A Practical Two-Step Synthesis of Tetraselenafulvalene (TSF)

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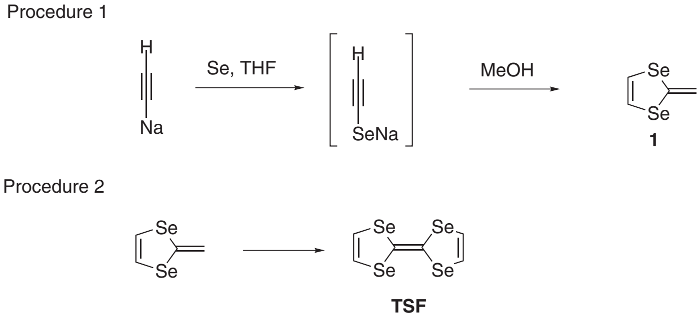
Abstract: The preparation of tetraselenafulvalene (TSF) from commercially available sodium acetylide in xylene–light mineral oil and selenium powder is described.

Keywords, tetraselenafulvalenes, selenium, sodium acetylide, electron donors



Scheme 1 Synthesis of TSF

Tetraselenafulvalene (TSF) derivatives have been important electron donors in the field of organic conductors, since Engler et al. first synthesized the parent TSF and its highly conducting charge-transfer complex with tetracyanoquinodimethane (TCNQ).[1] Since then, the first organic superconductor was generated from the radical cation salt of tetramethyltetraselenafulvalene (TMTSF).[2] Furthermore, new superconductors based on heterocycle-fused TSF derivatives, such as bis(ethylenedithio)tetraselenafulvalene (BETS),[3] methylenedithio-tetraselenafulvalene (MDT-TSF),[4] and methylenediseleno-tetraselenafulvalene (MDS-TSF)[5] have been reported one after another.

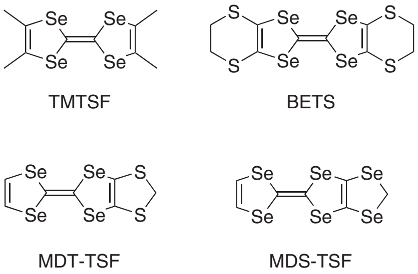


Figure 1

The development of materials chemistry based on TSF-type electron donors is, however, so far limited, because the synthesis of TSF and its derivatives usually require highly toxic selenium reagents such as carbon diselenide (CSe_2)[6] and hydrogen selenide (H_2Se). In order to expand TSF-based chemistry, like the well-established TTF-based chemistry, it is thus desirable to develop practical synthetic methods for such TSF compounds using readily available, nontoxic selenium reagents.[7] In this regard, Cava et al. reported an unconventional synthesis of TSF, as shown in Scheme 2, which involves the following two intriguing reactions: (i) the formation of 2-methylene-1,3-diselenole (**1**) by spontaneous decomposition of 1,2,3-selenadiazole (**2**) prepared from acetaldehyde semicarbazone and selenium dioxide and (ii) dimerization of **1** to TSF induced by iodine–morpholine.[8] In addition, Cava's group reported that various TSF derivatives could be obtained by functionalization of TSF itself.[9] Our group also demonstrated that some elaborate heterocycle-fused TSF derivatives including BETS and MDT-TSF could be tailored from TSF.[10] Cava's approach to TSF is quite promising in terms of the favorable use of nontoxic selenium dioxide, but has the disadvantages of low yield in the first reaction (25–30%).[11] It is speculated that in the first reaction, **2** decomposes to ethyneselenol (**3**), which is in equilibrium with selenoketene **4**, and dimerizes to **1**. We expected that, if the intermediate **3** is readily generated using a common acetylene reagent, then Cava's approach to TSF would become more attractive and useful. In this pa-

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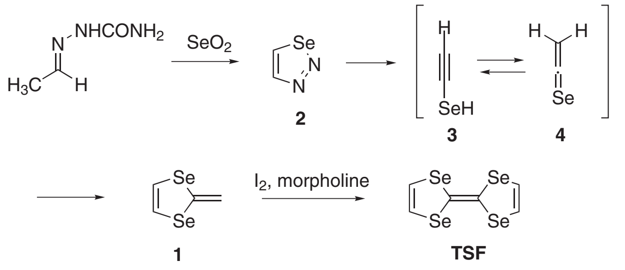
per, we report a one-pot synthesis of **1** from commercial sodium acetylide and elemental selenium. In combination with Cava's conversion procedure of **1** to TSF it has turned out that this procedure provides a practical two-step, gram-scale synthesis of TSF.



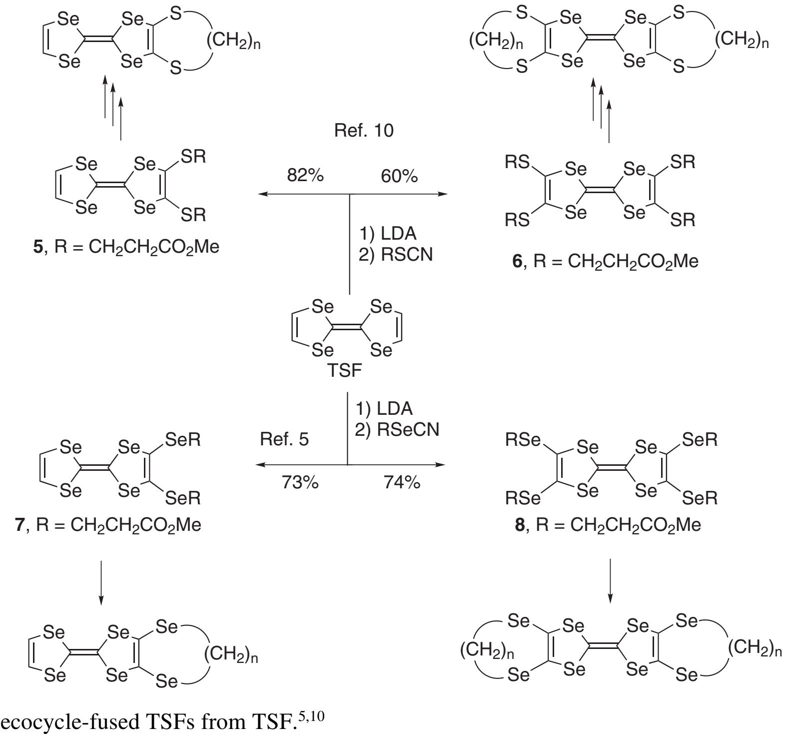
Scheme 2 Cava's method for the synthesis of TSF.

Sodium acetylide is a commercial reagent available as slurry in xylene–light mineral oil. As a result of the chemical instability of 2-methylene-1,3-diselenole (**1**)[8] we were afraid that the existence of these stabilizing solvents with high boiling points would make purification of **1** difficult. Thus, the solvents were first removed from solid sodium acetylide by repeated centrifugation/washing (anhydrous hexane) cycles, and the resulting solvent-free sodium acetylide was utilized in the reaction with selenium powder in THF. This reaction proceeded smoothly, as was observed by the gradual consumption of selenium powder, in situ, producing ethyneselenate anion, which was then protonated by the addition of methanol and dimerized into **1**. In Cava's method, compound **1** was isolated by precipitation from DMF–water. In the present case, however, precipitation of **1** by the addition of even a large amount of water to the reaction mixture did not take place. Instead, extraction with pentane turned out to be satisfactory (69% yield) for the isolation of **1**. Treatment of **1** with an iodine–morpholine mixture in DMF gave TSF in almost the same yield (25–37%) as the literature.[8]

We also examined the synthesis of TSF without isolation of **1**. Reaction of sodium acetylide in xylene–light mineral oil with selenium powder in THF, followed by the addition of methanol gave a solution of **1** in xylene–light mineral oil after the same workup as above. This solution without further purification was successfully utilized to synthesize TSF and the yield of TSF, based on the amount of selenium powder used in the first step, is basically the same as above. By both reactions, more than 2 g of TSF was routinely obtained from sodium acetylide in xylene–light mineral oil (32 mL, ca. 0.1 mol) and selenium powder (7.6 g).

As reported in the proceeding papers, alkylenedithio-, bis(alkylenedithio)-, and alkylenediseleno-TSFs via the protected TSF-dithiolate (**5**),[10] -tetrathiolate (**6**),[10] and -diselenolate (**7**)[5] were synthesized from TSF. In a similar manner, protected TSF tetraselenolate **8** was prepared as shown in Scheme 3. With these intermediates in hand, various kinds of heterocycle-fused TSF derivatives are easily obtained via the deprotection/realkylation protocol.[12]

In conclusion, we have established a convenient and practical synthesis of TSF from commercially available sodium acetylide. The present procedure has the advantage of using cheap, non-toxic selenium powder as the selenium source, only two synthetic steps are required, and the method is suitable for laboratory-scale preparation (>2 g batch). In combination with their functionalization as pro-



Scheme 3 Synthesis of hetecocycle-fused TSFs from TSF.[5,10]

tected thiolate or selenolate moieties, followed by their deprotection/realkylation chemistry, the present method paves a practical way to various heterocycle-fused TSF-type donors, including MDT-TSF and MDS-TSF which can be used to produce superconducting radical cation salts.

All chemicals and solvents used were of reagent grade. Sodium acetylide was purchased from Aldrich. All reactions were carried out under a nitrogen atmosphere with anhyd solvents. Column chromatography was carried out with Daisogel IR-60 (63–210 μm). Melting points are uncorrected. NMR spectra were obtained in $CDCl_3$ with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR, with TMS as the internal reference; chemical shifts (δ) are reported in ppm. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the selenium-containing compounds showed a typical selenium isotopic pattern, and all the selenium-containing mass peaks are reported for ^{80}Se.

2-Methylene-1,3-diselenole (1); Synthesis of TSF from Sodium Acetylide

Sodium acetylide (18% wt., slurry in xylene–light mineral oil, 32 mL, ca. 4.8 g, 0.1 mol) was transferred to four test tubes (16.5 mm diameter × 105 mm length) and centrifuged to precipitate the salt. The upper solvent layer was removed with a syringe, and the resulting solid was shaken with anhyd hexane (6 mL) under a nitrogen atmosphere, and then the mixture was once again centrifuged. This operation was repeated three times, and the resulting xylene–light mineral oil-free sodium acetylide was suspended in THF (100 mL) and transferred into a 500 mL three-necked flask via double-ended transfer needle. To this suspension cooled to –70 °C was added Se powder (7.6 g, 0.096 mol) in one portion, the resulting mixture was allowed to warm to 0 °C, and stirred for 1 h at 0 ºC. Then, MeOH (60 mL) was added at –78 °C, the resulting mixture was gradually warmed to 0 °C, and stirred for 2 h at the same temperature. The solution was diluted with H_2O (120 mL), extracted with pentane (4 × 80 mL), the extract was washed with H_2O (3 × 60 mL), dried over Na_2SO_4, and concentrated in vacuo (to avoid decomposition of **1**, it is advisable that this is carried out below r.t. in the dark) to give 2-methylene-1,3-dislenole (7.0 g, 69%). The product was used in the next reaction without further purification.

Mp 51–53 °C (Lit.[8] 58–60 °C).

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.93 (dd, *J* = 1.0, 1.5 Hz, 2 H), 5.62 (dd, *J* = 1.0, 1.5 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 107.98, 120.29, 132.41.

MS (EI): $m/z = 212$ (M^+, ^{80}Se).

Tetraselenafulvalene (TSF)

To a solution of **1** (7.0 g, 33 mmol) in DMF (140 mL) was added dropwise a mixture of iodine (17.1 g, 67 mmol) and morpholine (17.7 g, 0.2 mol) in DMF (140 mL) at r.t. An exothermic reaction took place, and it was necessary to cool the mixture with a water bath. After stirring for 2 h at r.t., the mixture was diluted with H_2O (100 mL), and extracted with CH_2Cl_2 (4 × 50 mL). The extract was washed with aq $Na_2S_2O_3{\cdot}5H_2O$ solution (2 × 150 mL), H_2O (3 × 60 mL), dried over $MgSO_4$, and concentrated to give a dark red residue. Column chromatography (silica gel, 6 cm × 20 cm; CH_2Cl_2–hexane, 1:2) gave TSF (2.4 g, 37%) as a red solid. This product was practically pure and can be used without further purification. An analytically pure sample was obtained by recrystallization from hexane.

Mp 132–133 °C (Lit.[1] 132.5–133 °C, Lit.[8] 132–133 °C); R_f 0.4 (CH_2Cl_2–hexane, 1:2).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.22 (s, 4 H).

MS (EI): $m/z = 396$ (M^+, ^{80}Se).

Anal. Calcd for $C_6H_4Se_4$: C, 18.39; H, 1.03. Found: C, 18.39; H, 1.02.

Synthesis of TSF without Isolation of 1

Sodium acetylide (18% wt., slurry in xylene–light mineral oil, 32 mL, ca. 4.8 g, 0.1 mol) was transferred to a 500-mL three-necked flask and diluted with anhyd THF (100 mL). This sodium acetylide suspension was used in the reaction with Se powder as mentioned above, and the reaction work-up was carried out in the same manner. The pentane extract was concentrated to give a dark red solution of **1**, which was treated with an iodine–morpholine mixture (26.5 g and 27.5 mL, respectively) in DMF (150 mL) in the same manner as above. Concentration of the CH_2Cl_2 extract gave a solution of TSF in xylene–light mineral, which was purified directly by column chromatography (silica gel, 6 cm × 20 cm; hexane was used as the first eluent until both the xylene and light mineral were completely eluted, and then CH_2Cl_2–hexane, 1:2).

Yield: 2.2–2.4 g (ca. 25%).

2,3,6,7-Tetrakis[(2-methoxycarbonyl)ethylseleno]tetraselenafulvalene (8)

To a solution of TSF (225 mg, 0.57 mmol) in anhyd THF (20 mL) was added freshly prepared LDA in THF–hexane (1.0 M, 2.4 mL, 2.4 mmol) at –90 °C, and the mixture was stirred for 40 min at –78 °C. Methyl selenocyanatopropionate (480 mg, 2.5 mmol) was added via syringe to the solution, the mixture was allowed to warm to –50 °C over a period of 1 h, and finally quenched by the addition of H_2O (30 mL). The mixture was extracted with CH_2Cl_2 (4 × 15 mL), the extract was washed with H_2O (30 mL), and dried over $MgSO_4$ (anhyd). The extract was concentrated in vacuo and the resulting residue was subjected to column chromatography (silica gel; CH_2Cl_2–EtOAc, 6:1). Recrystallization from $CHCl_3$–hexane (1:1) gave fine red needles.

Yield: 474 mg (78%); mp 107–108 °C (Lit.[12b] 108 °C); R_f 0.5 (CH_2Cl_2–EtOAc, 6:1).

Spectroscopic data were identical to those reported previously.

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