}C NMR ($CDCl_3$): δ 185.9, 160.4, 152.1, 136.3, 63.8, 42.1, 20.6, 16.7, 14.3. **7b**: yield quantitative ^{1}H NMR ($CDCl_3$): δ 4.46 (2H, q, J = 7.1 Hz), 4.07 (3H, s), 3.42 (2H, t, J = 7.2 Hz), 2.82 (3H, s), 1.93 (2H, m), 1.55 (2H, m), 1.43 (3H, t, J = 7.1 Hz), 0.99 (3H, t, J = 7.2 Hz) ^{13}C NMR ($CDCl_3$): δ 184.2, 158.6, 149.6, 136.1, 63.9, 42.2, 39.1, 29.9 22.2, 16.8, 14.4, 13.8. Then **7** were dissolved in acetonitrile (20 mL). The resulting solution was injected in one portion into a stirred solution of NaHSe under argon, obtained in 30 min from selenium (0.23 g, 2.88 mmol for **3** and 0.51 g, 6.52 mmol for **4**) and sodium borohydride (0.12 g, 3.16 mmol for **3** and 0.27 g, 7.17 mmol for **4**) in absolute EtOH (20 mL for **3** and 30 mL for **4**). The reaction mixture was stirred for 1 h. After, water (100 mL) was added into the reaction mixture and product was extracted with CH_2Cl_2 (5 × 30 mL). The combined organic layers were washed with water (50 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residual yellow solid was recrystallized from MeOH to furnish 4-ethoxycarbonyl-3,5-dimethyl-1,3-selenazole-2-selone **8**. Yield 0.30 g (67%) *from* **3** or 0.51 g (50%) *from* **4**, yellow needles, R_f (CH_2Cl_2) = 0.58, mp 95 °C. ^{1}H NMR ($CDCl_3$): δ 4.45 (2H, q, J = 7.1 Hz), 3.95 (3H, s), 2.54 (3H, s), 1.45 (3H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 185.1, 159.2, 141.9, 134.1, 62.3, 41.6, 16.1, 14.2. Anal. Calcd for $C_8H_{11}NO_2Se_2$: C, 30.89; H, 3.56; N, 4.50. Found: C, 30.70; H, 3.50; N, 4.76%.

4-Butoxycarbonyl-3,5-dimethyl-1,3-selenazole-2-selone 9. Same procedure as for **8** using 2-alkylthio-4-butoxycarbonyl-5-methyl-1,3-selenazole (**5**: 0.40 g, 1.37 mmol or **6**: 0.93 g, 2.78 mmol) in CH_2Cl_2 (15 mL) and trimethyloxonium tetrafluoroborate (0.20 g, 1.37 mmol for **5** and 0.41 g, 2.78 mmol for **6**) in $MeNO_2$ (8 mL for **5** and 10 mL for **6**).

The solution of NaHSe was prepared from selenium (0.22 g, 2.74 mmol for **5** and 0.44 g, 5.56 mmol for **6**) and sodium borohydride (0.11 g, 3.01 mmol for **5** and 0.23 g, 6.12 mmol for **6**) in absolute EtOH (30 mL). Purification was achieved by recrystallization from MeOH to furnish 4-butoxycarbonyl-3,5-dimethyl-1,3-selenazole-2-selone **9**. Yield 0.23 g (50%) *from* **5** or 0.35 g (37%) *from* **6**, yellow needles, R_f (CH_2Cl_2) = 0.60, mp 61 °C. ^{1}H NMR ($CDCl_3$): δ 4.33 (2H, t, J = 6.7 Hz), 3.89 (3H, s), 2.50 (3H, s), 1.74 (2H, m, J = 6.8 Hz), 1.44 (2H, m, J = 7.3 Hz), 0.96 (3H, t, J = 7.3 Hz).^{13}C NMR ($CDCl_3$): δ 185.5, 159.7, 142.2, 134.6, 66.6, 41.6, 30.9, 19.6, 16.5, 14.1. Anal. Calcd. for $C_{10}H_{15}NO_2Se_2$: C, 35.41; H, 4.46; N, 4.13. Found: C, 35.43; H, 4.37; N, 4.37%.

Diselenadiazafulvalenes 10 and 11. A stream of nitrogen was bubbled for 15 min through a solution of 3,5-dimethyl-4-substituted-1,3-selenazole-2-selone (**8**: 20.0 mg, 0.064 mmol, **9**: 20.0 mg, 0.059 mmol) in distilled toluene (3 mL). The yellow clear solution was heated to reflux under nitrogen and distilled triethylphosphite (27.5 μL, 0.16 mmol for **8**, 25.3 μL, 0.15 mmol for **9**) was added dropwise with a Hamilton syringe. The reaction mixture was stirred at reflux for 30 min giving an orange clear solution. The donor containing solution was cooled to room temperature and then transferred into an electrochemical cell under nitrogen to a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. The CV of the donor containing solution was recorded after the addition of aluminium oxide (activated, basic, 150 mesh).

Diethyl hydrazine-1,2-diylidenebis(3,5-dimethyl-2,3-dihydro-1,3-selenazole-4-carboxylate) 12. To a stirred solution of 4-ethoxycarbonyl-3,5-dimethyl-2-methylthio-1,3-selenazolium tetrafluoroborate **7a** (0.87 g, 2.38 mmol) in EtOH–MeCN = 1 : 1 (4 mL) was added NEt_3 (0.48 g, 4.77 mmol) in MeCN (2 mL) and $H_2N–NH_2·H_2O$ (60 mg, 1.19 mmol) in MeCN (2 mL). The mixture was stirred at room temperature for 60 min. The precipitated product was filtered off, washed with EtOH (10 mL), washed with water (20 mL) and dried to give yellow powder, which was recrystallized from petrol ether–CH_2Cl_2 to furnish **12**. Yield 0.20 g (34%), yellow powder, R_f (CH_2Cl_2) = 0.29, mp 229 °C. ^{1}H NMR ($CDCl_3$): δ 4.26 (4H, q, J = 7.2 Hz), 3.39 (6H, s), 2.35 (6H, s), 1.31 (6H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 160.74, 160.33, 129.28, 126.81, 61.62, 35.48, 16.90, 14.65. HRMS: Calcd. for $C_{16}H_{22}N_4O_4Se_2$: 493.9972. Found: 493.9980. Anal calcd for $C_{16}H_{22}N_4O_4Se_2$: C, 39.04; H, 4.50; N, 11.38. Found: C, 38.91; H, 4.61; N, 11.52%.

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