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One-Pot Synthesis of Heterocycle-Fused 1,3-Diselenole-2-selones as the Key Precursors of Tetraselenafulvalene-Type Electron Donors

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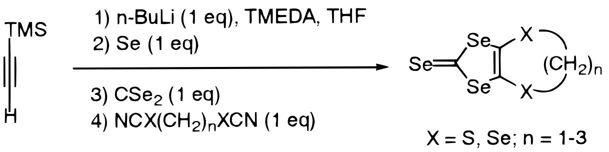
ABSTRACT



A simple one-pot synthetic method of a series of 4,5-alkylenedichalcogeno-substituted 1,3-diselenole-2-selones by successive treatments of trimethylsilylacetylene with butyllithium, selenium, carbon diselenide, and finally α,ω-bis(chalcogenocyanato)alkanes is described.

Since the discovery of a number of organic superconductors based on BEDT−TTF,[1] analogous heterocycle-fused TTF-type donors have been systematically studied with the purpose of searching for new organic superconductors with high *Tc*.[2] In particular, the TSF variants such as **1** have attracted considerable interest,[3] because the introduced selenium atoms can contribute to an increase of intermolecular interactions.[4] However, when compared with the TTF-type donors, such heterocycle-fused TSF-type donors are generally inaccessible and have been obtained by only limited methods.[5] The heterocycle-fused 1,3-diselenole-2-selones (**2**) and the corresponding ketones are very important as the key precursors of **1**, and accordingly the ready synthetic methods of these compounds are highly desirable. We now would like to report a simple one-pot synthesis of **2**, together with 4,5-bis(methylthio)-1,3-diselenole-2-selone (**3**), from commercially available trimethylsilylacetylene (Figure 1).

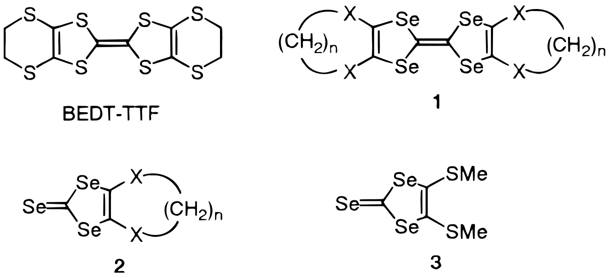


Figure 1.

Recently we reported an efficiently improved one-pot preparation of 1,3-dithiole-2-thiones (**5**, X = S) and 1,3-

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(1) For an excellent review on organic superconductors, see: Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (including Fullerenes)*; Prentice Hall: Englewood Cliffs, 1992.

(2) For an extensive review on TTF-type electron donors, see: Schukat, G.: Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1−294.

(3) (a) Kobayashi, H.; Udagawa, T.; Tomita, H.; Bun, K.; Naito, T.; Kobayashi, A. *Chem Lett*. **1993**, 1559−1562. (b) Kobayashi, A.; Udagawa, T.; Tomita, H.; Naito, T.; Kobayashi, H. *Chem Lett*. **1993**, 2179−2182. (c) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368−377. (d) Kobayashi, H.; Naito, T.; Sato, A.; Kawano, K.; Kobayashi, A.; Tanaka, H.; Saito, T.; Tokumoto, M.; Brossard, L.; Cassoux, P. *Mol. Cryst. Liq. Cryst.* **1996**, *284*, 61−72.

(4) (a) Cowan, D.; Kini, A. *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 2; Patai, S., Ed.; John Wiley & Sons: Chichester, 1987; pp 463−494. (b) Wudl, F. *Organoselenium Chemistry*; Liotta, D., Ed.; John Wlley & Sons: New York, 1987; pp 395−409.

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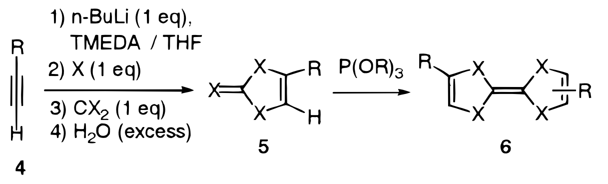
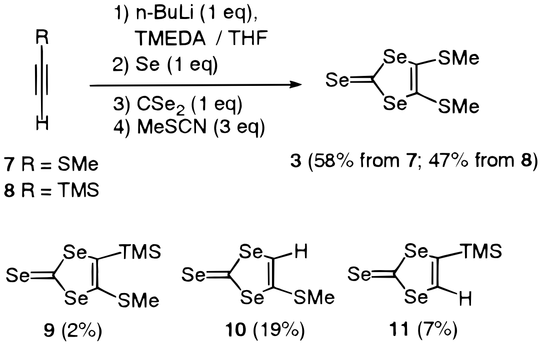
diselenole-2-selones (**5**, X = Se) from readily available acetylenes **4** (Scheme 1).[6] This reaction in combination with a conventional trialkyl phosphite-promoted coupling reaction[7] provides a ready access to TTF and TSF derivatives (**6**); in particular, it is very advantageous to the synthesis of less accessible TSF derivatives.[8]

Scheme 1



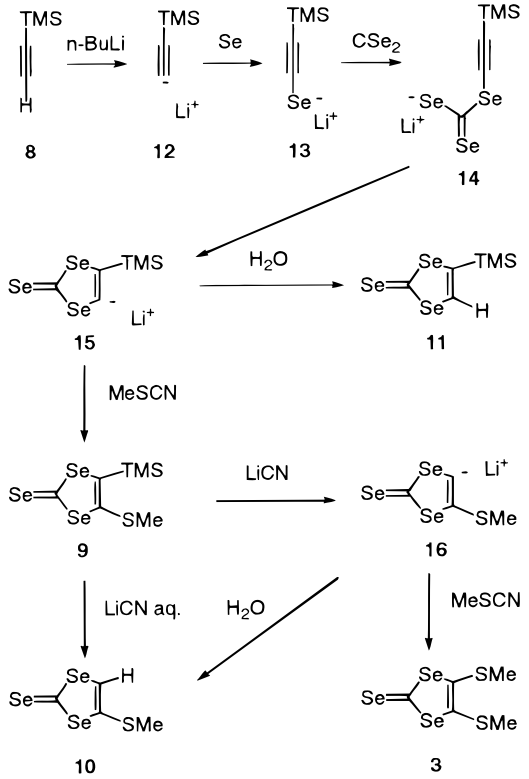
The thus obtained TSF donors (**6**) are of a bifunctional type and usually comprise both *cis* and *trans* forms that are readily interconvertible to each other and often cause crystallographic disorder. In this regard, symmetrical tetrafunctional TSF donors such as **1** are generally preferable and of greater value. This has prompted us to explore the synthetic method of the disubstituted 1,3-diselenole-2-selones **2** and **3.** The one-pot preparation of **5** involves a successive reaction sequence of an acetylene with 1 molar equiv of butyllithium, 1 molar equiv of selenium, 1 molar equiv of carbon diselenide, and finally excess water. With the aim of introducing an additional substituent group, we examined quenching with an appropriate electrophile instead of water. After many fruitless attempts, alkyl thiocyanates turned out to be an effective electrophile for this purpose. Thus, when a reaction mixture from methylthioacetylene (**7**) was quenched with excess methyl thiocyanate, 4,5-bis(methylthio)-1,3-diselenole-2-selone (**3**) was obtained in 58% yield (Scheme 2). In the course of our detailed examination on a similar reaction using trimethylsilylacetylene (**8**), we found an interesting result: the expected 4-methylthio-5-trimethylsilyl derivative **9** was detected in only 2% yield and instead the 4,5-bis(methylthio) derivative **3** (47% yield) was formed together with the two byproducts **10** (19%) and **11** (7%).

Scheme 2



The formation of **3**, **10**, and **11** is well explained by a plausible reaction mechanism, as shown in Scheme 3: quenching the cyclic intermediate **15** with methyl thiocyanate leads to the expected product **9** and with water to **11**. For the formation of **3** and **10**, however, it is proposed that the resultant **9** further reacts in situ with lithium cyanide concomitantly formed by the above quenching to give another intermediate (**16**), which subsequently with methyl thiocyanate leads to **3** and with water to **10**. As a direct evidence of the desilylation, we observed that treatment of **9** with aqueous lithium cyanide afforded **10** in almost quantitative yield.

Scheme 3



This serendipitous bis-methylthiolation reaction allowed us to develop a short access to the heterocycle-fused 1,3-diselenole-2-selone system (**2**). When the reaction mixture of **8** was finally quenched with 1 molar equiv of α,ω-bis-(chalcogenocyanato)alkane, a cyclofunctionalization reaction

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(5) (a) Lee, V. Y.; Engler, E. M.; Schumaker, R. R.; Parkin, S. S. P. *J. Chem. Soc., Chem. Commun*. **1983**, 235−236. (b) Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Met.* **1987**, *19*, 629−634. (c) Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Met.* **1991**, *42*, 2093−2096. (d) Zambounis, J. S.; Mayer, C. W. *Tetrahedron Lett.* **1991**, *32*, 2741−2742. (e) Kato, R.; Aonuma, S.; Okano, Y.; Sawa, H.; Kobayashi, A.; Kobayashi, H. *Synth. Met*. **1993**, *56*, 2084−2089. (g) Courcet, T.; Malfant, I.; Pokhodnia, K.; Cassoux, P. *New J. Chem.* **1998**, 585−589.

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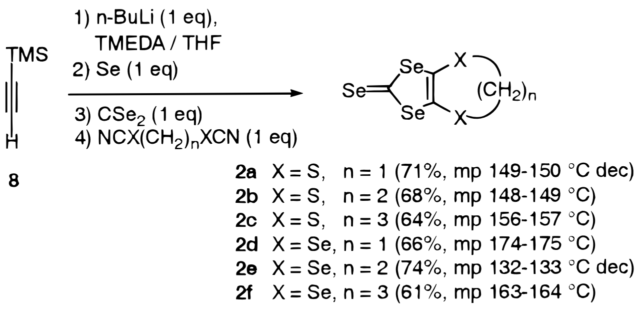
(7) (a) Bechgaard, K.; Cowan, D. O.; Bloch, A. N. *J. Org. Chem.* **1975**, *40*, 746−749. (b) Engler, E. M.; Scott, B. A.; Etemad, S.; Penney, T.; Patel. V. V. *J. Am. Chem. Soc.* **1977**, *99*, 5909−5916.

(8) Takimiya, K.; Oharuda, A.; Morikami, A.; Aso, Y.; Otsubo, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 619−622.

occurred to give the desired **2** in a good yield (Scheme 4).[10]

Scheme 4



2a X = S, n = 1 (71%, mp 149-150 °C dec)
2b X = S, n = 2 (68%, mp 148-149 °C)
2c X = S, n = 3 (64%, mp 156-157 °C)
2d X = Se, n = 1 (66%, mp 174-175 °C)
2e X = Se, n = 2 (74%, mp 132-133 °C dec)
2f X = Se, n = 3 (61%, mp 163-164 °C)

This reaction is widely applicable to the synthesis of a series of 1,3-diselenole-2-selones (**2**) with different methylene numbers, $n = 1-3$, and different chalcogen elements, S and Se, of the fused heterocyclic ring. Thus we believe that, in consideration of its simplicity and versatility, the present synthetic method of alkylenedichalcogeno-substituted 1,3-diselenole-2-selones greatly contributes to the development of TSF-based organic conductors.

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Supporting Information Available: Compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Pan, W.-H.; Fackler, J. P., Jr. *Inorganic Syntheses*, Vol. 21; Fackler J. P., Jr., Ed.; John Wiley & Sons: New York, 1982; pp 6−11.

[10] **Representative Experimental Procedure.** To a mixture of trimethylsilylacetylene (**8**) (0.282 mL, 2 mmol) and TMEDA (0.61 mL, 4 mmol) in dry THF (10 mL) cooled at −78 °C was added a hexane solution of n-BuLi (1.6 n, 1.25 mL, 2 mmol), and the resulting solution was stirred for 30 min at the same temperature. To the resulting lithium acetylide solution, selenium (158 mg, 2 mmol) was added in one potion, and the reaction mixture was allowed to warm to 0 °C during the period of 2 h and stirred for an additional 2 h at 0 °C. Then the mixture was cooled again to −90 °C, and carbon diselenide (0.14 mL, 2.2 mmol), prepared according to the literature procedure,[9] was added. The mixture was stirred for 3 min, then quenched by the addition of 1,2-bis(thiocyanato)ethane (288 mg, 2 mmol), and allowed to warm to room temperature. Water (30 mL) was added to the reaction mixture, and the insoluble material was filtrated, washed with MeOH (60 mL), and then recrystallized from carbon disulfide to give red plates of 4,5-(ethylenedithio)-1,3-diselenole-2-selone (**2b**). The filtrate and washings were combined and concentrated in vacuo. The residue was then taken up with dichloromethane (30 mL), washed with water (90 mL), dried ($MgSO_4$), and finally purified by column chromatography on silica gel with carbon disulfide and then recrystallization from carbon disulfide to give additional red plates of **2b**. The total yield is 499 mg (68%), and the physical and spectroscopic data are as follows: mp 148−149 °C; ^{1}H NMR ($CDCl_3$) δ 3.39 (s, 4H, CH_2); IR (KBr) ν 905 cm^{-1} (C=Se); MS *m*/*z* 366 (M^+) with an isotropic pattern of three selenium atoms. Anal. Calcd for $C_5H_4S_2Se_3$: C, 16.45; H, 1.10. Found: C, 16.63; H, 1.15.