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 $(MDT-TTF)_2AuI_2^2$, 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 crosscoupling 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 thiolates⁵ is attractive for several non-phosphite coupling routes to the central C=C bond of unsymmetrical TTFs.⁶ Although Mori and Inokuchi⁷ 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 dihydrotetra-

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Figure 1. Organotin compounds and esters.



Figure 2. DHTTF derivatives and their related compounds.

thiafulvalene (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 acids⁹ and also that the DHTTF derivatives become new electron donors.

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 5d¹⁰ with MeMgBr (3.3 equiv) in THF, followed by trapping with Cl_2SnBu_2 at -78 °C (eq 1). Although



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 TiCl₄, Me₂AlCl, and Me₃Al (entries 1-3). Trimethylaluminum gave the best result among the Lewis acids

(12) Esters 3a and 3b were obtained from Tokyo Kasei Co.

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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 AuI₂: 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 IBr₂: Kikuchi, K.; Murata, K.; Honda, V.; Mariti, T.; Saito, K.; Lehiguro, T.; Kikuchi, K.; Murata, K.; Honda, V.; Mariti, T.; Saito, K.; Lehiguro, T.; Kikuchi, K.; Murata, K.; Honda, Y.; Namiki, T.; Baito, K.; Murata, K.; Honda, Y.; Namiki, T.; Saito, K.; Murata, K.; Honda, Y.; Namiki, T.; Murata, K.; Honda, Y.; Namiki, T.; Murata, K.; Honda, Y.; Namiki, T.; Murata, K.; Honda, Y.; Namiki, Y.; Murata, K.; Honda, Y.; Namiki, T.; Yahu, **196**, 56, 4241–4244. $X = 1_3$ and $15I_2$. Kikuchi, K.; Murata, K.; Hohda, 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.;

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⁽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.

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

			rea	ction condit			
entry	organotin compound	ester	Lewis acid	temp, °C	time	product	isolated yield, %
1	1a	3a	TiCl ₄	$-78 \rightarrow rt^a$	overnight	6a	28 ^{b,d}
2	1a	3a	Me ₂ AlCl	-78 → rt	overnight	6a	$44^{b,d}$
3	1a	3a	Me ₃ Al	-78 → rt	overnight	ба	57 ^{b,d}
4	1a	3b	Me ₃ Al	-78 → rt	overnight	6b	61 ^{b,d}
5	1b	3a	Me ₃ Al	-78 → rt	overnight	7a	9 ^{c,e}
6	1b	3a	Me ₃ Al	-78 - 15	3 h	7a	36 ^{c,e}
7	1b	3b	Me ₃ Al	—78 → rt	6 h	7b	22 ^{b,e}
8	1c	3a	Me ₃ Al	rt	3 days	8	67 ^{<i>b</i>,<i>f</i>}
9	2a	3a	Me ₃ Al	rt	6 days	9	83 ^b
10	2b	3a	Me ₃ Ai	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-CHCl₃) followed by recrystallization from CHCl₃-EtOH. ^{*d*} Overall yield from **5a**. ^{*c*} Overall yield from **5b**. ^{*f*} Overall yield from **5c**. ^{*g*} Overall yield from 1,2-dibromocyclopentene.

examined.¹³ Similarly, the Me₃Al-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

(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.

-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 Me₃Al (2 equiv), DMET (**11**) was obtained in 43% yield (eq 2).¹⁶ Similarly, the Me₃Al (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**-TCNQ¹⁹, **8**-TCNQ¹⁹, **9**-TCNQ,¹⁹ and **10**-TCNQ¹⁹ could be obtained by recrystallization from both THF and CH₃CN, respectively.²⁰ The crystal growth of **6a**-AsF₆¹⁹ and **10**-ClO₄¹⁹ was carried out by electrocrystallization at a constant current (0.9 μ 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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(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 CH₃CN, were not so good.

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

⁽¹³⁾ The procedure of entry 3 is representative. To a solution of 1a (2 mmol based on 5a) in CH₂Cl₂ (30 mL) was added at -78 °C under nitrogen a solution of Me₃Al 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 NaHCO₃ was dropwise added at 0 °C, and the resulting mixture was filtered through Celite. The organic layer was separated, dried over anhydrous MgSO₄, and condensed. The product was isolated by silica gel column chromatography using *n*-hexane-CH₂Cl₂ as an eluent. (14) An alternative synthetic method of 8 is as follows. Similarly to