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Preparation of 4,5-(Alkylmethylenedithio)-1,3-dithiole-2-chalcogenones: Building Blocks for the Mono-alkylated TTF Donors

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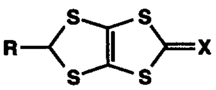
Abstract: 4,5-(Methoxymethylenedithio)-1,3-dithiole-2-chalcogenones **3** and **4** have been alkylated by using R_3Al and RMgX (X = Cl or Br)/$TiCl_4$ complex reagent to give the title compounds **1** and **2**. Cross-coupling of **1a–d** with **5** furnished the mono-alkylated MET derivatives **6a–d**, and the ClO_4 and PF_6 salts of **6b** exhibited metallic conducting behavior for compressed pellets.

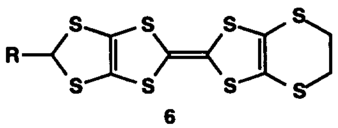
Keywords: dithioles; coupling reactions; electron donors; physical properties

Extensive studies on the preparation of functionalized 1,3-dithiole-2-chalcogenones have been made, since the resulting products serve as building blocks in the TTF synthesis.[1] We have been studying the synthesis of TTF donors with the periphery extended by addition of heterocycles to develop new organic metals,[2] and have found that, as their building blocks, the 1,3-dithiole-2-chalcogenones condensed with a cis-fused heterobicyclic system or a biheterocycle can be prepared via Lewis acid-promoted reactions.[3] However, we have investigated only the utilization of saturated heterocycles for extending the outer hemisphere of the TTF core, and an open question remains concerning the synthesis of TTF donors appending a simple alkyl group. Considering the molecular symmetry to avoid chirality problems,[4] the achiral 4,5-(alkylmethylenedithio)-1,3-dithiole-2-chalcogenones (**1** and **2**) are a good source of the mono-alkylated TTF donors with potentially attractive characteristics,[5] but a practically systematic preparation of **1** or **2** has not been realized.[6] In this communication, we describe the alkylation of 4,5-(methoxymethylenedithio)-1,3-dithiole-2-chalcogenones (**3** and **4**) using an organometallic reagent and an organometallic/Lewis acid complex reagent to obtain **1a–d** and **2a**, the conversion of **1a–d** into the mono-alkylated MET [methylenedithio(ethylenedithio)tetrathiafulvalene] derivatives **6a–d**, and the electrical conducting behavior of their charge-transfer (CT) materials.



R = alkyl
1: X = O
2: X = S

a: R = Me
b: R = Et
c: R = *n*-Bu
d: R = *n*-C_8H_{17}



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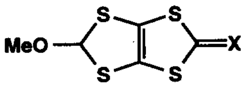

3: X = O
4: X = S

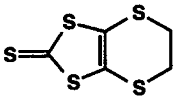

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Table 1. Alkylation of **3** and **4**[a]

Entry	Substrate	Reagent (equiv.)	Condition(s)	Product (yield[b], %)
1	**3**	Me_2Zn (0.5)/$TiCl_4$ (1.0)	–78 °C → 0 °C	**1a** (3)
2	**3**	MeMgBr/$TiCl_4$ (1.0)	–78 °C → 0 °C	**1a** (13)
3	**3**	MeLi/$TiCl_4$ (1.0)	–78 °C → 0 °C	**1a** (20)
4	**3**	Me_3Al (1.2)	rt[c], 8 min	**1a** (47)
5	**4**	Me_3Al (1.2)	rt, 10 min	**2a** (55)
6	**3**	Me_3Al (2.0)	rt, 5 min	**1a** (63)
7	**3**	Et_3Al (2.0)	rt, 5 min	**1b** (31)
8	**3**	Et_3Al (1.2)	rt, 10 min	**1b** (56)
9	**3**	BuLi/BF_3·OEt_2 (1.0)	–78 °C → 0 °C	**1c** (3)
10	**3**	BuLi/$TiCl_4$ (1.0)	–78 °C → 0 °C	**1c** (10)
11	**3**	BuLi/$TiCl_4$ (2.0)	–78 °C → 0 °C	**1c** (20)
12	**3**	BuLi/$TiCl_4$ (3.0)	–78 °C → 0 °C	**1c** (19)
13	**3**	BuMgCl/$TiCl_4$ (2.0)	–78 °C → 0 °C	**1c** (30)
14	**3**	BuMgCl/$TiCl_4$ (3.0)	–78 °C → 0 °C	**1c** (28)
15	**3**	BuMgCl/$TiCl_4$ (2.0)	–78 °C → rt	**1c** (34)
16	**3**	C_8H_{17}MgBr/$TiCl_4$ (2.0)	–78 °C → 0 °C	**1d** (29)
17	**3**	C_8H_{17}MgBr/$TiCl_4$ (3.0)	–78 °C → 0 °C	**1d** (27)
18	**3**	C_8H_{17}MgBr/$TiCl_4$ (2.0)	–78 °C → rt	**1d** (38)

[a] All reactions were carried out in dry CH_2Cl_2 under nitrogen on a 0.5 or 1.0 mmol scale. [b] Isolated yield after column chromatography on silica gel. [c] Room temperature.

Our preparation of **1a–d** and **2a**[7] was based on the reaction of **3**[8] and **4**[9] with an alkylating reagent such as $R_2Zn/TiCl_4$,[10] RMgX (X = Cl or Br)/$TiCl_4$,[10] RLi/$TiCl_4$,[10] R_3Al, or RLi/BF_3·OEt_2. The results are summarized in Table 1. For methylation of **3**, the $TiCl_4$-mediated reactions with Me_2Zn, MeMgBr, and MeLi gave the desired product **1a** in 3–20% yields along with small amounts of the recovered **3** (entries 1–3), whereas the reaction with Me_3Al alone enhanced the yield of **1a** (47%, entry 4). Similarly, reaction of **4** with Me_3Al afforded the methylated thione **2a** in 55% yield (entry 5).[11] More encouraging was the yield of up to 63% when **3** was reacted with 2 equiv. of Me_3Al (entry 6). Contrarily, the use of 2 equiv. of Et_3Al in place of 1.2 equiv. of Et_3Al resulted in a decrease in yield of the ethylated product **1b** (entries 7 and 8). For introduction of the *n*-butyl and *n*-octyl groups into **3**, we examined the reactions with the readily available organolithium and Grignard reagents in the presence of a Lewis acid. Although varying the Lewis acid used for reaction of **3** with BuLi from BF_3·OEt_2 to $TiCl_4$ led to an increase in yield of the butylation product **1c** (entries 9 and 10),[12] the yield was low (10%). Our attempt to improve this low yield was somewhat successful with the use of 2 equiv. of BuLi/$TiCl_4$ (entry 11), but the use of a more equiv. of this complex reagent had a negligible influence on the yield of **1c** (entry 12). On the other hand, under the same reaction conditions as employed for entries 11 and 12, higher yields of **1c** were obtained by using BuMgCl/$TiCl_4$ instead of BuLi/$TiCl_4$ (entries 13 and 14). Eventually, the reaction conditions shown in entry 15 gave the best result. Also, an analogous tendency as can be found in entries 13–15 was observable for the reaction of **3** with C_8H_{17}MgBr/$TiCl_4$ (entries 16–18).

The $(MeO)_3P$-promoted cross-coupling of the resultant ketones **1a–d** with 2 equiv. of thione **5** in toluene at 110 °C for 2 h produced the alkylated MET derivatives **6a–d** in 66%, 59%, 40%, and 43% yields, respectively. Table 2 shows their oxidation potentials measured by cyclic voltammetry together with those of MET. Compounds **6a–d** showed three pairs of reversible redox wave, and their values of E_1 and E_2 are all comparable to those of MET independent of the type of alkyl group.

Table 2. Oxidation potentials of MET and **6a–d**[a]

Compound	E_1	E_2	E_3	$\Delta E\ (E_2\text{-}E_1)$
MET	0.58	0.85	1.54	0.27
6a	0.59	0.85	1.61	0.26
6b	0.59	0.85	1.70	0.26
6c	0.58	0.84	1.72	0.26
6b	0.59	0.85	1.71	0.26

[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 methylated and ethylated MET derivatives [Me-MET (**6a**) and Et-MET (**6b**)] reacted with TCNQ to give CT complexes with relatively high room temperature conductivities for compressed pellets [**6a**·TCNQ, σ_{rt} = 6.3 S cm^{-1} (E_a = 0.13 eV); **6b**·TCNQ, σ_{rt} = 0.21 S cm^{-1} (E_a = 0.13 eV)]. Moreover, despite the presence of long alkyl chains such as the n-butyl and n-octyl groups, **6c,d** also formed TCNQ complexes, though their compressed pellets exhibited low conductivities (**6c**·TCNQ, $\sigma_{rt} = 2.8 \times 10^{-6}$ S cm^{-1}; **6d**·TCNQ, $\sigma_{rt} = 1.6 \times 10^{-6}$ S cm^{-1}). In addition, while the single crystals of the AuI_2, BF_4, ClO_4, and PF_6 salts of Me-MET[13] were semiconductive (Table 3), the temperature dependence of resistance of the Et-MET salts with ClO_4^- and PF_6^- anions[13] exhibited metallic conducting behavior for compressed pellets, as shown in Figure 1.[14]

Further investigation of the incorporation of not only a longer alkyl chain but also another functional group into **1** or **2** via our synthetic method reported herein, followed by construction of the achiral mono-functionalized TTF donors, is in progress.

Table 3. Conducting behavior of the **6a,b** salts

D[a]	A[b]	D:A[c]	σ_{rt} / S cm^{-1}[d]
6a	AuI_2^-	5:2	8.4×10^{-3}[e] (E_a = 0.23 eV)
6a	BF_4^-	3:2	5.5×10^{-4}[e,f] (E_a = 0.19 eV)
6a	ClO_4^-	–[g]	4.2×10^{-3}[e] (E_a = 0.18 eV)
6a	PF_6^-	5:2	1.4×10^{-1}[e] (E_a = 0.12 eV)
6b	AuI_2^-	1:1	1.3×10^{-3}[h] (E_a = 0.30 eV)
6b	BF_4^-	5:2	2.5[h] (E_a = 0.083 eV)
6b	ClO_4^-	–[g]	26[h] (metallic)
6b	PF_6^-	5:2	17[h] (metallic)

[a] Donor. [b] Anion. [c] Determined by elemental analysis. [d] Room temperature conductivity measured by a four-probe technique unless otherwise noted. [e] Measured on a single crystal. [f] Measured by a two-probe technique. [g] Not determined because this complex may explode during analysis. [h] Measured on a compressed pellet.

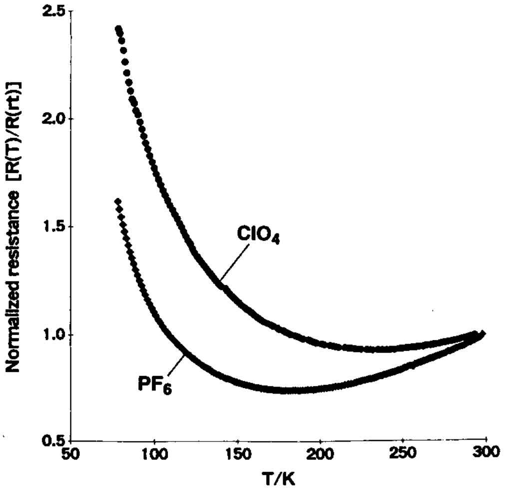

Figure 1. Temperature dependence of relative electrical resistance of the metallic Et-MET (**6b**) salts

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4. For example, in the case of the preparation of chiral 5,6-dihydro-5,6-dialkyl-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-chalcogenones, the availability of a chiral source is limited, see: Matsumiya, S.; Izuoka, A.; Sugawara, T.; Taruishi, T.; Kawada, Y. *Bull. Chem. Soc. Jpn.*, **1993**, *66*, 513–522, and references therein.
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7. Selected date for **1a**: mp 37 °C from CS_2; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (d, J = 6.8 Hz, 3 H), 5.20 (q, J = 6.8 Hz, 1 H); MS (EI) m/z 208 (M^+); calcd for $C_5H_4OS_4$ m/z 207.9145, measured m/z 207.9137. For **1b**: brown viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, J = 7.3 Hz, 3 H), 2.00 (quintet, J = 7.3 Hz, 2 H), 5.06 (t, J = 7.3 Hz, 1 H); MS (EI) m/z 222 (M^+); calcd for $C_6H_6OS_4$ m/z 221.9302, measured m/z 221.9301. For **1c**: brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 7.3 Hz, 3 H), 1.24–1.48 (m, 4 H), 1.95 (q, J = 7.3 Hz, 2 H), 5.08 (t, J = 7.3 Hz, 1 H); MS (EI) m/z 250 (M^+); calcd for $C_8H_{10}OS_4$ m/z 249.9615, measured m/z 249.9614. For **1d**: mp 31–32 °C from EtOH; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3 H), 1.25 (br, 10 H), 1.39–1.46 (m, 2 H), 1.99 (q, J = 7.3 Hz, 2 H), 5.13 (t, J = 7.3 Hz, 1 H); MS (EI) m/z 306 (M^+); calcd for $C_{12}H_{18}OS_4$ m/z 306.0241, measured m/z 306.0238. **2a**: mp 98–99 °C from CH_2Cl_2–EtOH; ^1H NMR (400 MHz, $CDCl_3$) δ 1.81 (d, J = 6.8 Hz, 3 H), 5.40 (q, J = 6.8 Hz, 1 H); MS (EI) m/z 224 (M^+); calcd for $C_5H_4S_5$ m/z 223.8917, measured m/z 223.8916.
8. Compound **3** could be obtained by basic cleavage of thiapentalenedione with NaOMe (2 equiv.) in MeOH followed by treatment with dichloromethyl methyl ether (2 equiv.) in 53% yield.
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11. In marked contrast to the preparation of 4,5-methylenedithio-1,3-dithiole-2-thione, reaction of $(Bu_4N)_2[Zn(dmit)_2]$ with 1,1-dibromoethane under similar conditions gave a trace amount of **2a**, see ref. 3a.
12. In the absence of a Lewis acid, reaction of **3** with BuLi afforded only 2% yield of **1c**.
13. These radical-cation salts were prepared in 1,1,2-trichloroethane by the controlled-current electrocrystallization method, see: (a) Anzai, H.; Delrieu, J. M.; Takasaki, S.; Nakatsuji, S; Yamada, J. *J. Cryst. Growth*, **1995**, *154*, 145–150. (b) Nishikawa, H.; Sato, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Anzai, H.; Yamada, J. *J. Mater. Chem.*, **1999**, *9*, 693–696.
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