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# A Rearrangement Approach to the Synthesis of New Electron Donors: TTF and DSDTF Derivatives with a 1,3-Dioxolane Ring

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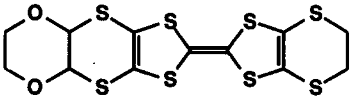
**Abstract:** The synthesis of TTF (tetrathiafulvalene) and DSDTF (diselenadithiafulvalene) derivatives with a 1,3-dioxolane ring (2-5) has been accomplished via the $MeAl_3$-promoted reaction of the organotin thiolate (7) with esters (**8a-c** and **9**). The electrical resistivity of the TCNQ complex of **2** exhibited metallic temperature dependance on a compressed pellet. © 1997 Elsevier Science Ltd.

We have already reported the synthesis of the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] derivative fused with a 1,4-dioxane ring (**1**) via cross-coupling reaction between ketone **6** and 4,5-ethylenedithio-1,3-dithiole-2-thione.[1] Meanwhile, though an attempt to prepare **1** by the $Me_3Al$-promoted reaction[2] of organotin thiolate **7**[1] with ester **8a** was unsuccessful, this reaction resulted in the production of a new TTF derivative with a 1,3-dioxolane ring (**2**) on the basis of the $Me_3Al$-mediated rearrangement of the existing two S,O-acetals in the two fused six-membered heterocycles to the five-membered O,O- and S,S-acetals. Thus, our search for new organic metals has led us to explore the metallic charge-transfer (CT) complexes using such a TTF derivative and its analogs as π-electron donors. In this paper, we describe the synthesis of the TTF and DSDTF derivatives with a 1,3-dioxolane ring (**2-5**), their electrochemical properties, the molecular structure of **2**, and the temperature dependance of the resistivity of the TCNQ (tetracyanoquinodimethane) complex with **2**.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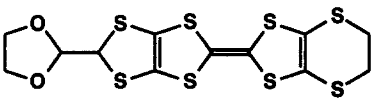
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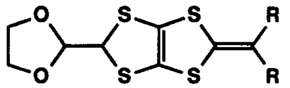
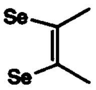


**3**: R-R =


**4**: R-R =


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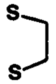

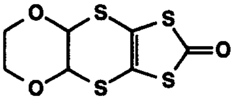
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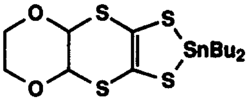
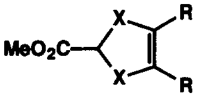
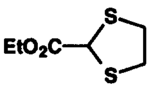


**7**



**8a**: X=S, R-R =$S(CH_2)_2S$
**8b**: X = S, R = R = H
**8c**: X = Se, R = R = Me



**9**

The results of the $Me_3Al$-mediated reaction of organotin thiolate **7**, derived from ketone **6** via a Grignard reaction,[1] with esters **8a-c** and **9** are summarized in Table 1.[3] As to the synthesis of **2**, the addition order of $Me_3Al$, tin thiolate **7**, and ester **8a** affected the yield of the product. Initially, to a $CH_2Cl_2$ solution of **7** was added at -78 °C a hexane solution of $Me_3Al$, and then an ester **8a**/$CH_2Cl_2$ solution was added (entry 1). Under these operating conditions, clean reaction did not occur, and the yield of **2** was only 3%. The alternative addition order: (i) ester **8a**, (ii) $Me_3Al$, and then (iii) tin thiolate **7** resulted in an increase in the yield of **2** (entry 2). However, the length of the reaction time had little effect on the yield of **2** (entry 3).[4] Similarly to the preparation of **2**, reaction with ester **8b** gave the TTF derivative **3** (entry 4), and reaction with **8c** produced the DSDTF derivative **4** (entry 5). In addition, the DHTTF (dihydrotetrathiafulvalene) derivative **5** could be obtained by reaction with **9** in 14% yield from ketone **6** (entry 6).

**Table 1.** Synthesis of **2-5** via $Me_3Al$-mediated reaction of **7** with esters

| Entry | Ester | Reaction temp. | Reaction time | Product | Isolated yield (%)[a] |
|---|---|---|---|---|---|
| 1 | **8a** | -78 °C → rt[b] | 4 days | **2** | 3[c] |
| 2 | **8a** | -78 °C → rt | overnight | **2** | 14[c] |
| 3 | **8a** | -78 °C → rt | 2 days | **2** | 16[c] |
| 4 | **8b** | -78 °C → rt | 2 days | **3** | 14[d] |
| 5 | **8c** | -78 °C → rt | 2 days | **4** | 27[c] |
| 6 | **9** | -78 °C → rt | 2 days | **5** | 14[c] |

[a]Overall yield from ketone **6**. [c]Room temperature. [c]After column chromatography on silica gel followed by recrystallization. [d]After column chromatography on silica gel.

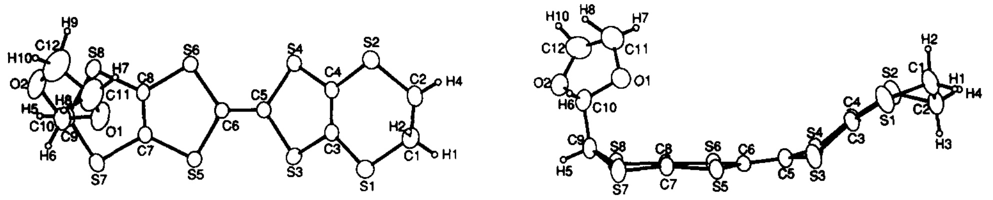
Electrochemical properties of new compounds **2-5** were investigated by cyclic voltammograms (CVs), and the results are summarized in Table 2. The CVs of compounds **2** and **4** showed three pairs of reversible redox waves, whereas the CV of the TTF derivative **3** consisted of two pairs of reversible redox waves though the $\pi$-electron system of **3** is the same as that of **2** or **4**. The CV of the DHTTF derivative **5** exhibited two pairs of reversible redox waves, and the $E_1$ value of **5** (0.62 V) is higher by 0.09 V than that of **3**. The $E_1$ values of **3** (0.53 V in PhCN and 0.54 V in $CH_3CN$) are slightly higher than those of MDT-TTF (methylenedithio-tetrathiafulvalene, 0.47 V in PhCN and 0.49 V in $CH_3CN$), suggesting that the electron-donating ability of **3** is somewhat decreased by the existence of a 1,3-dioxolane ring.

**Table 2.** Oxidation potentials of **2-5** [a]

| Compound | $E_1$ | $E_2$ | $E_3$ | $\Delta E$ ($E_2$-$E_1$) |
|---|---|---|---|---|
| **2** | 0.57 | 0.84 | 1.58 | 0.27 |
| **3** | 0.53 | 0.92 | | 0.39 |
| **4** | 0.53 | 0.83 | 1.58 | 0.30 |
| **5** | 0.62 | 1.02 | | 0.40 |

[a]V vs. saturated calomel electrode (SCE), 0.1 M n-$Bu_4NClO_4$ in PhCN, Pt electrode, at room temperature, under nitrogen, scan rate 50 mV $s^{-1}$.

The single crystal of **2** was obtained by recrystallization from $CS_2$, and its molecular structure was determined by X-ray diffraction.[5] As depicted in Fig. 1, compound **2** has a nonplanar structure, in which the 1,3-dioxolane ring is bonded perpendicularly to the MET [methylenedithio(ethylenedithio)tetrathiafulvalene] molecule and the MET skeleton itself is forced to incline toward the dioxolane ring. Accordingly, the dioxolane ring added to the MET framework makes it bulkier than most donors so far prepared.



(a) (b)

**Figure 1.** Molecular structure of **2**: (a) the over view; (b) the side view

Next, we examined the formation of TCNQ complexes with **2**-**5** and their conducting behavior. Preparation of TCNQ complexes was carried out by treatment of **2**-**5** with TCNQ (1 equiv) in TCE (1,1,2-trichloroethane) or $CH_3CN$ followed by recrystallization of the resulting black or dark green solid from TCE or $CH_3CN$ by slow cooling. Table 3 summarizes the electrical conductivities of the CT complexes thus obtained. In spite of the presence of the bulky 1,3-dioxolane ring, the TTF derivatives **2** and **3** produced the conducting TCNQ complexes with room temperature compaction conductivities of high values (12 and 9.1 $Scm^{-1}$), respectively. In addition, surprisingly, the TCNQ complex with **2** exhibited metallic temperature dependance of the resistivity in cooling and warming processes with metal to semiconductor transitions (Fig. 2).

**Table 3.** Electrical properties of the TCNQ complexes

| Donor | Solvent | D:TCNQ[a] | $\sigma_{rt}$ / $Scm^{-1}$[b] |
|---|---|---|---|
| **2** | TCE | 1:1 | 12[c] (metallic) |
| **3** | $CH_3CN$ | 5:4 | 9.1[c] (Ea = 60 meV) |
| **4** | TCE | 1:2 | < $10^{-6}$[c] |
| **5** | $CH_3CN$ | 1:1 | < $10^{-6}$[c] |

[a] Determined by elemental analysis. [b] Room temperature conductivity measured by a four-probe technique. [c] Measured on a compressed pellet.

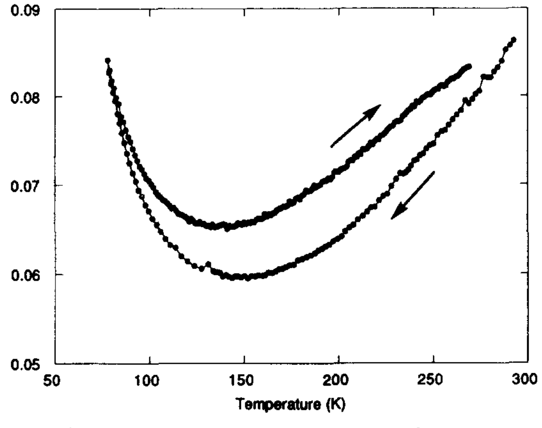


**Figure 2.** Temperature dependance of the resistivity of the TCNQ complex with **2**

In conclusion, we developed a synthetic method for the construction of TTF and DSDTF derivatives with a 1,3-dioxolane ring, and found that the MET derivative with a bulky 1,3-dioxolane ring produced the metallic TCNQ complex. On the other hand, for the π-electron donors leading to metallic conducting salts, it has been pointed out that the planar structure of donor molecules is necessary to form the segregating donor stack.[6]

Therefore, this finding will open up a way to new molecular designs of π-electron donors. Further investigation on the preparation and X-ray analysis of radical-cation salts derived from new donors **2** and **3** is in progress.[7]

## References and Notes

1. Yamada, J.; Nishimoto, Y.; Tanaka, S.; Nakanishi, R.; Hagiya, K.; Anzai, H. *Tetrahedron Lett.*, **1995**, *36*, 9509-9512.
2. (a) Yamada, J.; Amano, Y.; Takasaki, S.; Nakanishi, R.; Matsumoto, K.; Satoki, S.; Anzai, H. *J. Am. Chem. Soc.*, **1995**, *117*, 1149-1150. (b) Yamada, J.; Satoki, S.; Mishima, S.; Akashi, N.; Takahashi, K.; Masuda, N.; Nishimoto, Y.; Takasaki, S.; Anzai, H. *J. Org. Chem.*, **1996**, *61*, 3987-3995.
3. Selected physical and spectroscopic data, **2**: mp 175 °C (decomp); $^1$H NMR (400MHz, $CDCl_3$) $\delta$ 5.22 (d, J = 5.6 Hz, 1 H), 5.07 (d, J = 5.6 Hz, 1 H), 4.07-3.96 (m, 4 H), 3.35-3.23 (m, 4 H); MS m/z (% relative intensity) 444 (13, $M^+ + 2$), 442 (37, $M^+$), 73 (100); calcd for $C_{12}H_{10}O_2S_8$ m/z 441.8447, measured m/z 441.8467. **3**: mp 113-114 °C; $^1$H NMR (400MHz, $CDCl_3$) $\delta$ 6.33 (bs, 2 H), 5.23 (d, J = 5.9 Hz, 1 H), 5.06 (d, J = 5.9 Hz, 1 H), 4.09-3.95 (m, 4 H); MS m/z (% relative intensity) 354 (26, $M^+ + 2$), 352 (100, $M^+$), 73 (48); calcd for $C_{10}H_8O_2S_6$ m/z 351.8849, measured m/z 351.8848. **4**: mp 198 °C (decomp); $^1$H NMR (400MHz, $CDCl_3$) $\delta$ 5.22 (d, J = 5.6 Hz, 1 H), 5.03 (d, J = 5.6 Hz, 1 H), 4.08-3.94 (m, 4 H), 2.00 (s, 6 H); MS m/z (% relative intensity) 476 (100, $M^+ + 2$), 474 (77, $M^+$), 73 (77); calcd for $C_{12}H_{12}O_2S_4{}^{80}Se_2$ m/z 475.8051, measured m/z 475.8052. **5**: mp 137 °C (decomp); $^1$H NMR (400MHz, $CDCl_3$) $\delta$ 5.22 (d, J = 5.9 Hz, 1 H), 5.04 (d, J = 5.9 Hz, 1 H), 4.08-3.94 (m, 4 H), 3.52-3.42 (m, 4 H); MS m/z (% relative intensity) 356 (20, $M^+ + 2$), 354 (71, $M^+$), 73 (100); calcd for $C_{10}H_{10}O_2S_6$ m/z 353.9005, measured m/z 353.8987.
4. A typical procedure: To a solution of ester **8a** (0.80 mmol) in $CH_2Cl_2$ (4.0 mL) was added at -78 °C under nitrogen a hexane solution of $Me_3Al$ (1.02 M × 1.6 mL), and then a solution of crude tin thiolate **7** (377mg, 0.80 mmol) in $CH_2Cl_2$ (8.0 mL) was added. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 2 days. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, and the resulting suspension was filtered through Celite®. After the mixture was extracted with several portions of $CHCl_3$, the extracts were combined, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification of the residue on silica gel column chromatography using hexane and hexane-$CH_2Cl_2$ as eluents followed by recrystallization from $CHCl_3$-EtOH gave 58 mg (0.13 mmol) of **2** in 16% yield from ketone **6**.
5. Crystal data for **2**: $C_{12}H_{10}O_2S_8$, M = 442.72, monoclinic, space group $P2_1/n$, a = 6.322(1) Å, b = 25.093(2) Å, c = 10.637(1) Å, $\beta$ = 93.62(1)°, V = 1684.1(3) Å$^3$, Z = 4, $D_c$ = 1.746 gcm$^{-3}$, R = 0.045 (Rw = 0.051) for 6244 observed reflections.
6. For a example, see: Miller, J. S. *Ann. N. Y. Acad. Sci.*, **1978**, *313*, 25-60.
7. Our preliminary investigation on the electrical properties of the $BF_4^-$ and $PF_6^-$ salts based on **2** revealed that these salts exhibited metallic conductive behavior. A detailed study will be reported in a subsequent paper.

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