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# Noncoupling Synthesis of Unsymmetrical Tetrathiafulvalene Derivatives. Dihydrotetrathiafulvalenes as New Electron Donors

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The development of synthetic methods that allow for the efficient construction of unsymmetrical tetrathiafulvalenes (TTFs) has been very important, because some of their radical cation salts, *i.e.*, $(DMET)_2X$[1] and $(MDT\text{-}TTF)_2AuI_2$,[2] exhibit superconductivities. In the conventional synthesis of TTF derivatives, the coupling reaction utilizing trialkyl phosphite is a synthetic approach to the construction of symmetrical TTFs.[3] However, when this coupling reaction is the case for the synthesis of unsymmetrical TTFs, two symmetrical self-coupling products are formed along with the unsymmetrical cross-coupling product. Especially in the case of the synthesis of diselenadithiafulvalene (DSDTF) derivatives, the separation of the desired cross-coupling product from self-coupling products is often troublesome.[4] On the other hand, the transformation of esters into dithioketene acetals by the use of aluminium thiolates[5] is attractive for several non-phosphite coupling routes to the central C=C bond of unsymmetrical TTFs.[6] Although Mori and Inokuchi[7] have reported the first application of this transformation for the synthesis of unsymmetrical TTFs, the synthesis of both the sulfur-rich TTF derivatives and the selenium analog of TTF derivatives is not described. Thus we report here that the noncoupling syntheses of dihydrotetrathiafulvalene (DHTTF) derivatives,[8] as well as DSDTF derivatives, are accomplished by the reactions of organotin thiolates **1** or organotin selenolates **2** with esters **3** or **4** (Figure 1) in the presence of Lewis acids[9] and also that the DHTTF derivatives become new electron donors.

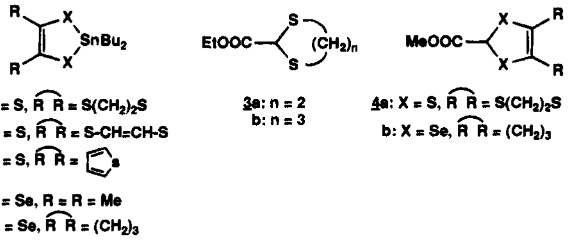


**Figure 1.** Organotin compounds and esters.

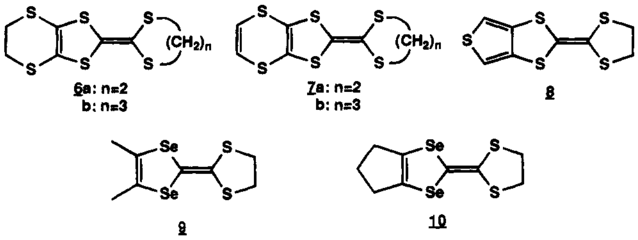
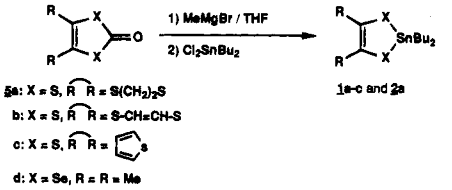


**Figure 2.** DHTTF derivatives and their related compounds.

Organotin thiolates **1a**−**c** and selenolate **2a** were prepared by reactions of the corresponding 1,3-dithiole-2-ones **5a**−**c** and 1,3-diselenole-2-one **5d**[10] with MeMgBr (3.3 equiv) in THF, followed by trapping with $Cl_2SnBu_2$ at −78 °C (eq 1). Although



(1)

tin thiolates **1a**−**c** could not be purified by column chromatography on silica gel, tin selenolate **2a** was able to be purified in the same way (81% yield). The organotin selenolate could also be prepared by an alternate route. Two consecutive stepwise reactions of 1,2-dibromocyclopentene in THF with 2 equiv of ${}^tBuLi$ and 1 equiv of elemental selenium,[11] followed by trapping with $Cl_2SnBu_2$ at −78 °C, enable us to prepare **2b**. Tin selenolate **2b** tended to decompose through silica gel.

The results of noncoupling syntheses of DHTTF derivatives and their related compounds (Figure 2) are summarized in Table 1. Tin thiolate **1a** reacted with **3a**[12] in the presence of Lewis acids such as $TiCl_4$, $Me_2AlCl$, and $Me_3Al$ (entries 1−3). Trimethylaluminum gave the best result among the Lewis acids

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[1] DMET = dimethyl(ethylenedithio)diselenadithiafulvalene; X = $Au(CN)_2$: Kikuchi, K.; Kikuchi, M.; Namiki, T.; Saito, K.; Ikemoto, I.; Murata, K.; Ishiguro, T.; Kobayashi, K. *Chem. Lett.* **1987**, 931−932. X = $AuCl_2$ and $AuI_2$: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K.; Anzai, H.; Kobayashi, K.; Ishiguro, T.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 4241−4244. X = $I_3$ and $IBr_2$: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K.; Ishiguro, T.; Kobayashi, K.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 3436−3439. X = $AuBr_2$: Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K.; Kobayashi, K.; Ishiguro, T.; Ikemoto, I. *J. Phys. Soc. Jpn.* **1987**, *56*, 2627−2628.

[2] MDT-TTF = methylenedithiotetrathiafulvalene: (a) Kini, A. M.; Beno, M. A.; Son, D.; Wang, H. H.; Carlson, K. D.; Porter, L. C.; Welp, U.; Vogt, B. A.; Williams, J. M.; Jung, D.; Evain, M.; Whangbo, M.-H.; Overmyer, D. L.; Schirber, J. E. *Solid State Commun.* **1989**, *69*, 503−507. (b) Papavassiliou, G. C.; Mousdis, G. A.; Zameounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Met.* **1988**, *27*, B379−B383.

[3] For general reviews, see: (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209−1252. (b) Bryce, M. R. *Aldrichim. Acta* **1985**, *18*, 73−77. (c) Schumaker, R. R.; Lee, V. Y.; Engler, E. M. *J. Phys.* **1983**, *44*, C1139−C1145. (d) Narita, M.; Pittman, C. U. *Synthesis* **1976**, 489−514.

[4] (a) Aonuma, S.; Okano, Y.; Sawa, H.; Kato, R.; Kobayashi, H. *J. Chem. Soc., Chem. Commum.* **1992**, 1193−1195. (b) Kobayashi, K.; Kikuchi, K.; Namiki, T.; Ikemoto, I. *Synth. Met.* **1987**, *19*, 555−558. (c) Kikuchi, K.; Namiki, T.; Ikemoto, I.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1472−1473.

[5] (a) Cohen, T.; Gapinski, R. E.; Hutchins, R. R. *J. Org. Chem.* **1979**, *44*, 3599−3601. (b) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1973**, 95, 5829−5831.

[6] (a) Gimber, Y.; Moradpour, A.; Dive, G.; Dehareng, D.; Lahlil, K. *J. Org. Chem.* **1993**, *58*, 4685−4690. (b) Sudmale, I. V.; Tormos, G. V.; Khodorkovsky, V. Yu.; Edzine, A. S.; Neilands, O. J.; Cava, M. P. *J. Org. Chem.* **1993**, *58*, 1355−1358. (c) Khodorkovsky, V. Yu.; Tormos, G. V.; Neilands, O. Ya.; Kolotilo, N. V.; Il'chenko, A. Ya. *Tetrahderon Lett.* **1992**, *33*, 973−976. (d) Jørgensen, M.; Lerstrup, K. A.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684−5688. (e) Mizuno, M.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 416−418. (f) Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369−370.

[7] Mori, T.; Inokuchi, H. *Chem. Lett.* **1992**, 1873−1876.

[8] For some recent work involving DHTTF dervatives, see: (a) Lorcy, D.; Paillard, M.-P. L.; Robert, A. *Tetrahedron Lett.* **1993**, *34*, 5289−5292. (b) Salle, M.; Gorgues, A.; Jubault, M.; Gouriou, Y. *Synth. Met.* **1991**, *41*−*43*, 2575−2578.

[9] For the Lewis acid-promoted reactions, see: Yamada, J.; Yamamoto, Y. *Rev. Heteroatom Chem.* **1991**, *5*, 250−269.

[10] Compounds **5a**−**d** were derived from the appropriate 1,3-dithiole-2-thiones and 1,3-diselenole-2-selenone by treatment with $Hg(OAc)_2$ in THF−AcOH and in the following yields: **5a**, 92%; **5b**, 82%; **5c**, 62%; **5d**, 68%. The thione for **5a** was obtained from Tokyo Kasei Co. The thiones for **5b** and **5c** were prepared essentially according to the lierature. The thione for **5b**: Nakamura, T.; Nogami, T.; Shirota, Y. *Bull Chem. Soc. Jpn.* **1987**, *60*, 3447−3449. The thione for **5c**: Chiang, L.-Y.; Shu, P.; Holt, D.; Cowan, D. *J. Org. Chem.* **1983**, *48*, 4713−4717. The selenone for **5d** was prepared according to the literature: Moradpour, A.; Peyrussan, V.; Johansen, I.; Bechgaard, K. *J. Org. Chem.* **1983**, *48*, 388−389.

[11] Okano, Y.; Sawa, H.; Aonuma, S.; Kato, R. *Chem. Lett.* **1993**, 1851−1854.

[12] Esters **3a** and **3b** were obtained from Tokyo Kasei Co.

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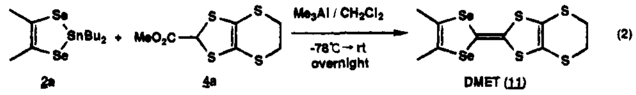
**Table 1.** Noncoupling Synthesis of DHTTF Derivatives and Their Related Compounds

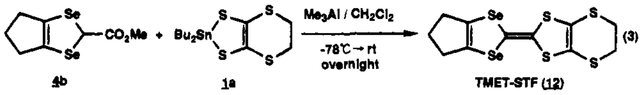
| | | | reaction conditions | | | | |
|---|---|---|---|---|---|---|---|
| entry | organotin compound | ester | Lewis acid | temp, °C | time | product | isolated yield, % |
| 1 | **1a** | **3a** | $TiCl_4$ | −78 → rt[a] | overnight | **6a** | 28[b,d] |
| 2 | **1a** | **3a** | $Me_2AlCl$ | −78 → rt | overnight | **6a** | 44[b,d] |
| 3 | **1a** | **3a** | $Me_3Al$ | −78 → rt | overnight | **6a** | 57[b,d] |
| 4 | **1a** | **3b** | $Me_3Al$ | −78 → rt | overnight | **6b** | 61[b,d] |
| 5 | **1b** | **3a** | $Me_3Al$ | −78 → rt | overnight | **7a** | 9[c,e] |
| 6 | **1b** | **3a** | $Me_3Al$ | −78 → 15 | 3 h | **7a** | 36[c,e] |
| 7 | **1b** | **3b** | $Me_3Al$ | −78 → rt | 6 h | **7b** | 22[b,e] |
| 8 | **1c** | **3a** | $Me_3Al$ | rt | 3 days | **8** | 67[b,f] |
| 9 | **2a** | **3a** | $Me_3Al$ | rt | 6 days | **9** | 83[b] |
| 10 | **2b** | **3a** | $Me_3Al$ | rt | 5 days | **10** | 33[b,g] |

[a] Room temperature. [b] After column chromatography on silica gel. [c] After column chromatography (silica gel, *n*-hexane−$CHCl_3$) followed by recrystallization from $CHCl_3$−EtOH. [d] Overall yield from **5a**. [e] Overall yield from **5b**. [f] Overall yield from **5c**. [g] Overall yield from 1,2-dibromocyclopentene.

examined.[13] Similarly, the $Me_3Al$-mediated reaction of **1a** with **3b**[12] gave the 1,3-dithiane derivative **6b** in 61% yield based on **5a** (entry 4). A vinylenedithio-annelated DHTTF **7a** seems to be sensitive to the acidic conditions, since the treatment of **1b** with **3a** for a prolonged period of time resulted in a decrease in yield of **7a** (entry 5). Therefore, we shortened the length of the reaction time when the treatment of **1b** with both **3a** and **3b** was carried out (entries 6 and 7). A thieno-annelated DHTTF **8**[14] could be formed slowly by reaction **1c** with **3a** (entry 8). The reaction of tin selenolates **2a** and **2b** was relatively very slow in comparison with the reaction of tin thiolates, but the selenium analogue of DHTTF derivatives **9** and **10** could be obtained by this new noncoupling reaction (entries 9 and 10).

Next, we investigated the synthetic method of the esters **4** so as to construct DSDTF derivatives by the noncoupling reaction. Transmetalation of **1a** and **2b** with *n*-butyllithium (2 equiv) at −78 °C, followed by treatment of methyl dichloroacetate, afforded the desired esters **4a** (32% yield based on **5a**) and **4b**[15] (54% yield based on 1,2-dibromocyclopentene), respectively. Tin selenolate **2a** reacted quite smoothly with **4a** in the presence of $Me_3Al$ (2 equiv), DMET (**11**) was obtained in 43% yield (eq 2).[16] Similarly, the $Me_3Al$ (2 equiv)-promoted reaction of ester **4b** with tin thiolate **1a** gave TMST-STF (**12**)[17] in 37% yield (eq 3).[18]





The DHTTF derivatives **6a**, **7a**, **8**, **9**, and **10** afforded their charge-transfer salts with TCNQ in various organic solvents. Single crystals of **6a**−TCNQ[19], **8**−TCNQ[19], **9**-TCNQ,[19] and **10**−TCNQ[19] could be obtained by recrystallization from both THF and $CH_3CN$, respectively.[20] The crystal growth of **6a**−$AsF_6$[19] and **10**−$ClO_4$[19] was carried out by electrocrystallization at a constant current (0.9 $\mu$A) in PhCl.[21] Thus, it was proved that the DHTTF derivatives, synthesized by us, possess the property of the electron donor sufficiently.

In conclusion, we are now in a position to synthesize unsymmetrical TTFs without tedious separation procedures. Further, a series of DHTTF derivatives may break a way to the new class of tetrathiafulvalenes. We are actively investigating the preparation and physical characterization of charge-transer complexes using unsymmetrical TTF derivatives with both inorganic and organic acceptors.

**Supplementary Material Available:** Characterization data for all new compounds **6**−**10** and also the established ones, **11** and **12** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) The procedure of entry 3 is representative. To a solution of **1a** (2 mmol based on **5a**) in $CH_2Cl_2$ (30 mL) was added at −78 °C under nitrogen a solution of $Me_3Al$ in hexane (Kanto Chemical Co., 1.02 M, 4 mmol), and then 2 mmol of **3a** was added. The reaction mixture was gradually warmed to room temperature. After the solution was stirred overnight, aqueous $NaHCO_3$ was dropwise added at 0 °C, and the resulting mixture was filtered through Celite. The organic layer was separated, dried over anhydrous $MgSO_4$, and condensed. The product was isolated by silica gel column chromatography using *n*-hexane−$CH_2Cl_2$ as an eluent.

(14) An alternative synthetic method of **8** is as follows. Similarly to preparation of **2b**, except for addition of elemental sulfur instead of Se powder, two consecutive stepwise reactions of 3,4-dibromothiophene, followed by treatment with $Cl_2SnBu_2$, gave **1c**. Noncoupling reaction of **1c** with **3a** afforded **8** in *ca.* 19% overall yield from 3,4-dibromothiophene. However, the isolated **8** via this synthetic route contained small amounts of impurities.

(15) Ester **4b** could also be prepared by the direct reaction of the dilithium salt of cyclopentene-1,2-diselenol with methyl dichloroacetate in 50% overal yield from 1,2-dibromocyclopentene.

(16) This reaction was carried out on a 0.3-mmol scale in $CH_2Cl_2$ (2 mL) under nitrogen.

(17) Trimethylene(ethylenedithio)diselenadithiafulvalene, see ref 11.

(18) This reaction was carried out on a 0.3-mmol scale in $CH_2Cl_2$ (5 mL) under nitrogen.

(19) The details of crystal structure and physical property will be reported in a subsequent paper.

(20) The single crystals of **7a**−TCNQ, prepared by recrystallization from $CH_3CN$, were not so good.

(21) Under the similar electrochemical oxidation conditions, **6a**−$ClO_4$ and **7a**−$ClO_4$ were obtained as powders.