COMMUNICATION

CSe₂-free synthesis of [1,3]diselenole-2-thione and its application to syntheses of iodinated tetraselenafulvalenes (TSeFs)

Tatsuro Imakubo* and Takashi Shirahata

*Imakubo Initiative Research Unit, RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan.
E-mail: imakubo@postman.riken.go.jp*

We developed a new CSe₂-free protocol for the synthesis of [1,3]diselenole-2-thione and converted it to tetraselenafulvalene derivatives without any selenium–sulfur exchange side reactions.

From the first organic superconductor (TMTSF)₂PF₆[1] to recent reports on superconductivity of BETS and MDT–TSF salts,[2] tetraselenafulvalene (TSeF) has been one of the most important frameworks for the development of organic superconductors. Synthesis of the parent TSeF was first reported in 1974 by Engler and Patel[3] and a large number of both symmetrical and unsymmetrical TSeFs have been synthesized within the last three decades. Except for the parent TSeF[4] and a few examples of heterocycle-fused TSeFs,[5,6] the highly toxic and bad smelling reagent CSe₂ was employed as a key material in the syntheses of [1,3]diselenole-2-selone derivatives, which are essential to TSeF synthesis. Some research groups still use CSe₂ for the syntheses of TSeFs, however, the trend is moving away from using such a highly toxic reagent considering the protection of the environment and researchers own safety. Under these circumstances, extensive research on new TSeFs has been held back in spite of the usefulness of the TSeF skeleton, and development of a new CSe₂-free synthetic method has long been expected. We report here a new and convenient CSe₂-free protocol for the synthesis of [1,3]diselenole-2-thione **1** as an alternative to [1,3]diselenole-2-selone together with its efficient conversion to TSeFs.

Bis(cyclopentadienyl)titanium pentaselenide **2** was chosen as the key starting material because it is easily obtained on a large scale and in a high yield from elemental selenium powder, which is a less-toxic selenium reagent and is easy to handle in conventional chemical facilities. According to the literature,[7] thione **4** is derived from **2** *via* diselenolene complex **3** and it can be converted quantitatively to the corresponding dicarboxylic acid **5** under acidic conditions. First, we tried to perform one-pot decarboxylation of **5** as well as the synthesis of [1,3]dithiole-2-thione,[8] however, it was unsuccessful in spite of investigating a wide range of reaction conditions and reagents. For example, heating of **5** in neat pyridine, most of **5** decomposed and only monocarboxylic acid **6** was obtained in a low yield (15–32%). A temperature over 80 °C produced an unidentified tarry mixture and we could not detect the formation of **1**. Addition of copper powder or changing the solvent to quinoline were also unsuccessful.

Although, Klingsberg reported two step synthesis of [1,3]dithiole-2-thione *via* methylation of 4,5-dicarboxy[1,3]dithiole-2-thione using iodomethane–nitromethane at a temperature around 40 °C,[9] Melby and co-workers reported that this method was not reproducible.[8] We successfully applied this iodomethane–nitromethane method to decarboxylation of **5**. We obtained the target molecule **1** in a high yield after tuning the amount of reagents and reaction conditions to resolve some differences between [1,3]dithiole and [1,3]diselenole (Scheme 1). Outline of the synthesis is as follows: overnight refluxing of **5**·H₂O (3.145 g) in 75 ml of a 1 : 2 mixture of iodomethane and nitromethane resulted in precipitation of ochre powder (3.580 g). We expected the powder to be decarboxylated iodide **7**, however, it was not **7** but a novel salt **8**. The salt **8** (3.422 g) was

suspended in 150 ml of benzene and heated to reflux with a large excess of pyridine (10 ml). After 14 hours, **1** was extracted to benzene and the crude product was purified by silica-gel chromatography using benzene or CS₂ as the eluent (1.442 g).

The molecular structure of **8** was characterized by NMR, X-ray diffraction and elemental analyses.† Fig. 1 shows the crystal structure of **8**.‡ The C(1)–S(1) distance (1.668(14) Å) is slightly longer than that of a usual C=S double bond and it is consistent with the divalent thiolium structure. The cation part of salt **8** is almost planar and there are short O···I and Se···I intermolecular interactions in the crystal. Salt **8** is air-stable at room temperature and it can be stored for several months without any special care. The distinct difference in the reactivity between **5** and the corresponding sulfur analogue in decarboxylation could be due to the difference of the electronic state of the [1,3]dichalcogenole ring. The lower electronegativity of selenium rather than sulfur decreases the electron withdrawing
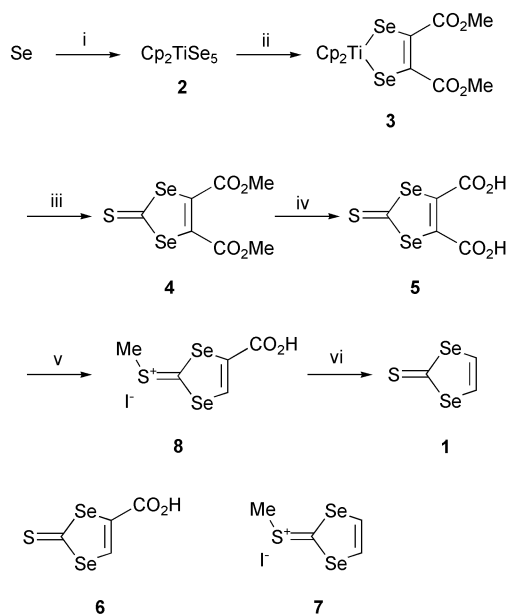
Scheme 1 *Reagents and conditions*: i, LiEt₃BH, THF, Cp₂TiCl₂ (78%); ii, DMAD, xylene, reflux (quant.); iii, Cl₂C=S, THF, reflux (68%); iv, AcOH–HCl aq. (91% as monohydrate); v, CH₃I–CH₃NO₂, reflux 16 h (92%); vi, pyridine–benzene, reflux 14 h (76%).
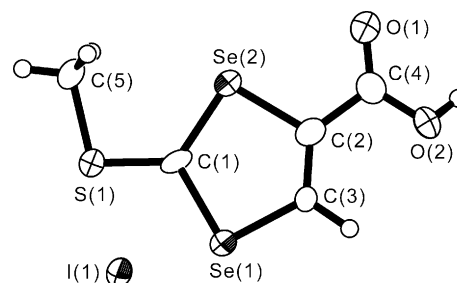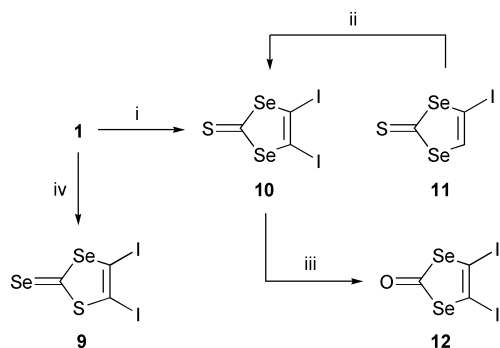

**Fig. 1** Crystal structure of **8**.

Scheme 2 *Reagents and conditions*: i, PFBI (12 eq.) then LDA (4 eq.), −78 °C (**10**: 38%, **11**: 43%); ii, PFBI (5.5 eq.) then LDA (2.2 eq.), −78 °C (51%); iii, Hg(OAc)$_2$, AcOH–CHCl$_3$ (97%); iv, LDA then ICl or PFBI.

nature of the [1,3]diselenole ring and the direct elimination of the two carboxyl groups on **5** is prevented. The electron density of the [1,3]diselenole ring of **8** is effectively lowered by the cationic methylation and the second decarboxylation proceeded smoothly. Decarboxylation of the monoacid **6** did not proceed under the same pyridine–benzene conditions, therefore the cationic methylation of the diacid **5** is essential for completion of decarboxylation.

For the utilization of thione **1** in syntheses of TSeFs, it is necessary to develop a conventional method of introducing substituents on the 4,5-positions. The most popular method is an electrophilic reaction with anionic species and we tried to react electrophile, iodine monochloride or perfluorobutyl iodide (PFBI) with 4,5-dilithio[1,3]diselenole-2-thione generated by the addition of LDA to **1** at −78 °C. The only identified product was, however, 4,5-diiodo[1,3]thiaselenole-2-selone **9**. This is consistent with the results reported by Poleschner *et al.* who suggested that the transformation of 4,5-dilithio[1,3]diselenole-2-thione to 4,5-dilithio[1,3]thiaselenole-2-selone is preferred in solution even at low temperature.[10] The formation of [1,3]thia-selenole-2-selone would occur by the ring-opening of the mono-lithio derivative[11] and an immediate quenching of the first carbanion on the [1,3]diselenole ring is needed to avoid unfavourable ring-opening. Considering this, we changed the reaction protocol: first we added the electrophile to the solution of **1** and then the lithiating reagent was added. Slow addition of LDA to the mixture of **1** and excess PFBI at −78 °C provided 4,5-diiodo[1,3]diselenole-2-thione **10** and 4-iodo[1,3]dise-nole-2-thione **11** as expected. No trace of [1,3]thiaselenole-2-selone was detected and the [1,3]diselenole skeleton remained complete. Monoiodide **11** is an alternative starting material of the iodination as shown in Scheme 2. A larger amount of PFBI and LDA raises the yield of **10**, however, the reaction becomes complicated probably due to the reaction between PFBI and LDA. The thione **10** is easily converted to the corresponding ketone **12** quantitatively by a usual Hg(OAc)$_2$–CHCl$_3$ method.

The TSeF skeletons were constructed by self- or cross-coupling reactions of **12** and **13**[5] (or **14**[6]) under P(OEt)$_3$–toluene reflux. It is interesting that de-iodination of the products which were reported in similar coupling reactions of the dithiole analogue[12,13] was not observed in these reactions of the diselenole **12**. TITSeF was obtained in 89% yield from **12**,
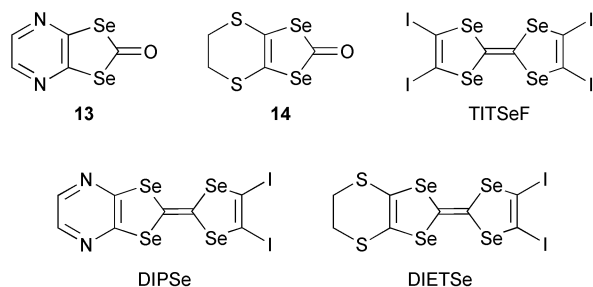
which is significantly higher than the reported yield from the corresponding selone (14%).[14] An organic π-donor DIPSe is the selenium analogue of DIPS, which provides supramolecular hexagonal crystals,[15] and DIETSe is also the selenium analogue of DIETS, which provides an organic superconductor.[16,17] The yields of cross-coupling reactions were 22% (DIPSe) and 28% (DIETSe) respectively. We previously reported multi-step synthesis of DIETSe without the use of CSe$_2$, however, the total yield was much lower (1%)[13] and the above one-step reaction is more convenient. Preparation of cation radical salts of these TSeFs is in progress and preliminary results show that the PF$_6$ salt of DIPSe crystallizes in a hexagonal crystal system tailored by the strong and directional I···N iodine bond and it is isostructural with that of DIPS salt.

Notes and references

† *Selected data of new compounds* **5**: ochre powder, mp 128 °C (decomp.); δ_H (300 MHz, CD$_3$OD) 2.40 (s, 1H), 8.41 (s, 3H); δ_C (75 MHz, DMSO-d$_6$) 21.39, 124.03, 124.18, 156.83, 162.75; ν_{max}(neat)/cm^{-1}: 1692 (C=O), 2790 (br, OH); Elemental analysis: calc. for C$_5$H$_5$O$_2$ISSe$_2$: C, 14.51; H, 1.22. Found: C, 14.24; H, 1.16; **10**: deep yellow wool, mp 182 °C (decomp.); m/z (EI, 70 eV): 482 (M$^+$ for C$_3$I$_2$S^{80}Se$_2$); Elemental analysis: calc. for C$_3$I$_2$SSe$_2$: C, 7.51. Found: C, 7.78; **11**: yellow crystals, mp 120 °C; δ_H (300 MHz, CDCl$_3$) 8.05 (s, 1H); m/z (EI, 70 eV): 356 (M$^+$ for C$_3$HIS^{80}Se$_2$); Elemental analysis: calc. for C$_3$HISSe$_2$: C, 10.18; H, 0.28. Found: C, 10.31; H, 0.31; **12**: white needles, mp 124 °C; m/z (EI, 70 eV): 466 (M$^+$ for C$_3$OI$_2$^{80}Se$_2$); ν_{max}(neat)/cm^{-1}: 1659 (C=O); Elemental analysis: calc. for C$_3$OI$_2$Se$_2$: C, 7.77. Found: C, 7.93; **DIPSe**: red crystals, mp 219 °C (decomp.); δ_H (300 MHz, CDCl$_3$) 8.13 (s, 2H); m/z (EI, 70 eV): 698 (M$^+$ for C$_8$H$_2$N$_2$I$_2$^{78}Se^{80}Se$_3$); Elemental analysis: calc. for C$_8$H$_2$N$_4$I$_2$Se$_4$: C, 13.81; H, 0.29; N, 4.03. Found: C, 13.78; H, 0.27; N, 3.80; CV(volt vs Cp$_2$Fe–Cp$_2$Fe$^+$ couple): $E_{1/2}^1$, 0.50; E_{ox}^2, 0.74.
‡ *Crystal data for* **5**; C$_5$H$_5$O$_2$ISSe$_2$, M = 413.97, red plate (0.40 × 0.20 × 0.02 mm), triclinic, $P\bar{1}$ (#2), a = 5.7670(13), b = 8.2412(18), c = 11.161(2) Å, α = 86.880(5), β = 79.191(4), γ = 70.423(4)°, V = 490.91(19) Å^3, μ = 10.840 mm^{-1}, Z = 2, 3505 reflections measured, 2346 unique (R_{int} = 0.0337). Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0789, $wR2$ = 0.2474. R indices (all data): $R1$ = 0.0927, $wR2$ = 0.2549. CCDC 210500. See http://www.rsc.org/suppdata/cc/b3/b304136k/ for crystallographic data in .cif or other electronic format.

1 D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.*, 1980, **41**, L95–L98.
2 H. Kobayashi, A. Kobayashi and P. Cassoux, *Chem. Soc. Rev.*, 2000, **29**, 325–333; K. Takimiya, Y. Kataoka, Y. Aso, T. Otsubo, H. Fukuoka and S. Yamanaka, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 1122–1125.
3 E. M. Engler and V. V. Patal, *J. Am. Chem. Soc.*, 1974, **96**, 7376–7378.
4 Y. A. Jackson, C. L. White, M. V. Lakshmikantham and M. P. Cava, *Tetrahedron Lett.*, 1987, **28**, 5635–5636.
5 G. C. Papavassiliou, S. Y. Yiannopoulos, J. S. Zambounis, K. Kobayashi and K. Umemoto, *Chem. Lett.*, 1987, 1279–1282.
6 R. Kato, H. Kobayashi and A. Kobayashi, *Synth. Met.*, 1991, **41–43**, 2093–2096.
7 C. M. Bolinger and T. B. Rauchfuss, *Inorg. Chem.*, 1982, **21**, 3947–3954.
8 L. R. Melby, H. D. Hartzler and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456–2458.
9 E. Klingsberg, *J. Am. Chem. Soc.*, 1964, **86**, 5290–5292.
10 H. Poleschner, R. Radeglia and J. Fuchs, *J. Organomet. Chem.*, 1992, **427**, 213–230.
11 E. M. Engler and V. V. Patel, *J. Org. Chem.*, 1975, **40**, 387–389.
12 A. S. Batsanov, M. R. Bryce, A. Chesney, J. A. K. Howard, D. E. John, A. J. Moore, C. L. Wood, H. Gershtenmen, J. Y. Becker, V. Y. Khodorkovsky, A. Ellern, J. Bernstein, I. F. Perepichka, V. Rotello, M. Gray and A. O. Cuello, *J. Mater. Chem.*, 2001, **11**, 2181–1291.
13 T. Imakubo, H. Sawa and R. Kato, *Synth. Met.*, 1997, **86**, 1883–1884.
14 K. Takimiya, Y. Kataoka, A. Morikami, Y. Aso and T. Otsubo, *Synth. Met.*, 2001, **120**, 875–876.
15 T. Imakubo, T. Maruyama, H. Sawa and K. Kobayashi, *Chem. Commun.*, 1998, 2021–2022.
16 T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1996, 1667–1668.
17 T. Imakubo, N. Tajima, M. Tamura, R. Kato, Y. Nishio and K. Kajita, *J. Mater. Chem.*, 2002, **12**, 159–161.

13   **14**   TITSeF

DIPSe   DIETSe