SYNTHESIS, ISOLATION, AND DIMERIZATION AND TRIMERIZATION OF MONOSUBSTITUTED THIOPHENE 1,1-DIOXIDES

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Abstract–Monosubstituted thiophenes were oxidized with dimethyldioxirane in acetone at –20 °C and then the solvent and volatile materials were removed below –40 °C. This allowed the isolation of kinetically labile 2-methyl-, 3-methyl-, 2-ethyl-, and 2-bromothiophene 1,1-dioxides (**3a**, **3b**, **3c**, and **3e**, respectively) in practically pure form. These were characterized by ^{1}H- and ^{13}C-NMR, IR, UV/Vis, and MS spectroscopies. The half-lives of the parent thiophene 1,1-dioxide (**1**), **3b**, **3a**, and **3c** were determined to be 14, 47, 68, and 76 min, respectively, at 313 K (40 °C) in 0.32 M $CDCl_3$ solutions. The 1,1-dioxide (**3a**) underwent a [4+2] cyclodimerization in which one molecule of **3a** acted as a diene and the other as a dienophile to provide two isomeric products (**4a** and **5a**). In addition, the trimeric product (**16a**) was formed owing to a further [4+2] cycloaddition of the major isomer (**4a**) with **3a** which took place in the endo and head-to-head mode. Dimeric and trimeric products formation was also observed on decomposition of **3b** and **3c**, whereas **3e** underwent only dimerization.

INTRODUCTION

Thiophene 1,1-dioxides in which the lone pair electrons of the sulfur atom are substituted by two oxygen atoms are no longer aromatic. Thus they undergo a wide variety of reactions as an unsaturated cyclic sulfone and hence have attracted much attention of synthetic as well as theoretical chemists. A recent exhaustive literature survey revealed that more than three hundred papers had dealt with the chemistry of thiophene 1,1-dioxides.[1,2] Thiophene 1,1-dioxides are highly reactive, and are stable enough to be isolated only when more than two substituents are introduced into the thiophene ring in order to decrease their reactivities at the double bonds. Thus, the parent thiophene 1,1-dioxide (**1**) had never been isolated and characterized in a definite way despite much efforts[3-5] until our recent success in its preparation, isolation, and characterization.[6] We now report here the preparation, isolation, and properties of monosubstitued thiophene 1,1-dioxides (**3**).

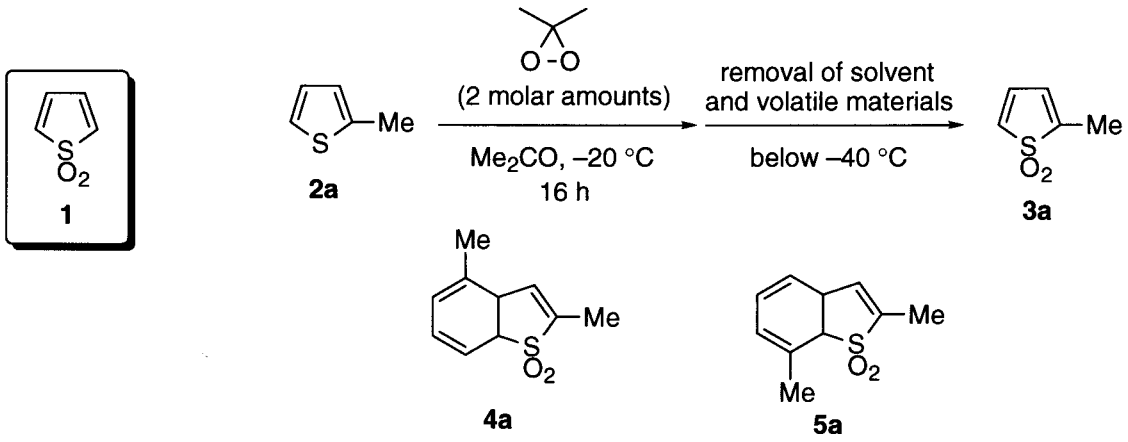
Dedicated to Professor Teruaki Mukaiyama on the occasion of his seventy-third birthday.

RESULTS AND DISCUSSION

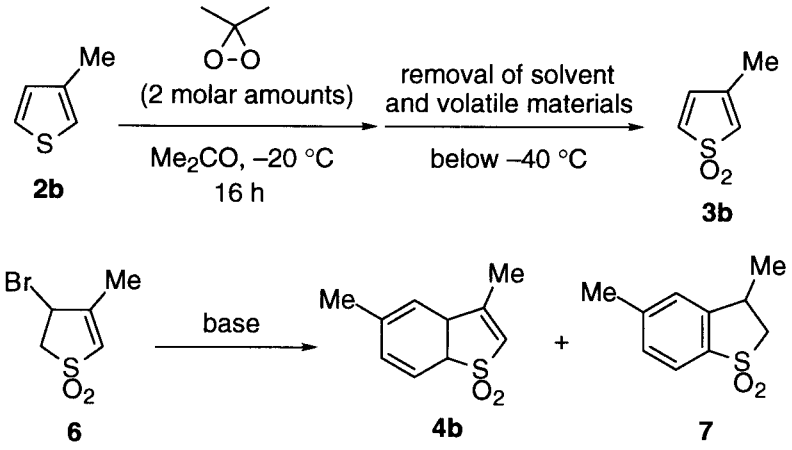
1. Preparation of Monosubstituted Thiophene 1,1-Dioxides (3)

The oxidation of thiophenes with peracids provides among the most convenient syntheses of thiophene 1,1-dioxides.[1,2] The method is not applicable to the parent thiophene 1,1-dioxide (**1**), however, and its synthesis and isolation required special devices and skills.[6] Also in the present study, the procedures developed for **1** were followed exactly. Thus, dimethyldioxirane (DMD),[7] which is a strong but neutral oxidant and would be capable of oxidizing thiophenes to the corresponding thiophene 1,1-dioxides at low temperature, was employed as the oxidant with purpose of isolating monosubstituted thiophene 1,1-dioxides (**3**) in pure form.[8] In this method, if the oxidation takes place cleanly, the resulting products are only **3** and acetone formed from DMD. Even if a thiophene and DMD remained unchanged, they are volatile or easily soluble in organic solvents and can be easily removed by distillation or washing with a volatile solvent (hexane).

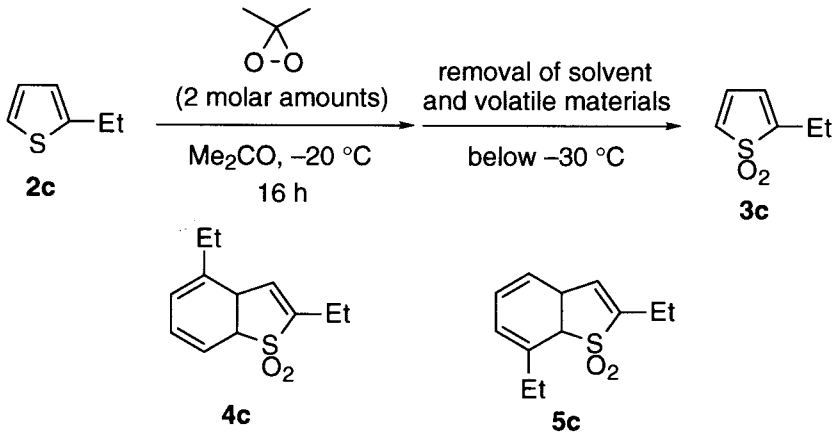
Thus, 2-methylthiophene (**2a**) was oxidized with two molar amounts of DMD at –20 °C for 16 h in acetone. Removal of the solvent and volatile materials at room temperature furnished a mixture of two isomeric products (**4a** and **5a**) that had been produced by dimerization of the expected thiophene 1,1-dioxide (**3a**). The mechanism of the formation of **4a** and **5a** is discussed later. These results suggest that the dioxide (**3a**) is kinetically labile and must be handled at low temperature. Thus, after the oxidation at –20 °C, the solvent and volatile materials were removed below –40 °C under reduced pressure to suppress the dimerization of **3a** when its solution was concentrated.[6] The colorless crystalline residue, obtained in this way, was washed with hexane and dried below –40 °C to give the practically pure **3a** that melted above 31 °C with decomposition. The yield of **3a** is nearly quantitative based on the consumed thiophene (**2a**).



In the same way as described above, 3-methylthiophene 1,1-dioxide (**3b**) was obtained as a thermally labile viscous oil. Chou *et al.* reported that the 1,1-dioxide (**3b**), produced by dehydrobromination of **6**, was kinetically labile and gave the dimeric products (**4b** and **7**).[3q] Actually, also at our hands, when the reaction mixture was evaporated at room temperature, the dimeric product **4b** was obtained as the sole product.

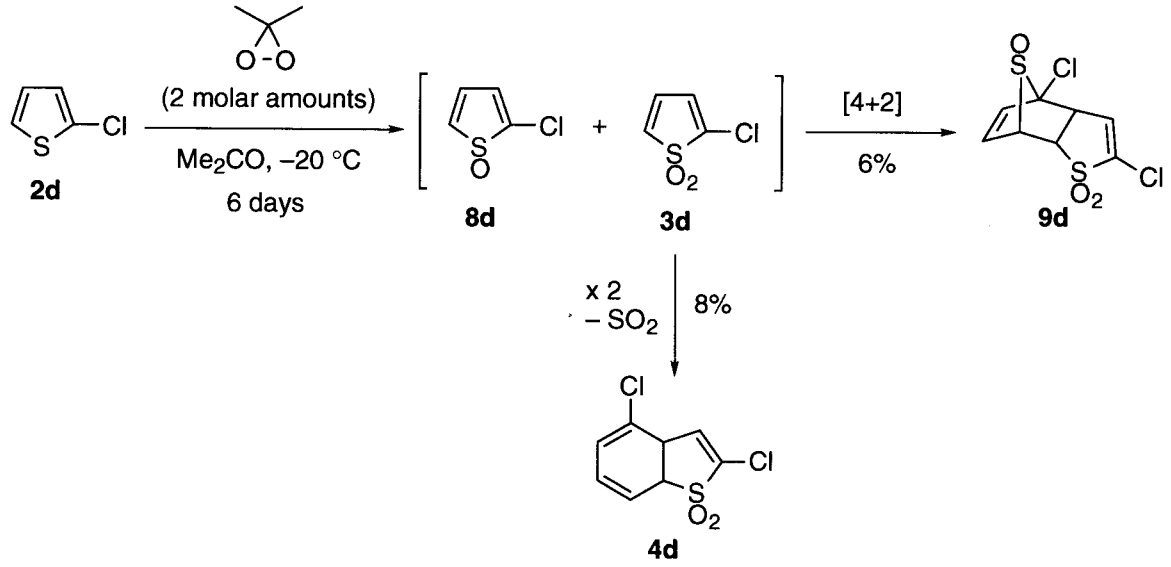


2-Ethylthiophene 1,1-dioxide (**3c**) is more stable thermally than the methyl derivatives (**3a**,**b**) and was obtained in pure form by solvent removal below –30 °C, after the oxidation of 2-ethylthiophene (**2c**) at –20 °C. Nevertheless, solvent removal at room temperature resulted in the decomposition of **3c** to give dimeric products (**4c** and **5c**). The colorless crystals of **3c** melted above 25 °C with decomposition.

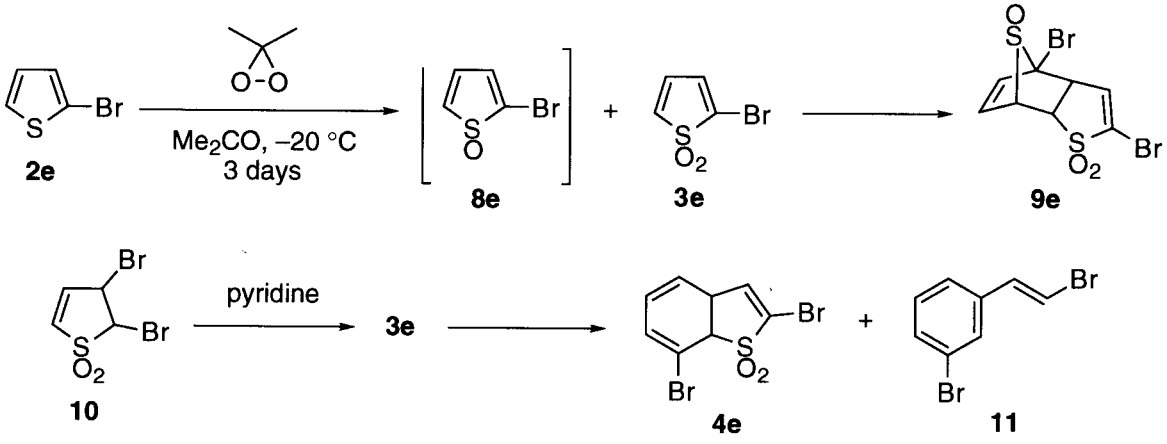


The oxidation of 2-chlorothiophene (**2d**) that carries an electron-withdrawing chlorine atom is slower than that of **2a-c**. Thus, **2d** was treated with two molar amounts of DMD for a prolonged time (6 days) at –20 °C and the solvent was removed below –40 °C. The residue was washed with hexane and then analyzed by ^{1}H NMR. The analysis disclosed that the oxidation produced a complex mixture containing **4d** and **9d** (8 and 6% isolated yields, respectively). The formation of **4d** is explained as the result of dimerization of the expected 1,1-dioxide (**3d**), whereas that of the sesquioxide (**9d**) as the result of [4+2] cycloaddition of 2-chlorothiophene 1-oxide (**8d**) and **3d**. The cycloaddition of a thiophene 1-oxide with the corresponding 1,1-dioxide was observed when the parent thiophene was oxidized with *m*-chloroperbenzoic acid.[3e] The interception of **8d** by **3d** indicates that the oxidation of **8d** to **3d** is slow compared to the same step in the oxidation of **2a-c**. When the crude product was analyzed by ^{1}H NMR immediately after the evaporation of

the solvent, signals, probably attributable to the expected 1,1-dioxide (**3d**), were observed at around δ 6.60 and 6.90, but exact structure proof for **3d** was not attained.

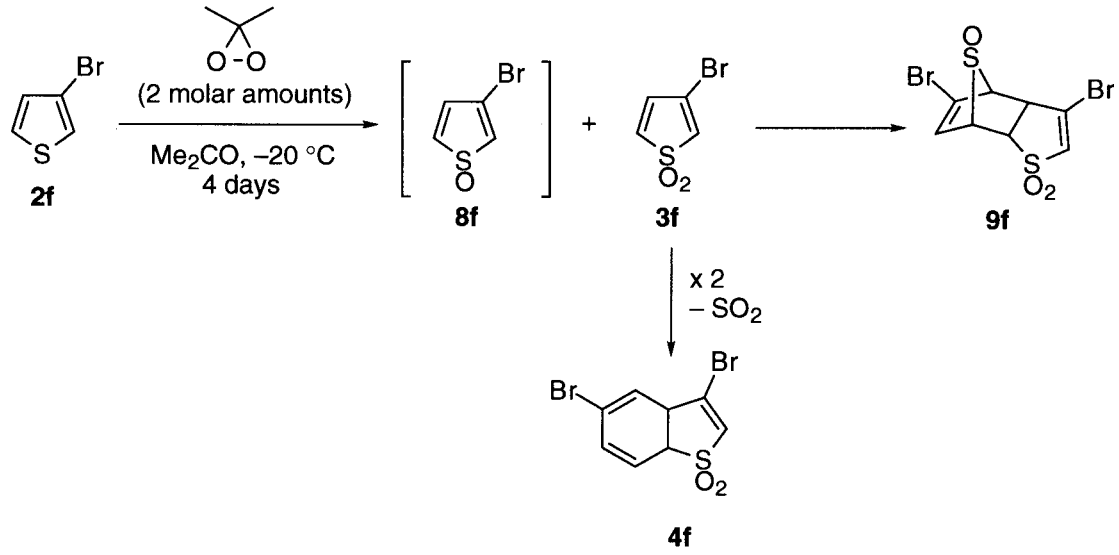


2-Bromothiophene (**2e**) was oxidized with two molar amounts of DMD and the mixture worked up as described above. The oxidation gave a mixture of the expected 1,1-dioxide (**3e**) and the sesquioxide (**9e**) that formed from the 1-oxide (**8e**) and **3e**. Crystallization of the mixture from CH_2Cl_2/hexane below –40 °C provided **3e** contaminated with a small amount of **9e**. Reportedly, **3e**, generated by dehydrobromination of the dibromide (**10**), gave the dimerization product (**4e**) in addition to **11** which was probably derived from **4e**.[3s]



The oxidation of 3-bromothiophene (**2f**) with DMD at –20 °C, followed by solvent removal and crystallization of the residue from CH_2Cl_2/hexane below –40 °C, furnished colorless crystals. The ^1H

NMR spectrum of the crystals showed the absorption, attributable to the expected 1,1-dioxide (**3f**) around at δ 6.70 which attenuated on being allowed to stand at room temperature for 24 h, in addition to the absorption due to **4f** (formed by dimerization of the expected **3f**) and **9f** [derived from **3f** and the 1-oxide (**8f**)]. Purification of the above crystals by GPC gave **4f** and **9f** in very low yields (2 and 3% yields, respectively).



2. Spectroscopy and Structure Proof of Thiophene 1,1-Dioxides (3)

The structure of thiophene 1,1-dioxides (**3**), which are highly reactive and were not capable of handling at room temperature, was determined by spectroscopies in solutions. ^{1}H- and ^{13}C-NMR data are summarized in Tables 1 and 2, respectively. Because of the loss of the aromaticity of the thiophene, *i.e.*, the loss of the ring current effect, up-field shifts of all of the ring hydrogens were observed on going from the thiophenes (**2**) to the corresponding 1,1-dioxides (**3**). For example, the three ring hydrogens of **2a** at δ 6.70-6.75 (m), 6.89 (dd), and 7.03 (d) moved to δ 6.28-6.34 (m), 6.78 (dd), and 6.55 (d), respectively, for **3a**.

IR spectra of **3** showed a weak absorption due to the C=C stretching vibration in the range of 1525-1551 cm^{-1} and very strong absorptions due to the SO_2 symmetric and asymmetric stretching vibrations in the ranges 1299-1310 and 1144-1170 cm^{-1}, respectively (Table 3).

UV/Vis spectra of **3a** and **3b** showed two absorption maxima as observed with the parent compound (**1**) (Table 3). A small bathochromic shift of the longer-wavelength absorption was observed on going from **1** to **3a** and **3b** by the effect of the methyl substituent.

Every **3** gave the molecular ion peak at the correct position in the MS spectra (Table 4). The most intense peak originates from M^{+}–SO, which corresponds to the furan radical cation. This fragmentation pattern, which could be depicted as below by consideration of the mechanism of the formation of furans from thiophene 1,1-dioxides on pyrolysis,[6,9] is seemingly characteristic of many thiophene 1,1-dioxides. High resolution MS spectra also gave satisfactory results (Table 4).

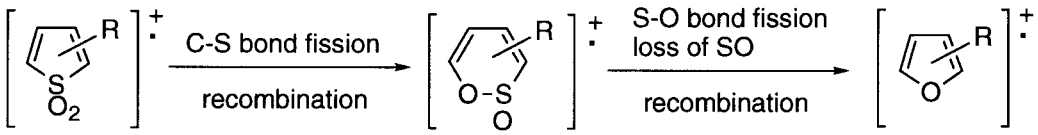


Table 1. ^{1}H NMR data of **1**[a] and **3** (solvent, $CDCl_3$; chemical shift values, δ).

	H at C2	H at C3	H at C4	H at C5
1	6.75-6.83 (m)	6.53-6.61 (m)		
3a[b]		6.28-6.34 (m)	6.78 (dd, J = 7.0/4.2 Hz)	6.55 (d, J = 7.0 Hz)
3b[c]	6.54-6.61[e] (m)		6.22-6.27 (m)	6.54-6.61[e] (m)
3c[d]		6.54-6.61 (m)	6.90 (dd, J = 6.8/4.5 Hz)	6.65 (d, J = 6.8 Hz)
3e		6.79 (d, J = 4.6 Hz)	6.86 (dd, J = 7.4/4.6 Hz)	6.72 (d, J = 7.4 Hz)

[a] Taken from ref. 6. [b] Me at δ 2.09 (d, J = 1.8 Hz). [c] Me at δ 2.06 (d, J = 1.8 Hz). [d] Et at δ 1.30 (t, J = 7.3 Hz) and 2.53 (q, J = 7.3 Hz). [e] These two signals are overlapped.

Table 2. ^{13}C NMR data of **1**[a] and **3**[b] (solvent, $CDCl_3$; chemical shift values, δ).

	C2	C3	C4	C5	Me (Et)
1	131.1	129.3			
3a	140.6	121.9	128.2	130.1	9.1
3b	123.5	141.7	132.8[c]	130.0[c]	17.4
3c	146.3	120.1	128.4	130.5	10.3, 17.0

[a] Taken from ref. 6. [b] Ring carbons of **3e**, δ = 121.9, 126.7, 129.1, 131.1 (not assigned). [c] This assignment might be reversed.

Table 3. IR and UV/Vis data of **1**[a] and **3**.

	IR ($CDCl_3$, cm^{-1})			UV/Vis ($CHCl_3$) nm (ε)
	$\nu_{C=C}$	ν_{SO2} (sym)	ν_{SO2} (asym)	
1	1530	1151	1305	245 (870), 288 (1070)
3a	1551	1144	1300	241 (1300), 296 (1460)
3b	1551	1170	1300	242 (2450), 293 (1350)
3c	1549	1151	1299	
3e	1525	1156	1310	

[a] Taken from ref. 6.

Table 4. MS spectra data of **1** and **3** (EI, 70 eV).

	MS (*m/z*)		HRMS	
	M^+	M^+–SO	Found	Calcd
1[a]	116	68		
3a[b]	130	82	130.0061	130.0088 ($C_5H_6O_2S$)
3b[b]	130	82	130.0093	130.0088 ($C_5H_6O_2S$)
3c[b]	144	96	144.0211	144.0245 ($C_6H_8O_2S$)
3e[b]	196 194	146	195.9027 193.9059	195.9017 ($C_4H_3Br(81)O_2S$) 193.9037 ($C_4H_3Br(79)O_2S$)

[a] Taken from ref. 6. [b] Other major peaks: for **3a**, *m/z* 97; **3b**, 97; **3c**, 70; **3e**, 165.

Dimerization and Trimerization of Thiophene 1,1-Dioxides (3)

We have shown that the parent thiophene 1,1-dioxide (**1**) decomposes to furnish not only dimerization but also trimerization products (**12** and **13**, respectively); decomposition in solution produced **12** as the major product, while decomposition of a neat sample gave **12** and **13** in a comparable amount.[6] Monosubstituted thiophene 1,1-dioxides (**3**) also undergo dimerization as well as trimerization. The formation of the dimerization products (**4** and **5**) has been already mentioned in connection with the synthesis of **3**. For monosubstituted derivatives, the formation of four isomeric dimerization products is possible regardless of the dimerization being either in the endo or exo mode. Thus, for thiophene 1,1-dioxides (**3a**,**c**,**e**), the

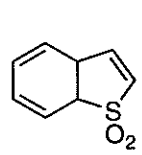
formation of **4**, **5**, **14**, and **15** is possible (only dimerization in the endo mode is given in the Scheme). Also, for the trimerization in the endo mode, formation of four isomeric products is possible. Only two isomers are shown in the Scheme since the other two isomers were not involved in the actual reactions. Also trimerization in the exo mode was excluded from the Scheme by the same reason.

When a pure neat sample of the 1,1-dioxide (**3a**) was warmed at 27 °C for 90 min, complete decomposition took place to give **4a**, **5a**, and **16a** in the molar ratio 100:6:12. When a 0.27 M $CDCl_3$ solution of **3a** was allowed to stand at 25 °C for 6 days, the decomposition also took place to provide **4a** and **5a** in the molar ratio 100:18 along with **16a** in a trace amount. The other dimeric products (**14a** and **15a**) were not formed in the both decompositions. The combined yield of the decomposition products is nearly quantitative. The isomers (**4a** and **5a**) were differentiated to each other by homonuclear decoupling experiments. In the ^{13}C NMR spectrum, the trimer (**16a**) showed ten peaks indicative of the presence of ten nonequivalent carbon atoms. The other isomer (**17a**) that possesses fifteen nonequivalent carbon atoms should show fifteen peaks. The stereochemistry of **16a** was determined by NOESY experiments where distinct correlations were observed between one of the two hydrogens attached at the central double bond (the inner hydrogen in the structure **16a**) and the β-hydrogens of the dihydrothiophene rings. The formation of **4a** and **5a** does not leave any memory as to whether the reaction took place either in the endo or exo mode. Meanwhile, the formation of **16a** discloses that the [4+2] cycloaddition of **4a** and **1a** occurred in the endo and head-to-head mode. Preferential formation of **4a** to **5a** reflects the fact that steric repulsions between the Me and SO_2 groups are avoidable in the transition state leading to **4a**. Noticeable is the formation of the head-to-head product (**16a**), keeping the formation of the head-to-tail product (**13**) from **1** in mind. These facts imply that the crucial factor that governs the trimerization product formation from **12** and **1** is the repulsive interactions between the two SO_2 groups, whereas that from **4a** and **3a** is the repulsive interactions between the Me and SO_2 groups, in other words, the latter repulsions are more important than the former since the formation of **16a** has overcome the former repulsions.

Thermolysis of 2-ethylthiophene 1,1-dioxide (**3c**) gave the results similar to those of 2-methyl derivative (**3a**). Warming a pure neat sample of **3c** at 30 °C for 60 min resulted in the complete decomposition of **3c** to provide **4c**, **5c**, and **16c** in the molar ratio 100:4:4. Meanwhile, a 0.12 M $CDCl_3$ solution of **3c**, on warming at 30 °C for 7 days, led to the incomplete decomposition of **3c** and provided a mixture of **3c**, **4c**, and **5c** in the molar ratio 17:100:5. No trimeric product formation was observed. Structures of **4c**, **5c**, and **16c** were determined by the same methods as described above.

A dilute solution of **3e** in $CDCl_3$ (0.03 M solution contaminated with **9e**), on warming at 35 °C for 5 days, provided **4e** as the sole dimerization product. The formation of **5e** (isomer of **4e**) and the trimer was not observed.

When a neat sample of 3-methylthiophene 1,1-dioxide (**3b**) was warmed at 30 °C for 60 min, complete decomposition took place, with emission of the smell of SO_2, to afford a mixture of the dimeric product (**4b**) and the trimeric product (**16b**) in the molar ratio 100:38. Decomposition of **3b** in a 0.16 M $CDCl_3$ solution (30 °C for 7 days) provided **4b** and **16b** in the molar ratio 100:20. The structure of **4b** was determined by ^1H- and ^{13}C-NMR spectra including homonuclear decoupling experiments, whilst that of **16b**, produced by cycloaddition of **4b** with **3b** in the endo and head-to-head mode, was determined by an X-Ray crystallographic analysis. The ORTEP diagram of **16b** is given in Figure 1.



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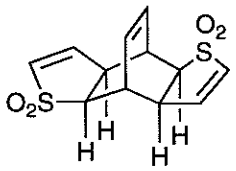

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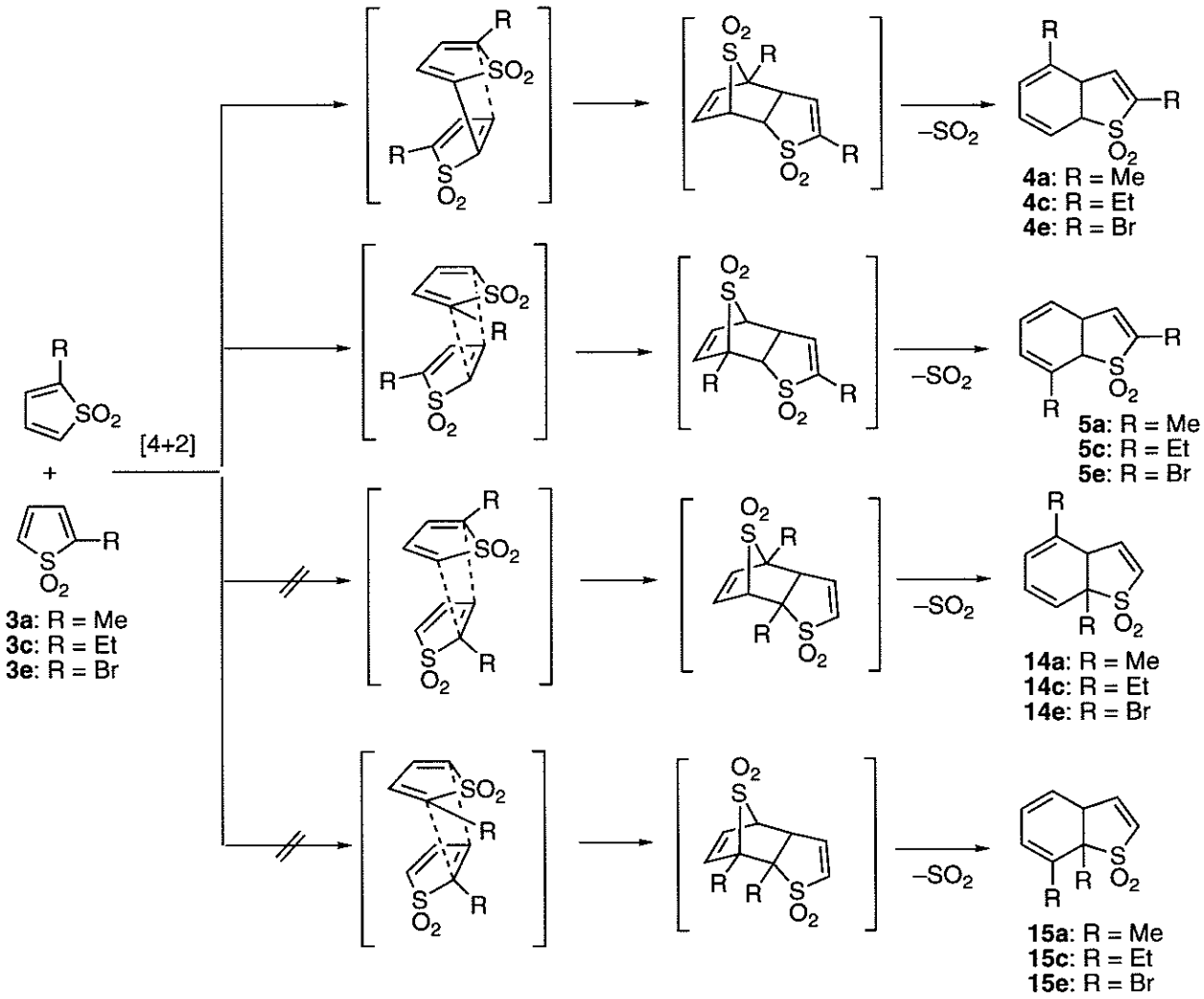
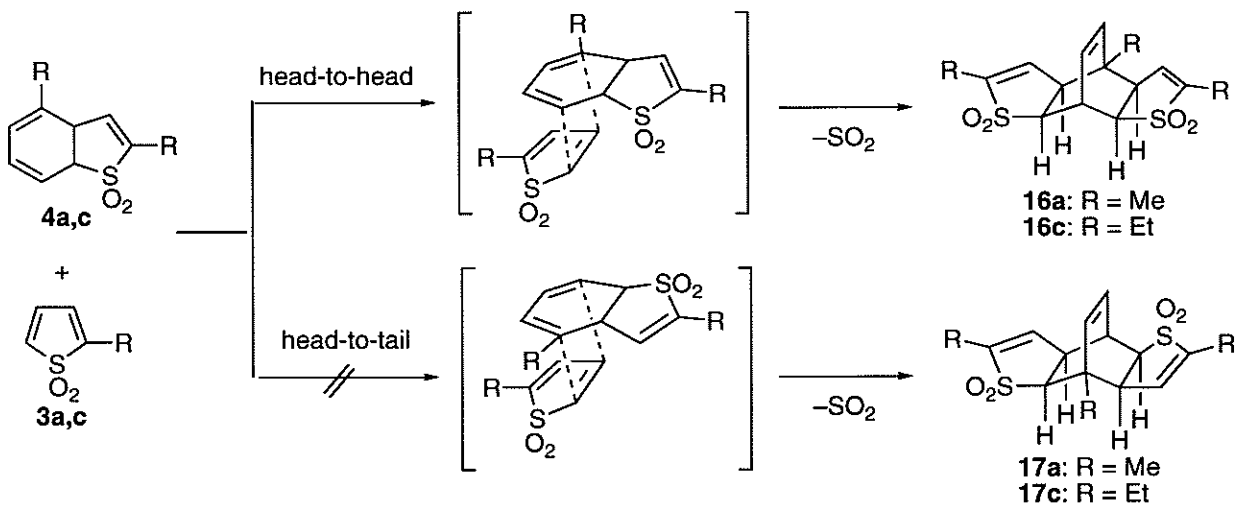
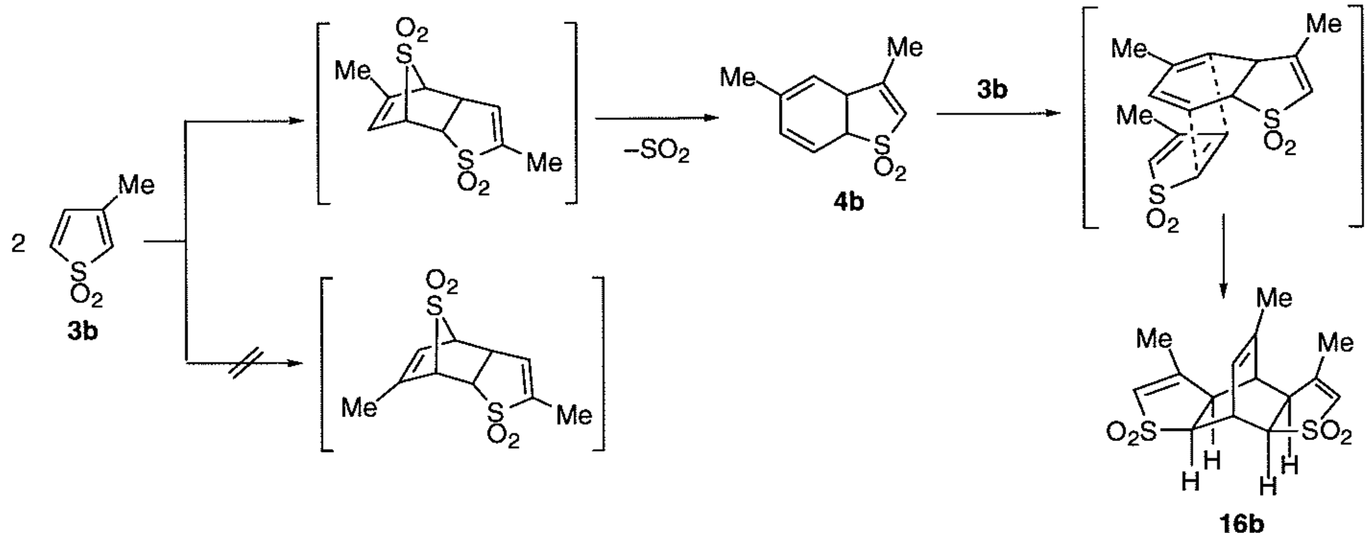
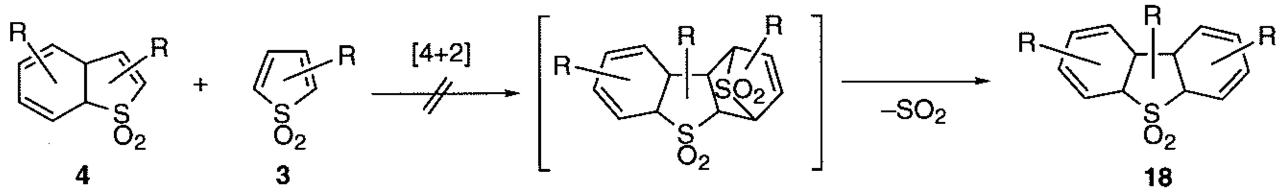

[4+2]
–SO2
4a: R = Me
4c: R = Et
4e: R = Br
5a: R = Me
5c: R = Et
5e: R = Br
14a: R = Me
14c: R = Et
14e: R = Br
15a: R = Me
15c: R = Et
15e: R = Br
3a: R = Me
3c: R = Et
3e: R = Br


head-to-head
head-to-tail
–SO2
4a,c
3a,c
16a: R = Me
16c: R = Et
17a: R = Me
17c: R = Et

Taken altogether, a [4+2] cycloaddition, in which **3** acted as a diene and **4** as a dienophile to form **18**, has never been observed.





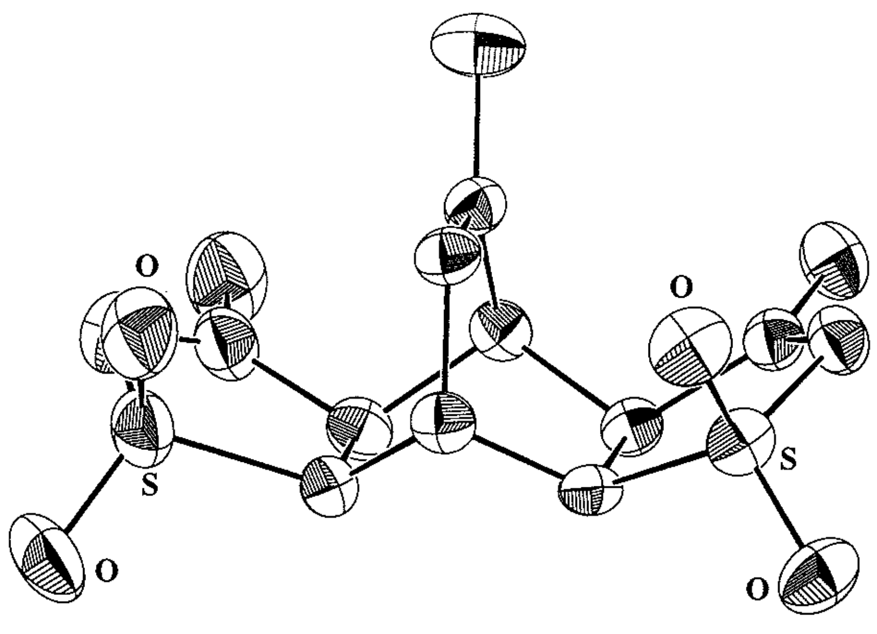


Figure 1. ORTEP diagram of the trimeric compound (**16b**).

Half-lives of Thiophene 1,1-Dioxides (3)

We have previously shown that the half-life of the parent thiophene 1,1-dioxide (**1**) in solution is dependent upon the concentration and is 419, 279, and 184, and 133 min at 303, 308, 313, and 318 K, respectively, in a very dilute $CDCl_3$ solution of 0.024 M.[6]

The half-lives of monosubstituted 1,1-dioxides (**3**) were also determined by ^1H NMR spectroscopy. Thus the half-life of **3a** was determined to be 225, 144, and 87 min at 303, 308, and 313 K, respectively, for a 0.25 M $CDCl_3$ solution, and that of **3b** to be 186, 151, and 116 min at 303, 308, and 313 K, respectively, for a 0.12 M $CDCl_3$ solution. The half-life of **3d** was determined to be 76 min at 313 K for a 0.32 M $CDCl_3$ soltuion.

The half-lives of these compounds were then extrapolated to the nomalized conditions by assuming that **1** and **3** are consumed only by bimolecular dimerization at the beginning of the decomposition. The extrapolation provided the half-lives of 14, 47, 68, and 76 min for **1**, **3b**, **3a**, and **3d**, respectively, at 313 K (40 °C) for a 0.32 M $CDCl_3$ solution, thus allowing the direct comparison of the rate of the dimerization. Thus the ethyl group is more effective in suppressing the dimerization than the methyl group, and the methyl at the 2-postion is more effective than that at the 3-position.

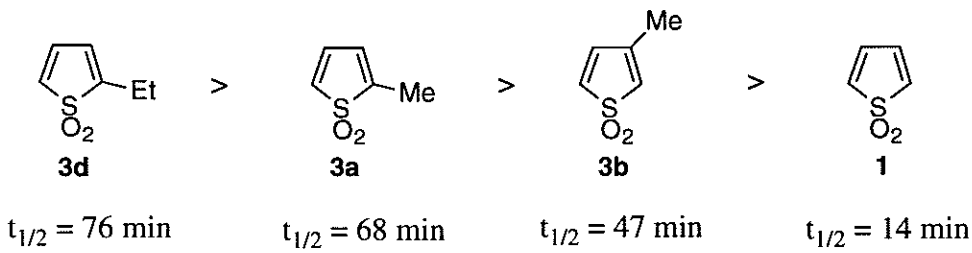


Figure 2. Half-lives of **1** and **3** under nomalized conditions: 313 K in 0.32 M $CDCl_3$ solutions.

In conclusion we have succeeded in the synthesis, isolation, and characterization of the parent thiophene 1,1-dioxide (**1**) and monosubstitued thiophene 1,1-dioxides (**3**) which had eluded isolation despite much efforts for a long time.

EXPERIMENTAL

General

Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H- and ^{13}C-NMR spectra were determined on a Bruker AM400, a Bruker ARX400, a Bruker AC300P, and a Bruker AC200 spectrometers using $CDCl_3$ as the solvent with TMS as the internal standard (400, 300, and 200 MHz for ^1H and 100.6, 75.5, and 50 MHz for ^{13}C, respectively). IR spectra were taken on a Hitachi 270-50 or a Perkin Elmer System 2000 FT-IR spectrophtometer. UV/Vis spectra were determined on a

Shimadzu UV-160A or a JASCO V-560 spectrophotometer. MS spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. GPC and HPLC were performed on a Japan Analytical Industry LC-908. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on Merck silica gel (7734, 70-230 mesh) and alumina column chromatography on Merck aluminum oxide 90 (70-120 mesh). Dimethyldioxirane (DMD) was prepared by the literature method as an acetone solution and the concentration of DMD was determined by titrimetry (oxidation of thioanisole to its sulfoxide derivative) prior to use.[7] The melting point of thermally labile **3a** and **3d** was determined in a room kept at –20 °C.

Preparation and Thermolysis of 2-Methylthiophene 1,1-Dioxide (3a)

Preparation. A mixture of 140 mg (1.4 mmol) of 2-methylthiophene (**2a**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –25 °C (molecular sieves were used to be freed of contaminating water which is otherwise difficult to remove at the workup stage). A 0.070 M solution (41 mL, 2.8 mmol) of DMD in acetone, cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 16 h at –20 °C and then cooled below –40 °C. The solvent and volatile materials were removed *in vacuo* below –40 °C (several hours might be required). The residue was washed with hexane (1 mL x 5) below –40 °C to provide the practically pure **3a** as colorless crystals. The yield of **3a** is nearly quantitative based on the consumed thiophene (*ca.* 30-40% based on the thiophene used). Spectroscopic data of **3a** were given in the text.

Thermolysis. The 1,1-dioxide (**3a**) is thermally unstable and cannot be weighed at rt. Therefore, thermolysis study of **3a** in $CDCl_3$ solution was examined in the following way. A fixed amount of *t*-butylbenzene (internal standard) and **3a** (obtained below –40 °C) were dissolved in $CDCl_3$. The solution was adjusted to a constant volume by dilution with $CDCl_3$. An aliquot was analyzed by ^1H NMR to determine the concentration of **3a**. A 0.27 M $CDCl_3$ solution of **3a**, prepared in this way, gave **4a** and **5a** in the molar ratio 100:18 along with **16a** in a trace amount, on warming at 25 °C for 6 days. During this period, the progress of the reaction was monitored by ^1H NMR at a constant interval to determine the half-life of **3a**. For decomposition study of a neat sample, **3a** which was obtained from 140 mg (1.4 mmol) of **2a** in the same way as described above, was warmed, without weighing, at 27 °C for 90 min. Purification of the resulting mixture by GPC and then by HPLC provided 36 mg of **4a**, 2 mg of **5a**, and 7 mg of **16a** (26, 1, and 4% yields, respectively, based on **2a**) in the molar ratio 100:6:12.

4a: mp 114-115 °C (from ether/hexane); ^1H NMR (300 MHz) δ: 1.86 (3H, s), 2.10 (3H, t, J = 2.2 Hz), 3.65-3.76 (1H, m), 4.14-4.24 (1H, m), 5.65-5.77 (2H, m), 6.07-6.16 (1H, m), 6.31-6.37 (1H, m); ^{13}C NMR (50 MHz) δ: 8.7, 20.7, 40.5, 59.7, 113.5, 118.7, 127.0, 131.87, 131.93, 139.7; IR (KBr) ν_{max} (cm^{-1}): 1122, 1148, 1152, 1286, 1310, 1596, 1658, 2948, 3048; MS (EI) *m/z*: 196 (M^+), 148, 131, 117, 92. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.17. Found: C, 61.13; H, 6.17.

5a: Colorless oil; ^1H NMR (300 MHz) δ: 2.04 (3H, s), 2.13 (3H, t, J = 1.5 Hz), 3.75-3.83 (2H, m), 5.40 (1H, d, J = 9.5 Hz), 5.86-5.94 (1H, m), 5.99-6.04 (1H, m), 6.36-6.40 (1H, m); ^{13}C NMR (50

MHz) δ: 9.3, 22.4, 38.3, 62.8, 120.2, 122.3, 123.1, 125.4, 132.7, 142.0; MS (EI) *m/z*: 196 (M^+), 148, 131, 117. HRMS Calcd for $C_{10}H_{12}O_2S$: 196.0558. Found: 196.0524.

16a: mp > 210 °C (decomp) (from MeCN); ^{1}H NMR (400 MHz) δ: 1.38 (3H, s), 1.94 (6H, t, *J* = 1.8 Hz), 2.90-2.97 (2H, m), 3.38 (2H, dd, *J* = 8.3, 2.4 Hz), 3.78-3.84 (1H, m), 5.47 (1H, d, *J* = 8.3 Hz), 6.04-6.11 (2H, m), 6.17 (1H, dd, *J* = 8.3, 6.4 Hz); ^{13}C NMR (100.6 MHz) δ: 8.1, 18.0, 31.9, 41.4, 48.2, 59.5, 129.0, 132.7, 133.1, 141.5; MS (EI) *m/z*: 326 (M^+), 278, 227, 195, 91. Anal. Calcd for $C_{15}H_{18}O_4S_2$: C, 55.19; H, 5.56. Found: C, 55.15; H, 5.52.

Preparation and Thermolysis of 3-Methylthiophene 1,1-Dioxide (3b)

Preparation. A mixture of 121 mg (1.2 mmol) of 2-methylthiophene (**2b**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –25 °C. A 0.070 M solution (35 mL, 2.4 mmol) of DMD in acetone, cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 16 h at –20 °C and then cooled below –40 °C. The solvent and volatile materials were removed in vacuo below –40 °C. The resiude was washed with hexane (1 mL x 5) and dried *in vacuo* for 3 h below –40 °C to provide the practically pure **3b** as a colorless oil. The yield of **3b** is nearly quantitative based on the consumed thiophene (*ca.* 40-45% yield based on the thiophene used). Spectroscopic properties of **3b** were discussed in the text.

Thermolysis. A 0.16 M $CDCl_3$ solution of **3b** was prepared in the same way as that of **3a**. The solution was warmed at 30 °C for 7 days. The progress of the reaction was monitored by ^{1}H NMR to determine the half-life of **3b**. The reaction finally gave a mixture of **4b** and **16b** in the molar ratio 100:20. For decomposition study of a neat sample, **3b** which was prepared from 117 mg (1.2 mmol) of **2b**, was warmed, without weighing, at 30 °C for 60 min. Purification of the resulting mixture by GPC provided 31 mg of **4b** (27% based on **2b**) and 20 mg of **16b** (15%) in the molar ratio 100:38.

4b: mp 103-104 °C (from ether/hexane) (previously reported as a colorless oil[3r]); ^{1}H NMR (300 MHz) δ: 1.79 (3H, s), 2.06 (3H, s), 3.69-3.83 (1H, m), 4.09 (1H, dd, *J* = 12.0, 4.4 Hz), 5.39 (1H, s), 5.86 (1H, dd, *J* = 9.2, 4.4 Hz), 6.12 (1H, d, *J* = 9.2 Hz), 6.51 (1H, s); ^{13}C NMR (50 MHz) δ: 14.0, 21.5, 42.9, 59.6, 115.5, 116.2, 125.8, 130.7, 131.2, 153.0; IR (KBr) ν_{max} (cm^{-1}): 1124, 1144, 1170, 1282, 1300, 1316, 1632, 2998; MS (EI) *m/z*: 196 (M^+), 148, 131, 117, 91. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 60.75; H, 6.16.

16b: mp > 181 °C (decomp) (from Me_2CO/hexane); ^{1}H NMR (200 MHz) δ: 1.67 (3H, s), 2.01 (6H, s), 3.13 (2H, d, *J* = 1.5 Hz), 3.29 (2H, d, *J* = 8.3 Hz), 3.42 (1H, dd, *J* = 8.2, 1.9 Hz), 3.74-3.85 (1H, m), 5.97 (1H, d, *J* = 6.3 Hz), 6.35 (2H, s); ^{13}C NMR (100.6 MHz) δ: 16.8, 21.7, 32.1, 39.8, 49.3, 60.9, 123.6, 129.6, 134.0, 149.6; IR (KBr) ν_{max} (cm^{-1}): 1106, 1140, 1152, 1212, 1228, 1288, 1634, 3064; MS (EI) *m/z*: 326 (M^+), 279, 227. Anal. Calcd for $C_{15}H_{18}O_4S_2$: C, 55.19; H,5.56. Found: C, 55.26; H, 5.55.

Preparation and Thermolysis of 2-Ethylthiophene 1,1-Dioxide (3c)

Preparation. A mixture of 137 mg (1.2 mmol) of 2-ethylthiophene (**2c**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –25 °C. A 0.070 M solution (34 mL, 2.4 mmol) of DMD in acetone,

cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 16 h at –20 °C and then cooled below –30 °C. The solvent and volatile materials were removed *in vacuo* below –30 °C. The resiude was washed with hexane (1 mL x 5) and dried *in vacuo* for 3 h below –40 °C to provide the practically pure **3c** as colorless crystals. The yield of **3c** is nearly quantitative based on the consumed thiophene (*ca.* 40-45% yield based on the thiophene used). Spectroscopic data of **3c** were given in the text.

Thermolysis. A 0.12 M $CDCl_3$ solution of **3c** was prepared in the same way as that of **3a**. The solution was warmed at 25 °C. The progress of the decomposition was monitored by ^1H NMR to determine the half-life of **3c**. After 7 days, the reaction gave a mixture of **3c**, **4c**, and **16c** in the molar ratio 17:100:5. For decomposition study of a neat sample, **3b** which was prepared from 137 mg (1.2 mmol) of **2c**, was warmed, without weighing, at 30 °C for 60 min. Purification of the resulting mixture by GPC and then by HPLC provided 56 mg of **4c**, 2 mg of **5c**, and 4 mg of **16c** (41, 2 and 3% yields, respectively, based on **2c**) in the molar ratio 100:4:4.

4c: mp 68-69 °C (from ether/hexane); ^1H NMR (400 MHz) δ: 1.12 (3H, t, J = 7.3 Hz), 1.25 (3H, t, J = 7.3 Hz), 2.10-2.26 (2H, m), 2.45-2.58 (2H, m), 3.75 (1H, d, J = 9.5 Hz), 4.14-4.24 (1H, m), 5.64-5.78 (2H, m), 6.13 (1H, ddd, J = 9.5, 5.9, 1.8 Hz), 6.20-6.26 (1H, m); ^{13}C NMR (100.6 MHz) δ: 11.5, 11.7, 17.2, 27.2, 39.4, 60.7, 114.1, 116.8, 127.1, 130.6, 137.5, 145.5; IR (KBr) ν_{max} (cm^{-1}): 1136, 1262, 1290, 1320, 1620, 1680, 2986, 3056; MS (EI) *m/z*: 224 (M^+), 207, 159, 117, 91. Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19. Found: C, 63.97; H, 7.19.

5c: Colorless oil; ^1H NMR (300 MHz) δ: 1.17 (3H, t, J = 7.4 Hz), 1.26 (3H, t, J = 7.4 Hz), 2.21-2.33 (1H, m), 2.37-2.47 (1H, m), 2.49-2.59 (2H, m), 3.85-3.98 (2H, m), 5.41 (1H, dd, J = 9.6, 2.2 Hz), 5.90-5.98 (1H, m), 6.01 (1H, d, J = 5.8 Hz), 6.34-6.40 (1H, m); ^{13}C NMR (50 MHz) δ: 11.4, 11.8, 17.5, 28.6, 36.3, 62.2, 120.4, 121.1, 122.3, 131.0, 131.2, 148.0; MS (EI) *m/z*: 224 (M^+), 176, 158, 131. HRMS Calcd for $C_{12}H_{16}O_2S$: 224.0871. Found: 224.0875.

16c: mp > 315 °C (decomp) (from $CHCl_3$/hexane); ^1H NMR (400 MHz) δ: 1.12 (3H, t, J = 7.6 Hz), 1.19 (3H, t, J = 7.4 Hz), 1.93 (2H, q, J = 7.6 Hz), 2.29-2.51 (4H, m), 3.26 (2H, dd, J = 8.4, 2.2 Hz), 3.44 (2H, dd, J = 8.6, 2.2 Hz), 3.80-3.88 (1H, m), 5.43 (1H, d, J = 8.2 Hz), 6.03 (2H, s), 6.24 (1H, dd, J = 8.2, 6.2 Hz); ^{13}C NMR (100.6 MHz) δ: 7.3, 11.9, 17.1, 23.5, 31.9, 44.16, 44.22, 61.0, 128.6, 130.2, 132.0, 149.7; MS (EI) *m/z*: 368 (M^+), 319, 269. HRMS Calcd for $C_{18}H_{24}O_4S_2$: 368.1116. Found: 368.1060.

Oxidation of 2-Chlorothiophene (2d)

A mixture of 125 mg (1.1 mmol) of 2-chlorothiophene (**2d**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –20 °C. A 0.070 M solution (33 mL, 2.3 mmol) of DMD in acetone, cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 6 days at –20 °C and then cooled below –40 °C. The solvent and volatile materials were removed *in vacuo* below –40 °C. The residue was washed with hexane (1 mL x 5) and dried *in vacuo* for 3 h below –40 °C. An ^1H NMR analysis disclosed that the residue is a complex mixture containing **4d** and **9d**. The signals, attributable to the expected 2-chlorothiophene 1,1-dioxide (**3d**), were also observed at about δ 6.6 and 6.9

and disappeared soon when the solution was allowed to stand at rt. Purification of the mixture by GPC gave 10 mg (8%) of **4d** and 9 mg (6%) of **9d**.

4d: mp 147-148 °C (from CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ: 4.10 (1H, dd, J = 11.4, 3.8 Hz), 4.47 (1H, ddd, J = 11.2, 4.4, 1.6 Hz), 5.81 (1H, dd, J = 5.8, 4.4 Hz), 6.10-6.21 (2H, m), 6.81 (1H, d, J = 3.8 Hz); ^{13}C NMR (100.6 MHz) δ: 41.4, 60.6, 114.5, 121.5, 126.8, 129.4, 130.5, 136.7; IR (KBr) ν_{max} (cm^{-1}): 1140, 1312, 1332, 1580, 1624, 2944, 3072; MS (EI) *m/z*: 240 (M^+), 238 (M^+), 236 (M^+), 201, 137, 112. Anal. Calcd for $C_8H_6O_2Cl_2S$: C, 40.52; H, 2.55. Found: C, 40.18; H, 2.66.

9d: mp 151-152 °C (decomp) (Me_2CO/hexane); ^{1}H NMR (400 MHz) δ: 4.26-4.33 (2H, m), 4.68 (1H, dd, J = 8.4, 4.0 Hz), 6.17 (1H, d, J = 7.0 Hz), 6.42 (1H, dd, J = 6.6, 4.0 Hz), 6.60 (1H, d, J = 3.6 Hz); ^{13}C NMR (100.6 MHz) δ: 50.2, 61.7, 62.0, 87.9, 127.4, 127.7, 130.6, 137.1; IR (KBr) ν_{max} (cm^{-1}): 1082, 1096, 1120, 1140, 1184, 1284, 1320, 1338, 1622, 3060, 3088; MS (EI) *m/z*: 286 (M^+), 284 (M^+), 238, 153, 137, 112. Anal. Calcd for $C_8H_6O_3Cl_2S_2$: C; 33.70; H, 2.12. Found: C, 33.83; H, 2.00.

Preparation and Thermolysis of 2-Bromothiophene 1,1-Dioxide (3e)

A mixture of 103 mg (0.63 mmol) of 2-bromothiophene (**2e**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –20 °C. A 0.07 M solution (18 mL, 1.3 mmol) of DMD in acetone, cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 4 days at –20 °C and then cooled below –40 °C. The solvent and volatile materials were removed *in vacuo* below –40 °C. The resiude was washed with hexane (1 mL x 5), crystallized from CH_2Cl_2/hexane, and dried *in vacuo* below –40 °C to provide colorless crystals of **3e** contaminated with **9e**. In a separate experiment, purification of the residue (obtained from 103 mg of **2e** in the manner described above) with GPC gave 8 mg of **4e** and 8 mg of **9e** (8 and 7% yields based on **2e**). Spectroscopic data of **3e** were given in the text.

A 0.03 M $CDCl_3$ solution of **3e** (contaminated with **9e**) was prepared in the same way as that of **3a**. The solution was warmed at 35 °C. The progress of the reaction was monitored by ^{1}H NMR to determine the half-life of **3e**. After 5 days, **3e** decomposed completely to give the dimeric product **4e** solely and nearly quantitatively.

4e: mp 154-155 °C (from CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ: 4.09-4.17 (1H, m), 4.44 (1H, ddd, J = 11.2, 4.0, 2.0 Hz), 5.88 (1H, dd, J = 9.6, 4.0 Hz), 6.01-6.09 (1H, m), 6.36 (1H, dd, J = 6.4, 2.0 Hz), 6.96 (1H, d, J = 3.6 Hz); ^{13}C NMR (100.6 MHz) δ: 45.0, 60.3, 115.3, 119.3, 124.2, 125.7, 127.1, 135.7; IR (KBr) ν_{max} (cm^{-1}): 1138, 1308, 1330, 1580, 1605, 2994, 3050; MS (EI) *m/z*: 328 (M^+), 326 (M^+), 324 (M^+), 183, 158, 102. Anal. Calcd for $C_8H_6O_2Br_2S$: C, 29.47; H, 1.86. Found: C, 29.47; H, 1.77.

9e: mp 120-121 °C (decomp) (Me_2CO/hexane); ^{1}H NMR (400 MHz) δ: 4.18 (1H, t, J = 5.0 Hz), 4.25 (1H, dd, J = 8.4, 5.0 Hz), 4.57 (1H, dd, J = 8.4, 5.0 Hz), 6.15 (1H, d, J = 7.0 Hz), 6.31 (1H, dd, J = 7.0, 5.0 Hz), 6.66 (1H, d, J = 1.8 Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 53.9, 61.4, 62.0, 77.7, 123.1, 129.0, 131.3, 134.8; IR (KBr) ν_{max} (cm^{-1}): 1075, 1091, 1118, 1136, 1311, 1335; MS (EI) *m/z*: 376 (M^+), 374 (M^+), 372 (M^+), 326, 275, 156. Anal. Calcd for $C_8H_6O_3Br_2S_2$: C; 25.69; H, 1.62. Found: C, 25.95; H, 1.69.

Oxidation of 3-Bromothiophene (2f)

A mixture of 125 mg (0.77 mmol) of 3-bromothiophene (**2f**) and molecular sieves 4A (*ca.* 200 mg) in acetone (5 mL) was cooled at –20 °C. A 0.070 M solution (22 mL, 1.5 mmol) of DMD in acetone, cooled at –20 °C, was then added to the mixture through a Teflon tubing. The resulting mixture was stirred for 4 days at –20 °C and then cooled below –40 °C. The solvent and volatile materials were removed *in vacuo* below –40 °C. The residue was washed with hexane (1 mL x 5) and crystallized from CH_2Cl_2/hexane below –40 °C to give colorless crystals. An ^1H NMR analysis disclosed that the crystals are a mixture containing **4f** and **9f**. The signals, which might be attributable to the expected 3-bromothiophene 1,1-dioxide (**3f**), were also observed around δ 6.7 and attenuated slowly at room temperature. Purification of the crystals by GPC gave 2 mg (2%) of **4f** and 5 mg (3%) of **9f** as the identifiable products.

4f: mp 156-157 °C (from CH_2Cl_2/hexane); ^1H NMR (400 MHz) δ: 4.10-4.18 (1H, m), 4.28 (1H, ddd, J = 11.0, 4.8, 1.6 Hz), 5.86 (1H, dd, J = 11.0, 3.8 Hz), 6.12 (1H, d, J = 3.8 Hz), 6.35 (1H, d, J = 10.0 Hz), 7.11 (1H, d, J = 1.6 Hz); ^{13}C NMR (100.6 MHz) δ: 47.9, 60.0, 117.6, 117.7, 120.3, 131.9, 132.4, 137.1; IR (KBr) ν_{max} (cm^{-1}): 1112, 1130, 1306, 1604, 3068; MS (EI) *m/z*: 328 (M^+), 326 (M^+), 324 (M^+), 278, 198, 183, 102. Anal. Calcd for $C_8H_6O_2Br_2S$: C, 29.48; H, 1.86. Found: C, 29.51; 1.79.

9f: mp 159-160 °C (decomp) (Me_2CO/hexane); ^1H NMR (400 MHz) δ: 4.25-4.30 (1H, m), 4.31-4.37 (1H, m), 4.56 (1H, dd, J = 8.2, 4.0 Hz), 4.72 (1H, ddd, J = 7.9, 3.9, 1.8 Hz), 6.58 (1H, dd, J = 4.8, 1.8 Hz), 6.77 (1H, d, J = 2.2 Hz); ^{13}C NMR (100.6 MHz) δ: 55.0, 64.6, 64.7, 71.4, 115.7, 128.6, 132.8, 136.1; IR (KBr) ν_{max} (cm^{-1}): 1078, 1098, 1108, 1118, 1136, 1282, 1310, 1604, 3050, 3098; MS (EI) *m/z*: 376 (M^+), 374 (M^+), 372 (M^+), 325, 278, 198, 183, 102. Anal. Calcd for $C_8H_6O_3Br_2S_2$: C; 25.69; H, 1.61. Found: C, 25.94; 1.48.

X-Ray Crystallographic Analysis of 16b

A single crystal of **16b** was analyzed at 295 K on a MAC MXC 18K diffractometer, Mo K_α (λ = 0.71073 Å) radiation with a graphite crystal monochronometer in the incident beam. The unit cell dimensions were obtained by a least-squares fit of 22 automatically centered reflections in the range of $31.7 < 2\theta < 34.5°$. Intensity data were collected using ω–2θ technique to a maximum 2θ of 55°. The scan width, Δω, for each reflections was 1.42 + 0.35tanθ, with a scan speed of 10.0° min^{-1}. The structure was solved by direct methods using SIR[10] in the CRYSTAN-GM program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares[11] to minimize the functions $\Sigma w(|Fo|-|Fc|)^2$. Chemical formula: $C_{15}H_{18}O_4S_2$, formula weight: 326.4, monoclinic, space group: $C_{2/c}$, crystal dimension: 0.28 x 0.18 x 0.14 mm, a = 32.959(5), b = 8.157(1), c = 11.845(2) Å, β = 103.83(2)°, V = 3092.0(9) $Å^3$, Z = 8, D_{calcd} = 1.402 Mgm^{-3}, μ = 3.41 mm^{-1}, number of measured reflections: 2909 [1755 observed with $I > 2\sigma(I)$], refined parameters: 262, R = 0.048, wR = 0.045, S = 1.454.

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