HETEROCYCLES, Vol. 60, No. 7, 2003, pp. 1689 - 1695
Received, 21st April, 2003, Accepted, 2nd June, 2003, Published online, 9th June, 2003

SYNTHESIS OF BENZO[1,2-*b*:5,4-*b*']DITHIOPHENE-4,8-DIONE DERIVATIVES

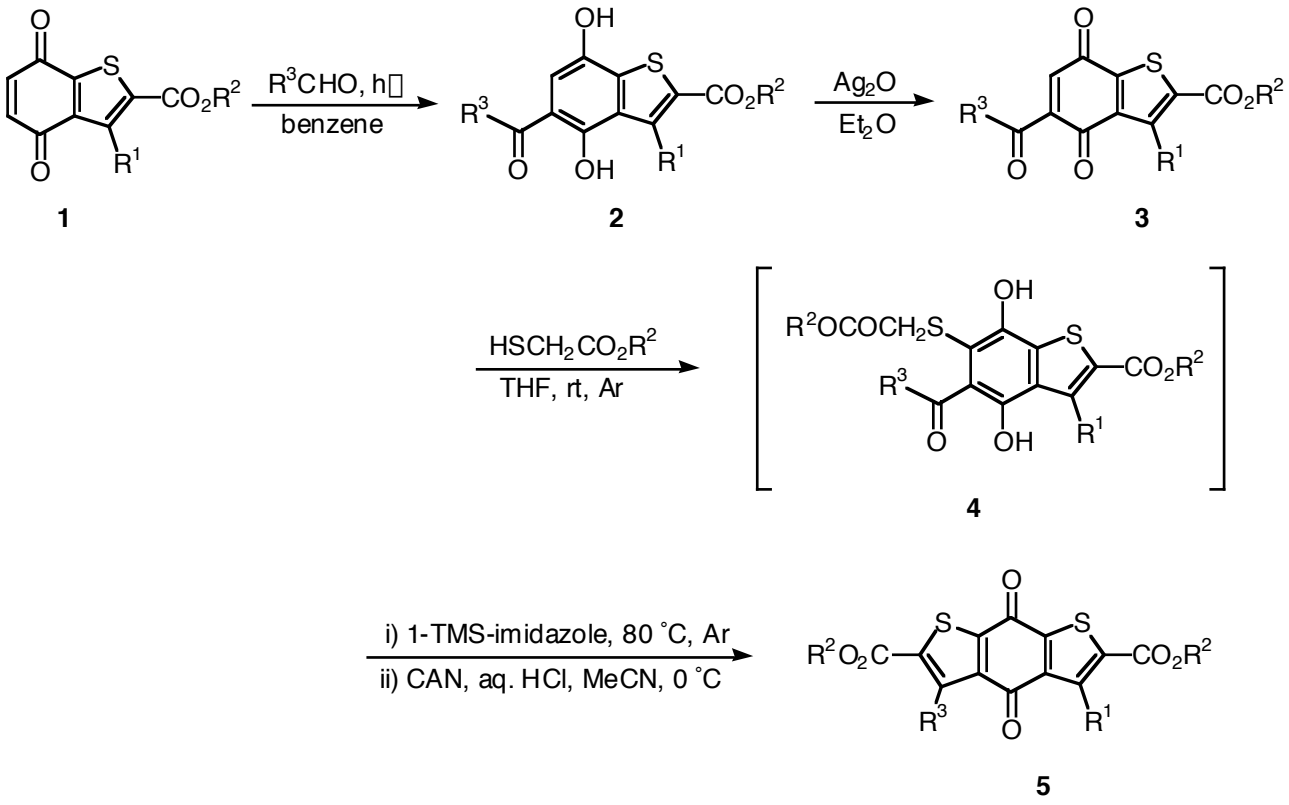
Kazuhiro Kobayashi,* Toshikazu Ogata, Kazuna Miyamoto, Osamu Morikawa, and Hisatoshi Konishi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-minami, Tottori 680-8552, Japan

Abstract- 4,7-Dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**1**) underwent regioselective acylation at the 5-position with a range of aldehydes under irradiation to give the corresponding 5-acyl-4,7-dihydroxybenzo[*b*]thiophene-2-carboxylates (**2**), which were then oxidized with Ag_2O to afford 5-acyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**3**). These acylated benzothiophenquinone derivatives were transformed in one-pot to 4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b'*]dithiophene-2,6-dicarboxylates (**5**) by treatment with mercaptoacetates, followed by 1-trimethylsilylimidazole-mediated cyclization and cerium(IV) ammonium nitrate (CAN) oxidation.

As part of our studies on the development of new methods for the synthesis of heterocycle-fused quinones,[1] we have investigated the possibility of synthesizing benzo[1,2-*b*:5,4-*b'*]dithiophene-4,8-dione derivatives.[2] These compounds are of interest since they exhibit interesting biological activities,[2b,c] synthetic[3] and practical utilities.[4] However, a general and convenient approach to this class of benzodithiophenequinone derivatives is lacking. We now report that 4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b'*]dithiophene-2,6-dicarboxylates (**5**) can be prepared by utilizing the 1-trimethylsilylimidazole-induced thiophene ring formation[5] from mercaptoacetates and 5-acyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**3**), as shown in the Scheme.

The acylated benzothiophenequinone derivatives (**3**) were readily obtained by photoacylation[6] of 4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**1**),[5,7] followed by Ag_2O oxidation[8] of the resulting 5-acyl-4,7-dihydroxybenzo[*b*]thiophene-2-carboxylates (**2**), as shown in the Scheme. Thus, irradiation of **1** in benzene in the presence of aldehydes with a 500 W high pressure mercury arc lamp for 2 days gave **2**. High regioselectivity could be obtained in this photoacylation, though the yields of **2** were



1 **2** **3** **4** **5**

Table. Preparation of benzo[1,2-*b*:5,4-*b'*]dithiophene-4,8-dione derivatives (**5**)

Entry	**1**	R^3	**2** (Yield/%)[a]	**3** (Yield/%)[a]	**5** (Yield/%)[a]
1	**1a** (R^1 = Me, R^2 = Et)	Et	**2a** (41)	**3a** (98)	**5a** (71)
2	**1a**	*n*-Pr	**2b** (42)	**3b** (98)	**5b** (74)
3	**1a**	*i*-Pr	**2c** (33)	**3c** (98)	**5c** (65)
4	**1a**	*i*-Bu	**2d** (38)	**3d** (97)	**5d** (70)
5	**1a**	Ph	**2e** (37)	**3e** (99)	**5e** (64)
6	**1b** (R^1 = H, R^2 = Me)	*n*-Pr	**2f** (54)	**3f** (94)	**5f** (60)

[a]Isolated yields.

moderate,[9] as summarized in the Table. The regioselective acylation at the 5-position was confirmed by NOE experiments of **2c**. Thus, irradiation of the signal at δ 3.06 due to 3-Me resulted in an enhancement (15%) of the signal at δ 13.95 due to 4-OH. An enhancement (19%) of the signal at δ 7.15 due to 6-H was observed on irradiation of the signal at δ 5.14 due to 7-OH. The Ag_2O oxidation of **2** led to rapid and excellent yield conversion to 5-acyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (**3**), as shown in the Table.

The 1-trimethylsilylimidazole-mediated construction of thiophene ring can be applied to these acylthiophenequinones (**3**). Transformation of **3** into benzodithiphenedione derivatives (**5**) was conducted under conditions similar to those described for the preparation of 3-substituted 4,7-dioxo-4,7-

dihydrobenzo[*b*]thiophene-2-carboxylates from 2-acyl-1,4-benzoquinones and mercaptoacetates.[5] Thus, addition of mercaptoacetates to **3** occurred rapidly at room temperature (<5 min), leading to 5-acyl-6-alkoxycarbonylmethylthio-4,7-dihydroxybenzo[*b*]thiophene-2-carboxylates (**4**). By adding 1-trimethylsilylimidazole and heating at 80 ˚C, protection of two hydroxyl groups and intramolecular cyclization reaction took place. After deprotection with hydrochloric acid, followed by oxidation with CAN, 4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b'*]dithiophene-2,6-dicarboxylates (**5**) were isolated in good yields, which are also listed in the Table.

In conclusion, we have demonstrated that benzo[1,2-*b*:5,4-*b'*]dithiophene-4,8-dione derivatives could be prepared by using the photoacylation of benzo[*b*]thiophene-4,7-dione derivatives and the 1-trimethylsilylimidazole-mediated thiophene ring formation. The method may be of value in heterocyclic quinone synthesis.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Perkin-Elmer 1600 Series FT IR spectrophotometer as KBr disk. The ^{1}H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) using TMS as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. *J* values are given in Hz. Low-resolution MS spectral analyses were performed on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). TLC was carried out on a Merck Kieselgel 60 PF_{254}. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. Ethyl 3-methyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (**1a**) was prepared according to the procedure reported by us.[5] Methyl 4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (**1b**) was prepared by the method of Valderrama *et al.*[7] All other chemicals used in this study were commercially available.

Ethyl 5-Propanoyl-4,7-dihydroxy-3-methylbenzo[*b*]thiophene-2-carboxylate (2a). Typical Procedure for the Photoacylation of 4,7-Dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylates (1). A solution of ethyl 3-methyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (**1a**) (0.96 g, 3.9 mmol) and propanal (2.2 g, 39 mmol) in benzene (60 mL) in a pyrex test tube under argon was irradiated with a 500 W mercury arc lamp for 2 days. After evaporation of the solvent, the residue was purified by chromatography on SiO_2 (2:1 hexane-AcOEt) to give **2a** (0.49 g, 41 %) as a pale yellow solid; mp 255-259 ˚C (decomp) (acetone–benzene); ν_{max}/cm^{-1} 3326, 1677, 1631; δ_H 1.26 (3H, t, *J* 7.3), 1.41 (3H, t, *J* 7.3), 3.00 (2H, q, *J* 7.3), 3.06 (3H, s), 4.39 (2H, q, *J* 7.3), 5.09 (1H, br s), 7.12 (1H, s), 13.73 (1H, s). Anal. Calcd for $C_{15}H_{16}O_5S$: C, 58.43; H, 5.23; S, 10.40. Found: C, 58.21; H, 5.22; S, 10.26.

Ethyl 5-Butanoyl-4,7-dihydroxy-3-methylbenzo[*b*]thiophene-2-carboxylate (2b): mp 257–260 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 3386, 1680, 1624; δ_H 1.04 (3H, t, *J* 7.3), 1.41 (3H, t, *J* 7.3), 1.80 (2H, sextet, *J* 7.3), 2.93 (2H, t, *J* 7.3), 3.05 (3H, s), 4.39 (2H, q, *J* 7.3), 4.98 (1H, s), 7.11 (1H, s), 13.80 (1H, s). Anal. Calcd for $C_{16}H_{18}O_5S$: C, 59.61; H, 5.63; S, 9.95. Found: C, 59.88; H, 5.57; S, 10.04.

Ethyl 4,7-Dihydroxy-3-methyl-5-(2-methylpropanoyl)benzo[*b*]thiophene-2-carboxylate (2c): mp 219-222 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 3339, 1681, 1623; δ_H 1.27 (6H, d, *J* 6.9), 1.41 (3H, t, *J* 7.3), 3.06 (3H, s), 3.51 (1H, septet, *J* 6.9), 4.39 (2H, q, *J* 7.3), 5.14 (1H, br s), 7.15 (1H, s), 13.95 (1H, s). Anal. Calcd for $C_{16}H_{18}O_5S$: C, 59.61; H, 5.63; S, 9.95. Found: C, 59.47; H, 5.70; S, 10.12.

Ethyl 4,7-Dihydroxy-3-methyl-5-(3-methylbutanoyl)benzo[*b*]thiophene-2-carboxylate (2d): mp 256–259 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 3403, 1687, 1621 ; δ_H (DMSO-d_6) 0.98 (6H, d, *J* 6.6), 1.33 (3H, t, *J* 7.3), 2.25–2.15 (1H, m), 2.88 (2H, d, *J* 6.6), 2.95 (3H, s), 4.33 (2H, q, *J* 7.3), 7.24 (1H, s), 10.07 (1H, s), 13.73 (1H, s). Anal. Calcd for $C_{17}H_{20}O_5S$: C, 60.70; H, 5.99; S, 9.53. Found: C, 60.68; H, 6.08; S, 9.50.

Ethyl 5-Benzoyl-4,7-dihydroxy-3-methylbenzo[*b*]thiophene-2-carboxylate (2e): mp 238–240 °C (decomp) (acetone-benzene); ν_{max}/cm^{-1} 3300, 1674, 1628; δ_H 1.42 (3H, t, *J* 7.3), 3.11 (3H, s), 4.40 (2H, q, *J* 7.3), 4.84 (1H, br s), 6.95 (1H, s), 7.5-7.7 (5H, m), 13.55 (1H, s). Anal. Calcd for $C_{19}H_{16}O_5S$: C, 64.03; H, 4.53; S, 9.00. Found: C, 63.96; H, 4.76; S, 9.02.

Methyl 5-Butanoyl-4,7-dihydroxybenzo[*b*]thiophene-2-carboxylate (2f): mp 253–256 °C (decomp) (acetone-benzene); ν_{max}/cm^{-1} 3296, 1674, 1624; δ_H (DMSO-d_6) 0.97 (3H, t, *J* 7.3), 1.68 (2H, sextet, *J* 7.3), 3.01 (2H, t, *J* 7.3), 3.89 (3H, s), 7.17 (1H, s), 7.26 (1H, s), 10.20 (1H, br s), 12.73 (1H, br s). Anal. Calcd for $C_{14}H_{14}O_5S$: C, 57.13; H, 4.79; S, 10.89. Found: C, 57.34; H, 5.02; S, 10.75.

Ethyl 3-Methyl-5-propanoyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (3a). Typical Procedure for the Oxidation of 5-Acyl-4,7-dihydroxybenzo[*b*]thiophene-2-carboxylates (2). A solution of **2a** (0.16 g, 0.52 mmol) in THF (5 mL) was added to a stirred suspension of Ag_2O [prepared from 0.44 g (2.6 mmol) of silver nitrate by the literature method[8]] in Et_2O (5 mL) in the presence of anhydrous sodium sulfate (3.0 g). After stirring for 25 min, the solids was filtered off and the filtrate was concentrated. The residual solid was recrystallized from Et_2O–hexane to give pure **3a** (0.16 g, 98%) as an orange solid: mp 158–160 °C (decomp); ν_{max}/cm^{-1} 1720, 1708, 1661; δ_H 1.19 (3H, t, *J* 7.3), 1.41 (3H, t, *J* 7.3), 2.87 (3H, s), 2.92 (2H, q, *J* 7.3), 4.40 (2H, q, *J* 7.3), 6.96 (1H, s). Anal. Calcd for $C_{15}H_{14}O_5S$: C, 58.81; H, 4.61; S, 10.47. Found: C, 58.81; H, 4.80; S, 10.32.

Ethyl 5-Butanoyl-3-methyl-4,7-dioxo-4,7dihydrobenzo[*b*]thiophene-2-carboxylate (3b): mp 120–125 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 1718, 1697, 1660; δ_H 0.99 (3H, t, *J* 7.3), 1.41 (3H,

t, *J* 7.3), 1.80 (2H, sextet, *J* 7.3), 2.87 (5H, s and t, *J* 7.3), 4.40 (2H, q, *J* 7.3), 6.94 (1H, s). Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.99; H, 5.03; S, 10.01. Found: C, 59.86; H, 5.24; S, 10.04.

Ethyl 3-Methyl-5-(2-methylpropanoyl)-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (3c): mp 133–136 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 1721, 1694, 1660; δ_H 1.19 (6H, d, *J* 6.9), 1.41 (3H, t, *J* 7.3), 2.86 (3H, s), 3.20 (1H, septet, *J* 6.9), 4.40 (2H, q, *J* 7.3), 6.86 (1H, s). Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.99; H, 5.03; S, 10.01. Found: C, 59.95; H, 5.25; S, 9.97.

Ethyl 3-Methyl-5-(3-methylbutanoyl)-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (3d): mp 140–142 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 1719, 1696, 1660; δ_H 0.99 (6H, d, *J* 6.9), 1.41 (3H, t, *J* 7.3), 2.15–2.3 (1H, m), 2.78 (2H, d, *J* 6.9), 2.87 (3H, s), 4.40 (2H, q, *J* 7.3), 6.92 (1H, s). Anal. Calcd for $C_{17}H_{18}O_5S$: C, 61.06; H, 5.43; S, 9.59. Found: C, 61.12; H, 5.53; S, 9.54.

Ethyl 5-Benzoyl-3-methyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (3e): mp 125–128 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 1721, 1682, 1660; δ_H 1.42 (3H, t, *J* 7.3), 2.84 (3H, s), 4.42 (2H, q, *J* 7.3), 6.89 (1H, s), 7.51 (2H, t, *J* 7.6), 7.66 (1H, t, *J* 7.6), 7.90 (2H, d, *J* 7.6). Anal. Calcd for $C_{19}H_{14}O_5S$: C, 64.40; H, 3.98; S, 9.05. Found: C, 64.18; H, 4.04; S, 8.85.

Methyl 5-Butanoyl-4,7-dioxo-4,7-dihydrobenzo[*b*]thiophene-2-carboxylate (3f): mp 84–87 °C (decomp) (Et_2O-hexane); ν_{max}/cm^{-1} 1713, 1693, 1669; δ_H 0.98 (3H, t, *J* 7.3), 1.72 (2H, sextet, *J* 7.3), 2.90 (2H, t, *J* 7.3), 3.97 (3H, s), 7.05 (1H, s), 8.14 (1H, s). Anal. Calcd for $C_{14}H_{12}O_5S$: C, 57.52; H, 4.14; S, 10.97. Found: C, 57.48; H, 4.30; S, 10.76.

Diethyl 3-Ethyl-5-methyl-4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5a). Typical Procedure for the Preparation of Dibenzothiophenequinone Derivatives (5). To a stirred solution of **3a** (80 mg, 0.26 mmol) in THF (1.6 mL) was added ethyl mercaptoacetate (31 mg, 0.26 mmol). After confirmation of the absence of the starting material using a TLC analysis (1:3 EtOAc-hexane) (*ca.* 5 min), THF was removed under reduced pressure. To the residue was added 1-trimethylsilylimidazole (0.18 g, 1.3 mmol) and the mixture was heated at 80 °C for 2 h. After cooling to 0 °C acetonitrile (3.9 mL) and 10% hydrochloric acid (0.55 mL) were added. The mixture was stirred at the same temperature for 10 min and then treated with CAN (0.29 g, 0.52 mmol) in water (1.6 mL) for 5 min. The precipitate was collected and recrystallized from hexane-CH_2Cl_2 to give pure **5a** (75 mg, 71%) as a yellow solid; mp 173–175 °C; ν_{max}/cm^{-1} 1725, 1699, 1667; δ_H 1.26 (3H, t, *J* 7.3), 1.41 (6H, t, *J* 7.3), 2.94 (3H, s), 3.48 (2H, q, *J* 7.3), 4.41 (4H, q, *J* 7.3 Hz); MS *m*/*z* 406 (M^+, 100). Anal. Calcd for $C_{19}H_{18}O_6S_2$: C, 56.14; H, 4.46; S, 15.78. Found: C, 55.93; H, 4.48; S, 15.82.

Diethyl 3-Methyl-4,8-dioxo-5-propyl-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5b): mp 157-160 °C (hexane-Et_2O); ν_{max}/cm^{-1} 1724, 1707, 1665; δ_H 1.04 (3H, t, *J* 7.3), 1.42 (6H, t, *J* 7.3), 1.65 (2H, sextet, *J* 7.3), 2.91 (3H, s), 3.42 (2H, t, *J* 7.3), 4.40 (4H, q, *J* 7.3);

MS *m/z* 420 (M^+, 100). Anal. Calcd for $C_{20}H_{20}O_6S_2$: C, 57.13; H, 4.79; S, 15.25. Found: C, 57.04; H, 4.64; S, 15.21.

Diethyl 3-Methyl-5-(1-methylethyl)-4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5c): mp 207–210 °C (acetone-hexane); ν_{max}/cm^{-1} 1726, 1696, 1673; δ_H 1.42 (combined 12H, t, *J* 7.3 and d, *J* 6.9), 2.93 (3H, s), 4.40 (4H, q, *J* 7.3), 4.55 (1H, septet, *J* 6.9); MS *m/z* 420 (M^+, 75), 374 (100). Anal. Calcd for $C_{20}H_{20}O_6S_2$: C, 57.13; H, 4.79; S, 15.25. Found: C, 57.22; H, 4.86; S, 15.35.

Diethyl 3-Methyl-5-(2-methylpropyl)-4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5d): mp 148–153 °C (CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1724, 1713, 1663; δ_H 0.96 (6H, d, *J* 6.6), 1.42 (6H, t, *J* 7.3), 1.9–2.05 (1H, m), 2.93 (3H, s), 3.42 (2H, d, *J* 6.6), 4.40 (4H, q, *J* 7.3); MS *m/z* 434 (M^+, 100). Anal. Calcd for $C_{21}H_{22}O_6S_2$: C, 58.05; H, 5.10; S, 14.76. Found: C, 57.96; H, 5.40; S, 14.74.

Diethyl 3-Methyl-4,8-dioxo-5-phenyl-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5e): mp 255–257 °C (CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1737, 1696, 1675, 1654; δ_H 1.14 (3H, t, *J* 7.3), 1.40 (3H, t, *J* 7.3), 2.79 (3H, s), 4.18 (2H, q, *J* 7.3), 4.39 (2H, q, *J* 7.3), 7.2–7.3 (3H, m), 7.45–7.5 (2H, m); MS *m/z* 454 (M^+, 89), 425 (100). Anal. Calcd for $C_{23}H_{18}O_6S_2$: C, 60.78; H, 3.99; S, 14.11. Found: C, 60.57; H, 4.03; S, 13.88.

Dimethyl 3-Propyl-4,8-dioxo-4,8-dihydrobenzo[1,2-*b*:5,4-*b*']dithiophene-2,6-dicarboxylate (5f): mp 140–143 °C (CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1734, 1724, 1669, 1658; δ_H 1.05 (3H, t, *J* 7.3), 1.54 (2H, sextet, *J* 7.3), 3.44 (2H, t, *J* 7.3), 3.94 (3H, s), 3.97 (3H, s), 8.20 (1H, s); MS *m/z* 378 (M^+, 100). Anal. Calcd for $C_{17}H_{14}O_6S_2$: C, 53.96; H, 3.73; S, 16.95. Found: C, 54.23; H, 3.83; S, 17.13.

ACKNOWLEDGEMENTS

We thank Mrs Miyuki Tanmatsu of this Department for determining the MS spectra and performing combustion analyses.

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9. It should be noted that the photoacylation of **1** (R^1 = Ph, R^2 = Et) with butanal gave only a very low yield of the desired acylated product.