Oxidation of Congested Thiophene 1,1-Dioxides with *m*-Chloroperbenzoic Acid. Formation of Epoxides and Thiete 1,1-Dioxides and Steric Acceleration

Hiroaki Kamiyama, Ryuji Hasemi, and Juzo Nakayama*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

Received 9 March 1993

ABSTRACT

A series of thiophene dioxides (3), including highly congested ones, were synthesized. Their oxidation with m-chloroperbenzoic acid (m-CPBA) was investigated either in the presence or in the absence of Na₂CO₃. The following conclusions were reached. (1) Oxidation in the presence of Na₂CO₃ affords the corresponding epoxides (4) in moderate to excellent yields. (2) Oxidation in the absence of Na₂CO₃ produces the ring-contracted thiete 1,1-dioxides (5) as the principal product, thus providing a novel synthesis of the sulfur-containing unsaturated four-membered ring system. If necessary, 5 can also be derived by treatment of 4 with BF₃·Et₂O. In an extreme case, the oxidation of 3,4-di(1-adamantyl)thiophene afforded the corresponding thiete dioxide 5b directly in 78% yield. (3) Oxidation takes place faster with a more congested 3, probably because of destabilization of the HOMO by steric repulsion between bulky substituents and also owing to relief of steric crowding on going from the ground to the transition state. (4) The formation of 5 from 3 in the absence of Na₂CO₃ can be explained by the occurrence of an acid-catalyzed rearrangement of 4 initially formed. However, a competitive pathway leading directly to 5 may also be operative.


Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

*To whom correspondence should be addressed.

INTRODUCTION

It is well known that the oxidation of α,β-unsaturated sulfones with HOO^- [1,2], t-$BuOO^-$ [2], ClO^- [3], and m-$ClC_6H_4CO_3^-$ [2] represents a convenient route to α,β-epoxy sulfones. To our knowledge, however, only a few reports describe the oxidation of thiophene 1,1-dioxides, a type of cyclic α,β-unsaturated sulfone. Thus, the oxidation of benzo[*b*]thiophene 1,1-dioxide with alkaline hydrogen peroxide affords 3-oxo-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (1), whereas the oxidation of the 3-alkyl- or 3-phenyl-substituted derivatives produces the corresponding 3-hydroxy-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxides (2) [4]. We have also reported that the oxidation of 3,4-di-*t*-butylthiophene 1,1-dioxide (3a) with *m*-chloroperbenzoic acid (*m*-CPBA) in refluxing 1,2-dichloroethane in the presence of Na₂CO₃ gives the epoxide 4a, while the oxidation of 3a in the absence of the base produces the ring-contracted thiete 1,1-dioxide 5a [5]. The formation of 5a was explained by the occurrence of acid-catalyzed rearrangement of 4a initially formed [6]. In our continuing study on congested thiophenes and related compounds, we have observed that the oxidation of 3,4-di(1-adamantyl)thiophene with excess *m*-CPBA affords not only the thiophene dioxide 3b but also either the epoxide 4b or the thiete dioxide 5b, depending on the presence or absence of Na₂CO₃, even at room temperature. These results mean that the sterically more congested 3b is more rapidly oxidized than 3a, because the *m*-CPBA oxidation of 3a was previously carried out in refluxing 1,2-dichloroethane and the fact that we have never observed the

formation of the epoxide **4a** or the thiete dioxide **5a** by *m*-CPBA oxidation of 3,4-di-*t*-butylthiophene at room temperature [5]. These findings prompted us to examine the *m*-CPBA oxidation of a series of congested thiophene dioxides, with emphasis being placed on the effect of bulky substituents on the rate of oxidation [7].

1

2
(R=alkyl or Ph)

3a   4a

5a   3b

4b   5b

3c   3d

3e   3f

3g   3h

3i
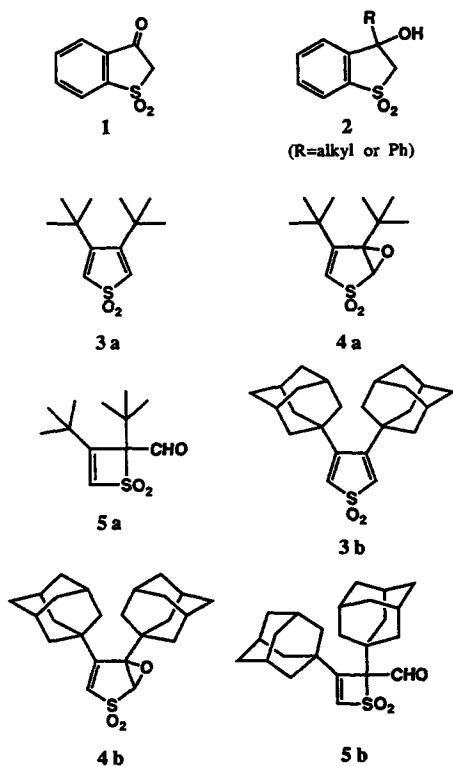
RESULTS AND DISCUSSION

Preparation of Thiophene 1,1-Dioxides (3)

Thiophene 1,1-dioxides **3a** [8] and **3b** [9] were prepared as previously reported by us. Thiophene dioxide **3c** was synthesized by *m*-CPBA oxidation of 2,4-di-*t*-butylthiophene which could be obtained by isomerization of the easily available 3,4-di-*t*-butylthiophene. Compounds **3d** and **3e** were synthesized from **3a** and **3c**, respectively, by lithiation with lithium diisopropylamide (LDA) followed by methylation with MeI. Compounds **3f** and **3i** were prepared by *m*-CPBA oxidation of 2,5-dimethyl-3-*t*-butyl- and tetramethylthiophenes, respectively. Highly congested thiophene dioxides **3g** and **3h** were synthesized by dilithiation of **3a** and **3b**, respectively, with LDA followed by methylation with MeI.

m-CPBA Oxidation of Thiophene 1,1-Dioxides (3)

m-CPBA purified by the literature method [10] was used throughout this work unless otherwise stated. All the oxidations were carried out both in the
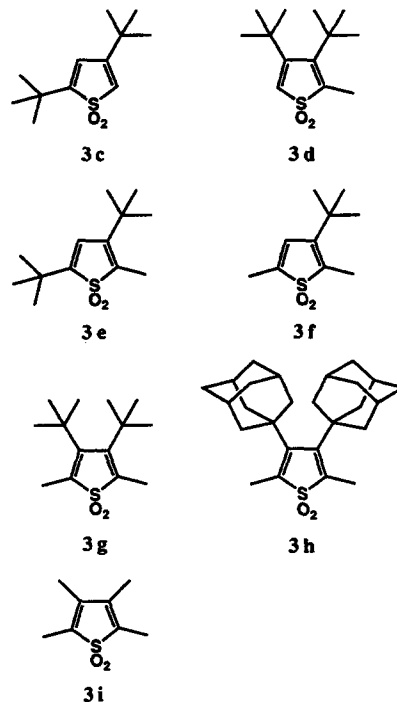
presence and absence of Na₂CO₃ and at room temperature, even though a long period of time was required for completion of the reaction.

First, we reexamined the oxidation of the thiophene dioxide **3a**, which revealed that the reaction proceeds even at room temperature, though very slowly. Thus, oxidation of **3a** with *m*-CPBA in the absence of Na₂CO₃ for 2 weeks gave the epoxide **4a** in 79% yield and the thiete dioxide **5a** in 3% yield, while the oxidation in the presence of Na₂CO₃ for 3 weeks produced **4a** exclusively in 82% yield.

The oxidation of **3b** for 9 days in the absence of Na₂CO₃ gave the epoxide **4b** in 78% yield and the thiete dioxide **5b** in a small amount. In the ^{1}H NMR spectrum of **4b**, signals due to the methine and vinyl protons appear as doublets (J = 2.2 Hz) at δ 4.56 and 6.15, respectively. Since such a coupling has also been observed with **4a** [5], this type of long range coupling seems to be general for the present ring system [11]. When the oxidation was carried out by using commercial *m*-CPBA without purification, the yield of **5b** increased to 40% and that of **4b** decreased to 52%, suggesting that the acidic impurities of the commercial product may catalyze the rearrangement of **4b** to **5b**. In accordance with this assumption, the oxidation in the presence of Na₂CO₃ gave **4b** exclusively in 71% yield with 10% recovery of **3b**. In an extreme case, the oxidation of 3,4-di(1-adamantyl)thiophene with excess *m*-CPBA directly gave **5b** in 78% yield. This is of particular importance from a viewpoint of thiete dioxide synthesis.

A 1:1 mixture of **3a** and **3b** was oxidized with

m-CPBA for 57 hours. ¹H NMR analysis showed that the mixture consisted of **3a**, **3b**, **4a**, and (**4b** + **5b**) in the ratio 78:43:22:57. This reveals that **3b** is oxidized about 3.4 times faster than **3a**.

The oxidation of 2,4-di-*t*-butylthiophene dioxide (**3c**) with excess *m*-CPBA for 8 days in the presence of Na₂CO₃ resulted in the recovery of **3c** in 78% yield and gave the epoxide **4c** in low yield (16%). On the other hand, the oxidation in the absence of Na₂CO₃ for 7 days resulted in the recovery of **3c** in 85% yield and gave the isomeric epoxide **4c′** (6%) but not **4c**. The identity of the structure **4c** was confirmed by spectroscopic data and also by chemical transformation to the thiete dioxide **4e** as described later. Although we cannot explain why either **4c** or **4c′** is formed exclusively, depending on the conditions, the recovery of **3c** in good yields under both conditions leads to the conclusion that the oxidation of the sterically less congested **3c** is slower than that of the more congested **3a** and **3b** which carry bulky substituents on the vicinal positions.

The oxidation of trisubstituted thiophene dioxide **3d** in the presence of Na₂CO₃ for 2 weeks produced the epoxides **4d** and **4d′** in 50 and 17% yields, respectively. During workup of the mixture by silica gel column chromatography, rearrangement of **4d** to the thiete dioxide **5d** was observed in a certain case. Properties of **4d′** are identical with those of the sample previously obtained in our laboratories by lithiation and subsequent methylation of **4a** [5]. In agreement with the above observation,
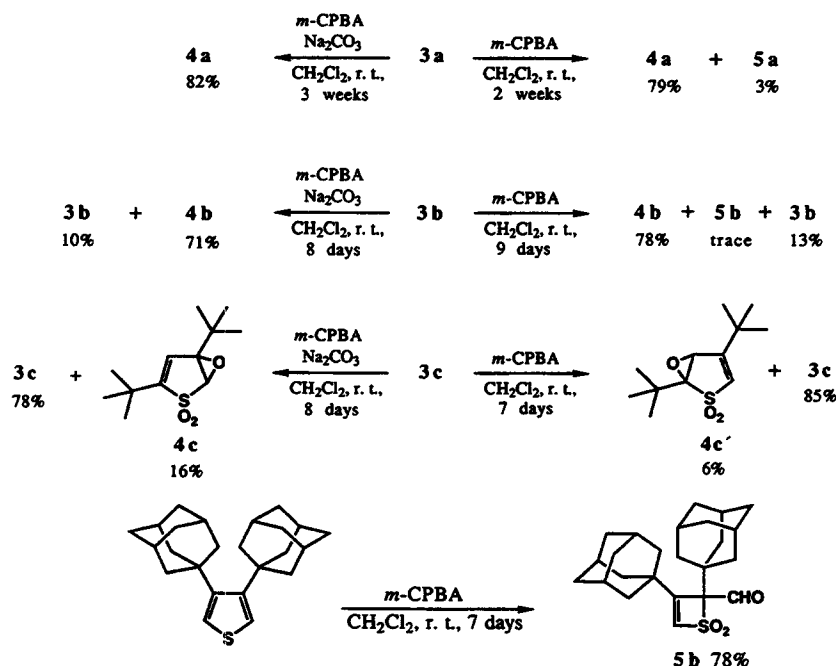
oxidation of **3d** in the absence of Na₂CO₃ gave the ring-contracted thiete dioxides **5d** and **5d′** in 44 and 19% yields, respectively. In a separate experiment, epoxide **4d′** was isolated in 12% yield along with **5d** in 59% yield. Thus, rearrangement of **4d** to **5d** takes place more easily than does that of **4d′** to **5d′**.

The oxidation of **3e** for 7 days in the presence of Na₂CO₃ gave a 33% yield of the epoxide **4e**, with 65% recovery of the starting material. Complete consumption of the starting material required a prolonged reaction time (7 weeks), affording **4e** in 41% isolated yield. The structure of **4e** was confirmed by an independent synthesis; lithiation of the epoxide **4c** with LDA, followed by methylation with MeI, gave **4e**. Oxidation of **3e** in the absence of Na₂CO₃ for 7 days gave a 77% yield of the starting material and a low yield (4%) of the thiete dioxide **5e**, which corresponds to the rearrangement product of the epoxide **4e**.
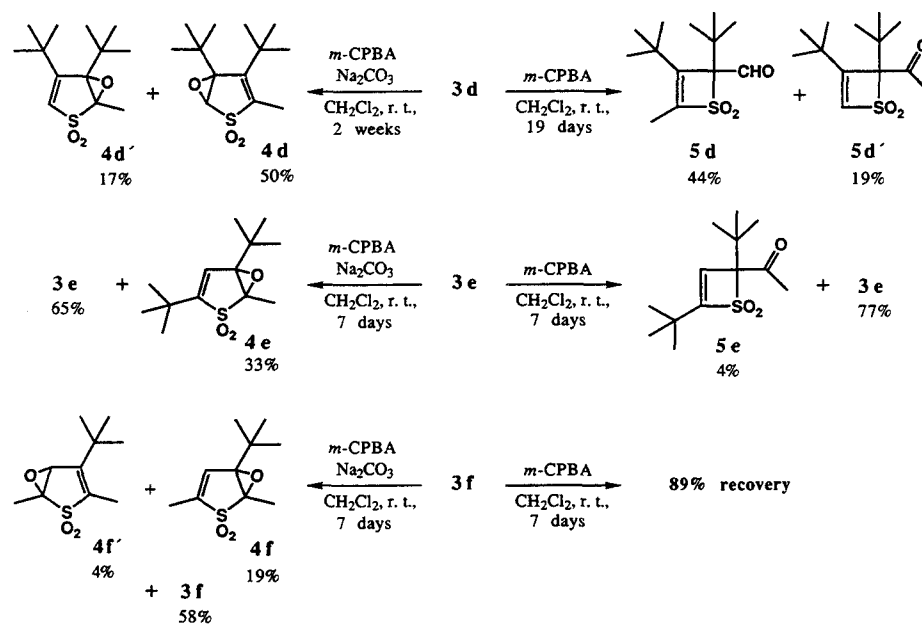
The oxidation of **3f** for 7 days in the presence of Na₂CO₃ afforded the epoxides **4f** and **4f′** in 19 and 4% yields, respectively, with 58% recovery of **3f**. On the other hand, oxidation of **3f** in the absence of Na₂CO₃ resulted in the 89% recovery of **3f**; any other products could not be isolated in pure form.

Results with the three trisubstituted compounds **3d–f** again revealed that the oxidation of the most congested **3d** takes place more easily than those of the less congested **3e** and **3f**.

Oxidation of the highly congested **3g** and **3h**

SCHEME 1

SCHEME 2

4d′ 17% + 4d 50%

m-CPBA Na₂CO₃ CH₂Cl₂, r. t., 2 weeks ← 3 d → *m*-CPBA CH₂Cl₂, r. t., 19 days

5 d 44% + 5 d′ 19%

3 e 65% + 4 e 33%

m-CPBA Na₂CO₃ CH₂Cl₂, r. t., 7 days ← 3 e → *m*-CPBA CH₂Cl₂, r. t., 7 days

5 e 4% + 3 e 77%

4 f′ 4% + 4 f 19% + 3 f 58%

m-CPBA Na₂CO₃ CH₂Cl₂, r. t., 7 days ← 3 f → *m*-CPBA CH₂Cl₂, r. t., 7 days

89% recovery

represents an extreme case. Thus, oxidation of **3g** in the presence of Na₂CO₃ was complete in 23 hours to afford the epoxide **4g** in 85% yield. Rearrangement of **4g** to the thiete dioxide **5g** on silica gel was observed during purification. On the other hand, the oxidation in the absence of Na₂CO₃ for 19 hours produced **5g** in 95% yield.

Oxidation of the most congested thiophene dioxide **3h** takes place very smoothly. Thus, the oxidation of **3h** in the presence of Na₂CO₃ for 21 hours afforded the epoxide **4h** in 99% yield. This epoxide rearranges to the thiete dioxide **5h** quantitatively on silica gel. When a sample of **4h** in a capillary tube was inserted into a melting point apparatus preheated at 150°C, it melted soon, then solidified, and melted again at 222–227°C, which corresponds to the melting point of **5h**. Oxidation in the absence of Na₂CO₃ for 40 hours gave **5h** in 97% yield. The driving force of the ready rearrangement of **4g** and **4h** must be attributed to relief of steric crowding on going from the ground to the transition state.

The oxidation of tetramethylthiophene dioxide **3i** is slower than those of **3g** and **3h**. Oxidation in the presence of Na₂CO₃ for 48 hours afforded the epoxide **4i** in 40% yield with 20% recovery of **3i**. The oxidation in the absence of Na₂CO₃ for 48 hours resulted in 53% recovery of **3i**, but any other products could not be isolated in pure form.

Results with the three tetrasubstituted compounds **3g–i** again led to the conclusion that the highly congested **3g** and **3h** are more easily oxidized than is the less congested **3i**.

The electron-donating properties of methyl, *t*-butyl, and 1-adamantyl groups are much the same; Hammett's σ_m-values of methyl and *t*-butyl are −0.07 and −0.10 [12], respectively, while that of 1-adamantyl is not available. Therefore, the en-

hanced reactivities of congested thiophene dioxides, mentioned previously should be independent of the electronic effect of substituents and must be ascribed to steric repulsion between bulky substituents which activates these molecules in two ways. First, the HOMO of congested molecules will be destabilized and activated since *p*-orbitals of these molecules are not parallel to each other, and thus, their overlapping is insufficient. Second, steric crowding in the ground state should decrease to some extent in the transition state, since the oxidation is accompanied by the change in hybridization of the reaction center from sp² to sp³.

Partial support for the preceding description comes from the PM3 calculations performed with MOPAC Version 5.0 [13]. Calculated torsion angles of thiophene dioxides **3a**, **3b**, **3g**, and **3i** are given in Table 1. As expected, the highly congested compound **3g** shows the large torsion angles, not only between *t*-butyl groups on the 3- and 4-positions, but also between methyl and *t*-butyl groups on the 2- and 3-positions (44 and 24°, respectively), while the tetramethyl compound **3i** is a nearly planar molecule. The torsion angles between the *t*-butyl groups of **3a**, determined by X-ray analysis, are 5.8 and 7.4° (**3a** exists in two different conformations in the crystals) [14] and are larger than the calculated torsion angle (3.3°). HOMO and LUMO energies of **3a**, **3b**, **3g**, and **3i** are summarized in Table 2. The HOMO of **3g** is the highest, and this may explain the enhanced reactivity of **3g**.

We need to discuss the mechanism of the formation of the thiete dioxides **5** in some detail. The most probable mechanism for the formation of **5** involves the acid-catalyzed rearrangement of the epoxides **4** initially formed, where acidic materials, such as *m*-CPBA and *m*-chlorobenzoic acid,
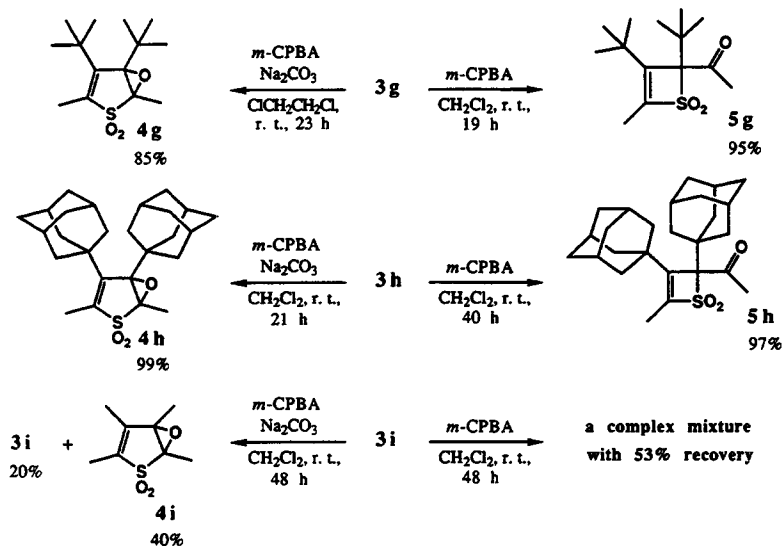
SCHEME 3

TABLE 1 Torsion Angles (°) of Thiophene 1,1-Dioxides **3**

Compounds	3a	3b	3g	3i
R_1-C_1-C_2-R_2	1.53	−2.83	23.96	−0.01
R_2-C_2-C_2-R_2	−3.32	5.39	−44.04	−0.02

act as catalysts [6] (Scheme 4). The following observations support this mechanism.

1. Thiete dioxides **5** are formed only in the absence of Na_2CO_3, namely, under acidic conditions.

2. The use of commercial *m*-CPBA, without

TABLE 2 HOMO and LUMO Energies of Thiophene 1,1-Dioxides **3**

| Compounds	3a	3b	3g	3i
HOMO (eV)	−10.49	−10.43	−9.70	−9.87
LUMO (eV)	−1.06	−1.04	−0.95	−1.05

purification, affords increased yields of **5** in compensation for **4**.

3. It was observed that some epoxides **4** rearranged to **5**. During the oxidation of **3d**, rearrangement of the epoxide **4d'** to the thiete dioxide **5d'** was confirmed by ¹H NMR spectroscopy. Epoxides **4d**, **4g**, and **4h** rearrange to **5d**, **5g**, and **5h**, respectively, on silica gel. By treatment with 1M H_2SO_4, **4g** rearranges to **5g**, although slowly.

However, the preceding mechanism is out of harmony with the following observations.

1. On treatment of **4b** and **4g** with *m*-chlorobenzoic acid, they remained unchanged. Epoxide **4b** did not undergo the rearrangement even in the presence of both *m*-CPBA and *m*-chlorobenzoic acid.

2. Treatment of **4a** and **4b** with 1M H_2SO_4 did not bring about the rearrangement. Treatment of **4a** with 18M H_2SO_4 afforded a complex mixture containing a small amount of **5a**.

3. Epoxides **4** smoothly rearrange to **5** only by use of a Lewis acid, such as $BF_3 \cdot Et_2O$. For example, treatment of **4b**, **4f**, and **4g** with $BF_3 \cdot Et_2O$ in CH_2Cl_2 at room temperature for 0.5 hours gave **5b**, **5f**, and **5g** in 52, 53, and 97% yields, respectively.

It is probable, therefore, that two mechanisms
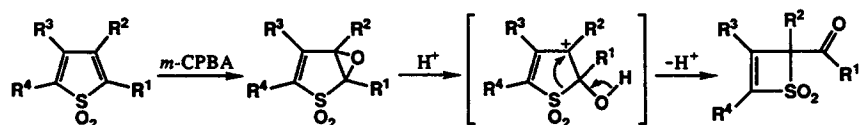
SCHEME 4
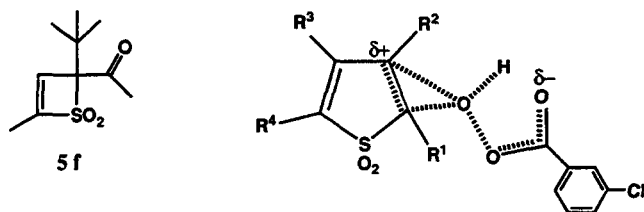
SCHEME 5

are competitively operative for the formation of **5**. One is the mechanism involving **4** as the intermediate. The other is shown in Scheme 5. In the epoxidation of thiophene dioxides carrying bulky substituents on β-positions, the hydroxylic oxygen of m-CPBA cannot form bonds with α- and β-carbons in equal strength, which results in the formation of an unsymmetrical transition state in which the greater partial positive charge is localized on the β-position. In such a transitional state, migration of the sulfur atom to the β-position with cleavage of the sulfur-carbon bond would directly give rise to the thiete dioxides **5**.

In conclusion, the oxidation of compounds **3** in the presence of Na_2CO_3 provides a convenient synthesis of epoxy sulfones **4** having a unique ring system. However, the oxidation in the absence of Na_2CO_3 provides an interesting synthesis of thiete dioxides **5** which are otherwise difficult to prepare. Finally, the present oxidation study represents a unique case of steric acceleration.

EXPERIMENTAL

General Procedures

Melting points were determined in open capillary tubes on a Mel-Temp melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a JEOL FX-90Q spectrometer (90 MHz) or on a Bruker AM-400 spectrometer (400 MHz) with Me_4Si as an internal standard; ^{13}C NMR on the above instruments (22.5 MHz and 100.6 MHz), with reference to the center of $CDCl_3$ (77.0). Infrared spectra were determined on a Hitachi 270-50 infrared spectrophotometer. Mass spectra were obtained at 70 eV on a Shimadzu QP-1000 spectrometer. High resolution mass spectra were determined on a JEOL DX-303 spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Silica gel used for column chromatography was 70–230 mesh ASTM, Merck 7734 Kieselgel. m-Chloroperbenzoic acid (Tokyo Kasei) was purified before use unless otherwise stated [10]; a benzene solution was washed with a buffer solution (pH 7.4), prepared from aqueous 0.1 M NaH_2PO_4 and 0.1 M NaOH solutions, dried over $MgSO_4$, and the benzene was removed carefully. Dichloromethane used

as the solvent for m-CPBA oxidation was washed with water, dried over $CaCl_2$, and distilled prior to use.

Preparation of Thiophene 1,1-Dioxides (3)

3,4-Di-t-butyl-, 3,4-di(1-adamantyl)-, and tetramethylthiophene 1,1-dioxides (**3a**, **3b**, and **3i**) are known compounds and were prepared by m-CPBA oxidation of the corresponding thiophenes [8,9,15]. 3,4-Di-t-butyl-2,5-dimethyl- and 3,4-di(1-adamantyl)-2,5-dimethylthiophenes (**3g** and **3h**) were prepared by dilithiation of **3a** and **3b** with LDA followed by methylation with methyl iodide. Preparation of these compounds will be reported in detail elsewhere.

Preparation of 2,4-Di-t-butylthiophene 1,1-Dioxide (**3c**). A mixture of 7.6 g (38.7 mmol) of 3,4-di-t-butylthiophene [8] and 6.2 g (46.4 mmol) of $AlCl_3$ in 150 mL of carbon disulfide was stirred for 6 days at room temperature. Usual workup of the mixture gave 5.8 g (75%) of 2,4-di-t-butylthiophene, bp 66–68°C/1 mmHg. To a stirred and ice-cooled solution of 4.7 g (24 mmol) of 2,4-di-t-butylthiophene in 100 mL of CH_2Cl_2 was added a solution of 13.0 g (75 mmol) of m-CPBA in 70 mL of CH_2Cl_2. The mixture was warmed slowly to room temperature and stirred for 7 hours. The m-chlorobenzoic acid, which had separated, was removed by filtration and the filtrate was washed with aq $NaHSO_3$, $NaHCO_3$, and then water and dried. Removal of the solvent and recrystallization of the solid residue from hexane gave 2.8 g (51%) of the thiophene dioxide, mp 136–137°C; results by ^1H NMR ($CDCl_3$, 90 MHz) δ 1.16 (s, 9H), 1.39 (s, 9H), 6.07 (d, J = 1.3 Hz, 1H), 6.33 (d, J = 1.3 Hz, 1H); by ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 27.46 (q), 29.08 (q), 33.17 (s), 34.58 (s), 120.61 (d), 120.61 (d), 152.68 (s), 154.36 (s). Anal. calcd for $C_{12}H_{20}O_2S$: C, 63.12; H, 8.83; found: C, 62.88; H, 8.67.

Preparation of 3,4-Di-t-butyl-2-methylthiophene 1,1-Dioxide (**3d**). To a stirred solution of 1.14 g (5 mmol) of 3,4-di-t-butylthiophene 1,1-dioxide (**3a**) in 50 mL of tetrahydrofuran (THF) was added a solution of LDA [prepared from 3.3 mL of a 1.68 M hexane solution of butyllithium and 557 mg (5.5 mmol) of diisopropylamine in 10 mL of THF] at −78°C through rubber septa and a Teflon tubing by applying argon pressure. After the mixture had been stirred for 3 hours at −78°C, a solution of 3.55 g (25 mmol) of MeI in 10 mL of THF was added. The mixture was stirred for 3 hours at −78°C and warmed slowly to room temperature, and the reaction was quenched by the addition of ice-water. Repeated purifications of the crude product by silica gel column chromatography (hexane/ether:2/1) followed by recrystallization from hexane gave 190 mg (17%) of the pure thiophene dioxide **3d**, mp

90–90.5°C; results by ^{1}H NMR (CDCl$_3$) δ 1.41 (s, 9H), 1.46 (s, 9H), 2.24 (s, 3H), 6.53 (s, 1H); by ^{13}C NMR (CDCl$_3$) δ 11.13 (q), 32.20 (q), 32.36 (q), 36.26 (s), 124.05 (d), 136.43 (s), 145.48 (s), 159.83 (s). Anal. calcd for C$_{13}$H$_{22}$O$_2$S: C, 64.42; H, 9.15; found: C, 64.20; H, 9.08.

Preparation of 3,5-Di-t-butyl-2-methylthiophene 1,1-Dioxide (**3e**). To a stirred solution of 1.56 g (7 mmol) of 2,4-di-*t*-butylthiophene 1,1-dioxide (**3c**) in 30 mL of THF was added a solution of LDA [prepared from 5.3 mL of a 1.66 M hexane solution of butyllithium and 885 mg (8.8 mmol) of diisopropylamine in 10 mL of THF] at −78°C under argon. After the mixture had been stirred for 4 hours at −78°C, a solution of 4.28 g (30 mmol) of MeI in 5 mL of THF was added at that temperature. The mixture was stirred for 3 hours at −78°C, warmed slowly to room temperature, and then treated with aq NH$_4$Cl. Chromatographic workup of the mixture gave 885 mg (52%) of the thiophene dioxide **3e**, mp 63.5–64°C; results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.24 (s, 9H), 1.38 (s, 9H), 2.14 (s, 3H), 6.41 (s, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 8.42 (q), 28.87 (q), 29.19 (q), 34.20 (s), 34.42 (s), 123.73 (d), 130.52 (s), 140.00 (s), 149.81 (s). Anal. calcd for C$_{13}$H$_{22}$O$_2$S: C, 64.42; H, 9.15; found: C, 64.32; H, 9.01.

Preparation of 3-t-Butyl-2,5-dimethylthiophene 1,1-Dioxide (**3f**). 3-*t*-Butyl-2,5-dimethylthiophene [16] (3.37 g, 20 mmol) was oxidized with 10.35 g (60 mmol) of *m*-CPBA in CH$_2$Cl$_2$ in the usual manner. The crude product was purified by recrystallization from hexane to give 1.55 g (39%) of the pure thiophene dioxide **3f**, mp 137–137.5°C; results by ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.24 (s, 9H), 2.13 (d, $J = 0.9$ Hz, 3H), 2.19 (s, 3H), 6.45 (q, $J = 0.9$ Hz, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 8.53 (q), 8.91 (q), 28.65 (q), 34.37 (s), 125.59 (d), 129.82 (s), 137.46 (s), 141.31 (s). Anal. calcd for C$_{10}$H$_{16}$O$_2$S: C, 59.96; H, 8.05; found: C, 59.73; H, 7.88.

m-CPBA Oxidation of Thiophene 1,1-Dioxides (**3**)

Oxidation of 3,4-Di-t-butylthiophene 1,1-Dioxide (**3a**). *(a) In the presence of Na$_2$CO$_3$.* A mixture of 114 mg (0.5 mmol) of **3a**, 129 mg (0.75 mmol) of *m*-CPBA, and 80 mg (0.75 mmol) of Na$_2$CO$_3$ in 5 mL of CH$_2$Cl$_2$ was stirred for 3 weeks. Usual workup of the mixture followed by purification with silica gel column chromatography gave 100 mg (82%) of the epoxide **4a**, mp 111–112°C, whose spectroscopic properties were identical with those of the specimen prepared previously in our laboratories [5]. *(b) In the absence of Na$_2$CO$_3$.* A mixture of 114 mg (0.5 mmol) of **3a** and 129 mg (0.5 mmol) of *m*-CPBA in 5 mL of CH$_2$Cl$_2$ was stirred for 15 days. Usual workup of the mixture followed by purifi-

cation with silica gel column chromatography gave 74 mg of the epoxide **4a** and 24 mg of a 5:1 mixture of **4a** and the thiete 1,1-dioxide **5a**. In a separate experiment, **5a**, mp 71.5–72°C, was isolated in pure form and its spectroscopic properties were identical with those of the specimen prepared previously in our laboratories [5].

Oxidation of 3,4-Di(1-adamantyl)thiophene 1,1-Dioxide (**3b**). *(a) In the presence of Na$_2$CO$_3$.* Thiophene dioxide **3b** (133 mg, 0.35 mmol) was oxidized with 119 mg (0.69 mmol) of *m*-CPBA in the presence of 14 mg (0.14 mmol) of Na$_2$CO$_3$ in 5 mL of CH$_2$Cl$_2$ for 8 days (after 4 days, an additional 43 mg of *m*-CPBA and 5 mg of Na$_2$CO$_3$ were added). Usual workup of the mixture and purification by column chromatography gave 92 mg (66%) of the epoxide **4b**, 17 mg of a 1:1 mixture of **4b** and the thiophene dioxide **3b**, and 14 mg (11%) of **3b**. **4b**, mp 214.5–215°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.6–2.2 (m, 30H), 4.56 (d, $J = 2.2$ Hz, 1H), 6.15 (d, $J = 2.2$ Hz, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 28.19 (d), 28.41 (d), 35.56 (s), 36.10 (t), 39.19 (t), 39.46 (s), 41.46 (t), 64.76 (d), 74.13 (s), 128.95 (d), 165.30 (s); by IR (KBr) 1574 (C=C), 1309, 1132 cm^{-1} (SO$_2$); MS, *m/z* 372 (M$^+$-CO), 336 (M$^+$-SO$_2$), 308 (M$^+$-CO-SO$_2$). Anal. calcd for C$_{24}$H$_{32}$O$_3$S: C, 71.96; H, 8.05; found: C, 71.98; H, 7.92. *(b) In the absence of Na$_2$CO$_3$.* A mixture of 77 mg (0.2 mmol) of **3b** and 52 mg (0.3 mmol) of *m*-CPBA was stirred at room temperature. After 7 days, 35 mg (0.2 mmol) of *m*-CPBA was added and the mixture was stirred for an additional 2 days. Column chromatographic purification of the mixture gave 63 mg (78%) of **4b**, 10 mg (13%) of **3b**, and a trace amount of the thiete dioxide **5b**. *(c) Use of m-CPBA without purification.* A mixture of 97 mg (0.25 mmol) of **3b** and 87 mg (0.5 mmol) of *m*-CPBA (commercial product was used without purification) was stirred for 9 days (after 5 days, an additional 58 mg of *m*-CPBA was added). Purification of the mixture by column chromatography gave 45 mg (45%) of the thiete dioxide **5b** and 48 mg of a 1:6 mixture of **5b** and **4b**. Thiete dioxide **5b**, mp 251–252°C (from benzene); results by ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.4–2.3 (m, 30H), 6.77 (s, 1H), 9.94 (s, 1H); by ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 28.21 (d), 28.36 (d), 35.99 (t), 36.38 (t), 37.31 (t), 38.28 (s), 42.22 (t), 106.92 (s), 142.56 (d), 168.30 (s), 194.81 (d); by IR (KBr) 1724 (C=O), 1288, 1120 cm^{-1} (SO$_2$); by MS, *m/z* 371, 336, 307. Anal. calcd for C$_{24}$H$_{32}$O$_3$S: C, 71.96; H, 8.05; found: C, 71.67; H, 7.86. *(d) One-pot preparation of thiete dioxide (**5b**) from 3,4-Di-(1-adamantyl)thiophene.* A mixture of 151 mg (0.43 mmol) of 3,4-di-(1-adamantyl)thiophene and 684 mg (5 mmol) of *m*-CPBA (not purified) in 6 mL of CH$_2$Cl$_2$ was stirred at room temperature for 7 days. Chromatographic workup of the mixture gave 123 mg (78%) of the pure thiete dioxide **5b**.

Competitive Oxidation of **3a** *and* **3b.** A mixture of 91 mg (0.4 mmol) of **3a** and 154 mg (0.4 mmol) of **3b** in 5 mL of CH$_2$Cl$_2$ was oxidized with 104 mg (0.6 mmol) of *m*-CPBA for 57 hours. Workup of the mixture gave 258 mg of a white solid. Analysis by ^{1}H NMR revealed that this was a mixture of **3a**, **4a**, **3b**, and (**4b** + **5b**) in the ratio 78:22:43:57.

Oxidation of 2,4-Di-t-butylthiophene 1,1-Dioxide (**3c**). *(a) In the presence of Na$_2$CO$_3$.* A mixture of 228 mg (1 mmol) of **3c**, 518 mg (3 mmol) of *m*-CPBA, and 318 mg (3 mmol) of Na$_2$CO$_3$ in 10 mL of CH$_2$Cl$_2$ was stirred for 8 days. Purification of the mixture by silica gel column chromatography gave 178 mg (78%) of the starting material and 39 mg (16%) of the epoxide **4c**, mp 102–105°C (dec) (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.07 (s, 9H), 1.33 (s, 9H), 4.47 (s, 1H), 6.54 (s, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 25.56 (q), 29.35 (q), 31.01 (s), 34.69 (s), 65.68 (d), 67.57 (s), 127.38 (d), 157.50 (s); by IR (KBr) 1619 (C=C), 1305, 1144, 1129 cm^{-1} (SO$_2$); by MS, *m/z* 244 (M$^+$). Anal. calcd for C$_{12}$H$_{20}$O$_3$S: C, 58.98; H, 8.25; found: C, 58.96; H, 8.12. *(b) In the absence of Na$_2$CO$_3$.* A mixture of 171 mg (0.75 mmol) of **3c** and 155 mg (0.9 mmol) of *m*-CPBA in 7.5 mL of CH$_2$Cl$_2$ was stirred for 7 days. Chromatographic workup of the mixture gave 146 mg (85%) of the starting material and 10 mg (6%) of the epoxide **4c′**, mp 81–83°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.01 (s, 9H), 1.36 (s, 9H), 4.74 (s, 1H), 6.38 (s, 1H); by ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 24.57 (q), 29.46 (q), 34.41 (s), 37.13 (s), 76.15 (s), 84.27 (d), 132.20 (d), 153.86 (s); by IR (KBr) 1657 (C=C), 1282, 1155 cm^{-1} (SO$_2$); by MS, *m/z* 159 (M$^+$-*t*-BuCO, 100%).

Oxidation of 3,4-Di-t-butyl-2-methylthiophene Dioxide (**3d**). *(a) In the presence of Na$_2$CO$_3$.* A mixture of 73 mg (0.3 mmol) of **3d**, 62 mg (0.36 mmol) of *m*-CPBA, and 38 mg (0.36 mmol) of Na$_2$CO$_3$ in 6 mL of CH$_2$Cl$_2$ was stirred for 2 weeks. Purification of the products by silica gel column chromatography gave 27 mg (35%) of the epoxide **4d** and 25 mg of a 1:1 mixture of **4d** and its isomeric epoxide **4d′**. This means that **4d** and **4d′** were formed in 50 and 17% yields, respectively. In a separate experiment, the epoxide **4d′** could be isolated in pure form and its spectroscopic data (^{1}H and ^{13}C NMR) agreed with those of the specimen obtained previously by methylation of **4a** [5]. Epoxide **4d**, mp 71–74°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.24 (s, 9H), 1.42 (s, 9H), 2.11 (s, 3H), 4.46 (s, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 11.62 (q), 29.46 (q), 31.33 (q), 34.47 (s), 36.75 (s), 66.11 (d), 73.42 (s), 138.92 (s), 151.71 (s); IR (KBr) 1594 (C=C), 1302, 1157, 1118 cm^{-1} (SO$_2$). This compound failed to give a satisfactory elemental analysis; calculated for C$_{13}$H$_{22}$O$_3$S: C, 60.43; H, 8.58; found: C, 61.30; H, 8.86. *(b) In the absence of Na$_2$CO$_3$.* A mixture of 242 mg (1 mmol) of **3d** and 207 mg

(1.2 mmol) of *m*-CPBA in 10 mL of CH$_2$Cl$_2$ was stirred at room temperature. ^{1}H NMR analysis revealed that the mixture consisted of **4d′**, thiete dioxides **5d** and **5d′**, and the starting material in the ratio 3:10:1:3 after 10 days and in the ratio 1:10:4:2 after 18 days. After 18 days, 207 mg (1.2 mmol) of *m*-CPBA was added and the mixture was stirred for an additional 2 days. Column chromatographic workup of the mixture gave 66 mg (25%) of pure **5d** and 94 mg of a 1:1 mixture of thiete dioxides **5d** and **5d′**. This means that **5d** and **5d′** were formed in 44 and 19% yields, respectively. Thiete dioxide **5d**, mp 97–98°C (hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.32 (s, 9H), 1.40 (s, 9H), 2.13 (s, 3H), 9.94 (s, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 9.96 (q), 28.11 (q), 30.55 (q), 35.23 (s), 35.34 (s), 106.58 (s), 151.81 (s), 158.86 (s), 195.24 (d); IR (KBr) 1716 (C=O), 1618 (C=C), 1283, 1135 cm^{-1} (SO$_2$). Anal. calcd for C$_{13}$H$_{22}$O$_3$S: C, 60.43; H, 8.58; found: C, 59.84; H, 8.39. Thiete dioxide **5d′**, which was contaminated with **5d**, showed the following ^{1}H and ^{13}C NMR data; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.35 (s, 9H, *t*-butyl), 1.38 (s, 9H, *t*-butyl), 2.50 (s, 3H, MeCO), 6.70 (s, 1H, vinyl H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 28.46 (q), 31.20 (q), 32.07 (q), 35.13 (s), 36.11 (s), 111.29 (s), 140.10 (d, thiete ring carbon carrying H), 171.92 (s, thiete ring carbon carrying *t*-butyl), 202.39 (s, C=O).

Oxidation of 3,5-Di-t-butyl-2-methylthiophene 1,1-Dioxide (**3e**). *(a) In the presence of Na$_2$CO$_3$.* A mixture of 182 mg (0.75 mmol) of **3e**, 155 mg (0.9 mmol) of *m*-CPBA, and 95 mg (0.9 mmol) of Na$_2$CO$_3$ in 7.5 mL of CH$_2$Cl$_2$ was stirred for 7 days at room temperature. Usual workup of the mixture gave 209 mg of a colorless oil which consisted of a 1:2 mixture of the epoxide **4e** and the starting material. Attempted purification of the mixture resulted in the decomposition of **4e** and gave the starting material in 65% yield. These results mean that the epoxide was formed in 33% yield. In a separate experiment, **3e** was treated with excess *m*-CPBA until it was completely consumed (7 weeks). This allowed us to isolate **3e** in pure form in 42% yield, mp 70–71°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.13 (s, 9H), 1.32 (s, 9H), 1.96 (s, 3H), 6.57 (s, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 8.64 (q), 26.54 (q), 29.30 (q), 32.52 (s), 34.47 (s), 68.71 (s), 75.27 (s), 129.03 (d), 154.36 (s); by IR (KBr) 1625 (C=C), 1298, 1163 cm^{-1} (SO$_2$); by MS, *m/z* 258 (M$^+$). Anal. calcd for C$_{13}$H$_{22}$O$_3$S: C, 60.43; H, 8.58; found: 60.14; H, 8.51. *(b) In the absence of Na$_2$CO$_3$.* A mixture of 182 mg (0.75 mmol) of **3e** and 155 mg (0.9 mmol) of *m*-CPBA in 7.5 mL of CH$_2$Cl$_2$ was stirred for 7 days. Chromatographic workup of the mixture gave 140 mg (77%) of the starting material and 8 mg (4%) of the thiete dioxide **5e**, mp 110–113°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.20 (s, 9H), 1.29 (s, 9H), 2.38 (s, 3H), 6.71 (s, 1H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 27.35 (q), 28.27 (q),

31.53 (q), 34.19 (s), 35.81 (s), 104.69 (s), 130.68 (d), 169.33 (s), 202.51 (s); by IR (KBr) 1706 (C=O), 1630 (C=C), 1292, 1142 cm^{-1} (SO$_2$); by MS, m/z 258 (M$^+$); by exact mass calculated for C$_{13}$H$_{22}$O$_3$S: 258.1290; found: 258.1269.

Derivation of **4e** *from* **4c**. Epoxide **4c** (32 mg, 0.13 mmol) was lithiated with LDA (0.26 mmol) at −78°C in THF in the usual manner and then methylated with MeI (1 mmol) (−78°C to room temperature). Workup of the mixture gave 26 mg of a 1:1 mixture of **4c** and **4e**. The ^{1}H NMR spectrum of this mixture agreed with that of **4e** derived from **3e** except for the signals due to **4c**.

Oxidation of 3-t-Butyl-2,5-dimethylthiophene 1,1-Dioxide (**3f**). (*a*) *In the presence of Na$_2$CO$_3$*. A mixture of 200 mg (1 mmol) of **3f**, 207 mg (1.2 mmol) of *m*-CPBA, and 127 mg (1.2 mmol) of Na$_2$CO$_3$ in 10 mL of CH$_2$Cl$_2$ was stirred for 7 days at room temperature. Workup of the mixture gave 237 mg of a yellow oil which was a mixture of the starting material, the epoxide **4f**, and the isomeric epoxide **4f'** in the ratio 58:19:4. Attempted separation of these compounds by silica gel column chromatography was unsuccessful. In a separate experiment, 0.60 g of **3f** was oxidized with excess *m*-CPBA until it was completely consumed. This enabled us to isolate 109 mg (17%) of **4f** and 110 mg of a 2:1 mixture of **4f** and **4f'**. Epoxide **4f**, mp 102–102.5°C (dec) (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.13 (s, 9H), 2.00 (s, 3H), 2.04 (d, J = 1.7 Hz, 3H), 6.61 (q, J = 1.7 Hz, 1H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 9.01 (q), 9.66 (q), 26.65 (q), 32.58 (s), 69.90 (s), 75.05 (s), 131.23 (d), 142.33 (s); by IR (KBr) 1298, 1163 cm^{-1} (SO$_2$); by MS, m/z 216 (M$^+$). Anal. calcd for C$_{10}$H$_{16}$O$_3$S: C, 55.53; H, 7.46; found: C, 55.50; H, 7.27. Epoxide **4f'**; results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.30 (s, 9H), 1.90 (s, 3H), 2.09 (s, 3H), 3.86 (s, 1H); by ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 9.03 (q), 9.35 (q), 28.97 (q), 35.43 (s), 58.41 (d), 68.13 (s), 134.95 (s), 147.40 (s). (*b*) *In the absence of Na$_2$CO$_3$*. Oxidation of 200 mg (1 mmol) of **3f** with 207 mg (1.2 mmol) of *m*-CPBA for 7 days gave 178 mg (89%) of the starting material; any other materials could not be isolated in pure form.

Oxidation of 3,4-Di-t-butyl-2,5-dimethylthiophene 1,1-Dioxide (**3g**). (*a*) *In the presence of Na$_2$CO$_3$*. A mixture of 128 mg (0.5 mmol) of **3g**, 185 mg (1.1 mmol) of *m*-CPBA, and 113 mg (1.1 mmol) of Na$_2$CO$_3$ in 5 mL of 1,2-dichloroethane was stirred for 23 hours at room temperature. Chromatographic workup of the mixture gave 115 mg (85%) of the epoxide **4g**, mp 77.5–79°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.29 (s, 9H), 1.41 (s, 9H), 2.04 (s, 3H), 2.09 (s, 3H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 11.45 (q), 13.57 (q), 30.27 (q), 31.09 (q), 34.75 (s), 36.75 (s), 76.40 (s), 77.81 (s), 136.38 (s), 154.31 (s); by IR (KBr) 1602 (C=C), 1291,

1165 cm^{-1} (SO$_2$); by MS, m/z 272 (M$^+$). Anal. calcd for C$_{14}$H$_{24}$O$_3$S: C, 61.73; H, 8.88; found: C, 61.60; H, 8.61. (*b*) *In the absence of Na$_2$CO$_3$*. Oxidation of 128 mg (0.5 mmol) of **3g** with 129 mg (0.75 mmol) of *m*-CPBA in 5 mL of CH$_2$Cl$_2$ at room temperature for 19 hours gave 130 mg (95%) of the thiete dioxide **5g**, mp 101–101.5°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.37 (s, 9H), 1.39 (s, 9H), 2.10 (s, 3H), 2.51 (s, 3H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 9.50 (q), 29.00 (q), 30.57 (q), 31.55 (q), 35.12 (s), 35.56 (s), 110.97 (s), 148.67 (s), 161.51 (s), 202.68 (s); by IR (KBr) 1697 (C=O), 1621 (C=C), 1284, 1135 cm^{-1} (SO$_2$); by MS, m/z 272 (M$^+$). Anal. calcd for C$_{14}$H$_{24}$O$_3$S: C, 61.73; H, 8.88; found: C, 61.52; H, 8.60.

Oxidation of 3,4-Di(1-adamantyl)-2,5-dimethylthiophene 1,1-Dioxide (**3h**). (*a*) *In the presence of Na$_2$CO$_3$*. Stirring of a mixture of 41 mg (0.1 mmol) of **3h**, 26 mg (0.15 mmol) of *m*-CPBA, and 16 mg (0.15 mmol) of Na$_2$CO$_3$ in 3 mL of CH$_2$Cl$_2$ at room temperature gave 43 mg (99%) of the pure epoxide **4h**. This epoxide readily rearranged to the thiete dioxide **5h** on silica gel column or on heating. Thus, when it was heated slowly in a capillary tube, it melted at 222–227°C, which corresponds to the melting point of **5h**, and when it was placed in a melting point apparatus preheated at 150°C, it melted soon, resolidified, and melted again at 222–227°C. Results by ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.6–2.5 (m, 30H), 2.11 (s, 3H), 2.14 (s, 3H); by ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 12.09 (q), 14.66 (q), 28.61 (d), 28.80 (d), 29.64 (s), 36.18 (t), 36.31 (t), 37.42 (s), 40.02 (t), 40.64 (t), 76.36 (s), 79.12 (s), 136.13 (s), 154.78 (s); by IR (KBr) 1288, 1160 cm^{-1} (SO$_2$); by MS, m/z 428 (M$^+$). Anal. calcd for C$_{26}$H$_{36}$O$_3$S: C, 72.86; H, 8.47; found: C, 72.75; H, 8.37. (*b*) *In the absence of Na$_2$CO$_3$*. Stirring of a mixture of 78 mg (0.19 mmol) of **3h** and 39 mg (0.23 mmol) of *m*-CPBA in 3 mL of CH$_2$Cl$_2$ at room temperature for 40 hours gave 78 mg of the pure thiete dioxide **5g** after purification by column chromatography, mp 227–228°C (from hexane); results by ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.6–2.4 (m, 30H), 2.13 (s, 3H), 2.51 (s, 3H); by ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 10.10 (q), 28.57 (d), 28.73 (d), 32.52 (q), 36.32 (t), 36.37 (t), 38.02 (t), 38.29 (s), 38.81 (s), 40.95 (t), 112.81 (s), 147.70 (s), 173.11 (s), 202.68 (s); by IR (KBr) 1705 (C=O), 1614 (C=C), 1285, 1153 cm^{-1} (SO$_2$); MS, m/z 428 (M$^+$). Anal. calcd for C$_{26}$H$_{36}$O$_3$S: C, 72.86; H, 8.47; found: C, 73.01; H, 8.44.

Oxidation of Tetramethylthiophene 1,1-Dioxide (**3i**). (*a*) *In the presence of Na$_2$CO$_3$*. A mixture of 86 mg (0.5 mmol) of **3i**, 152 mg (0.88 mmol) of *m*-CPBA, and 211 mg of Na$_2$CO$_3$ in 5 mL of CH$_2$Cl$_2$ was stirred for 48 hours at room temperature. Purification of the mixture by silica gel column chromatography gave 55 mg of a 2:1 mixture of the epoxide **4i** and the starting material. This result indicated the for-

mation of **4i** in 40% yield, with 20% recovery of the starting material. In a separate experiment, 138 mg (0.8 mmol) of **3i** was stirred with excess m-CPBA in the presence of Na_2CO_3 until it was completely consumed (2 weeks). This allowed us to isolate 62 mg (41%) of the pure epoxide **4i**, mp 92–95°C (from hexane); results by ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 3H), 1.82 (s, 3H), 1.93 (broad s, 3H), 1.96 (broad s, 3H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 7.34 (q), 7.44 (q), 12.05 (q), 12.37 (q), 64.32 (s), 72.50 (s), 134.80 (s), 140.71 (s); IR (KBr) 1655 (C=C), 1293, 1168, 1110 cm^{-1} (SO_2); by MS, m/z 188 (M$^+$). Anal. calcd for $C_8H_{12}O_3S$: C, 51.04; H, 6.43; found: C, 50.78; H, 6.16. *(b) In the absence of Na_2CO_3.* A mixture of 86 mg (0.5 mmol) of **3i** and 129 mg (0.75 mmol) of m-CPBA in 5 mL of CH_2Cl_2 was stirred for 48 hours at room temperature. Purification of the mixture by column chromatography gave 46 mg (53%) of the starting material. Any other products were not isolated in pure form.

Acid-Catalyzed Rearrangement of Epoxides 4 to Thiete Dioxides 5

With m-Chlorobenzoic Acid. Stirring of a mixture of 30 mg (0.08 mmol) of the epoxide **4b** and 6 mg (0.04 mmol) of m-chlorobenzoic acid in 3 mL of CH_2Cl_2 for 8 days at room temperature resulted in the quantitative recovery of **4b**. Under the same conditions, no rearrangement of **4g** was observed.

With m-CPBA + m-Chlorobenzoic Acid. Stirring of a mixture of 30 mg of **4b**, 6 mg of m-chlorobenzoic acid, and 7 mg of m-CPBA in 3 mL of CH_2Cl_2 for 7 days at room temperature resulted in the recovery of **4b** in 93% yield.

With Commercial m-CPBA. Stirring of 28 mg of **4b** with 34 mg of commercial m-CPBA in 3 mL of CH_2Cl_2 for 2 weeks resulted in the rearrangement to the thiete dioxide **5b** to some extent. After having been stirred for 6 weeks, **4b** rearranged to **5b** nearly quantitatively.

With H_2SO_4. Stirring of a mixture of 37 mg of **4a** in 3 mL of CH_2Cl_2 and 0.01 mL of 1M H_2SO_4 for 19 hours at room temperature resulted in the quantitative recovery of **4a**. Under similar conditions, **4b** also did not undergo the rearrangement. Stirring of a mixture of 68 mg of **4g** in 3 mL of CH_2Cl_2 with 25 mg of 1M H_2SO_4 for 4 days at room temperature gave the thiete dioxide **5g** in 9% yield, with recovery of **4g** in 89% yield. Stirring of a mixture of 37 mg of **4a** in 3 mL of CH_2Cl_2 with 3 mg of 18M H_2SO_4 for 9 days at room temperature gave a complex mixture containing the thiete dioxide **5a** in a small amount.

With $BF_3 \cdot Et_2O$. Stirring of a mixture of 68 mg (0.25 mmol) of **4g** and 7 mg (0.05 mmol) of $BF_3 \cdot Et_2O$ in 5 mL of CH_2Cl_2 for 0.5 hours at room temperature gave 60 mg (97%) of the thiete dioxide **5g** after purification by column chromatography. Under similar conditions, epoxides **4b** and **4f** also underwent the same rearrangement to give **5b** and **5f** in 52 and 53% yields, respectively. Thiete dioxide **5f**, mp 134–136°C (from hexane); results by ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 9H), 2.08 (d, J = 1.5 Hz, 3H), 2.38 (s, 3H), 6.83 (q, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.83 (q), 27.32 (q), 31.44 (q), 35.75 (s), 105.91 (s), 134.92 (d), 156.07 (s), 202.16 (s); IR (KBr) 1701 (C=O), 1630 (C=C), 1293, 1116 cm^{-1} (SO_2); MS, m/z 216 (M$^+$). Anal. calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46; found: C, 55.48; H, 7.22.

REFERENCES

[1] B. Zwanenburg, J. ter Wiel, *Tetrahedron Lett.*, 1970, 935.

[2] R. Curci, F. DiFuria, *Tetrahedron Lett.*, 1974, 4085.

[3] C. Clark, P. Hermans, O. Meth-Cohn, C. Moore, H. C. Taljaard, G. van Vuuren, *J. Chem. Soc., Chem. Commun.*, 1986, 1378.

[4] S. Marmor, *J. Org. Chem.*, 42, 1977, 2927.

[5] J. Nakayama, Y. Sugihara, *J. Org. Chem.*, 56, 1991, 4001.

[6] T. Durst, K.-C. Tin, *Tetrahedron Lett.*, 1970, 2369; D. F. Tavares, R. E. Estep, M. Blezard, *Tetrahedron Lett.*, 1970, 2373; A. A. M. Houwen-Claassen, J. W. McFarland, B. H. M. Lammerink, L. Thijs, B. Zwanenburg, *Synthesis*, 1983, 628; M. Yamamoto, K. Suzuki, S. Tanaka, K. Yamada, *Bull. Chem. Soc. Jpn.*, 60, 1987, 1523.

[7] A part of this work was preliminarily reported; J. Nakayama, H. Kamiyama, *Tetrahedron Lett.*, 33, 1992, 7539.

[8] J. Nakayama, S. Yamaoka, M. Hoshino, *Tetrahedron Lett.*, 29, 1988, 1161; J. Nakayama, S. Yamaoka, T. Nakanishi, M. Hoshino, *J. Am. Chem. Soc.*, 110, 1988, 6598.

[9] J. Nakayama, R. Hasemi, *J. Am. Chem. Soc.*, 112, 1990, 5654.

[10] D. D. Perrin, W. L. F. Armarego: *Purification of Laboratory Chemicals*, Pergamon, Oxford, p. 123 (1988).

[11] A similar long range coupling was also observed with the epoxide of cyclopentadienone; O. L. Chapman, T. C. Hess, *J. Org. Chem.*, 44, 1979, 962.

[12] L. P. Hammett: *Physical Organic Chemistry*, McGraw-Hill, New York, p. 356 (1970).

[13] J. J. P. Stewart, MOPAC Version 5.0, QCPE No. 455.

[14] M. Yasui, M. Morimoto, F. Iwasaki, J. Nakayama, *21st Symp. on Structural Organic Chemistry*, Tsukuba, Japan, October 1992, paper OB-9.

[15] J. Nakayama, M. Kuroda, M. Hoshino, *Heterocycles*, 24, 1986, 1233.

[16] N. Messina, E. V. Brown, *J. Am. Chem. Soc.*, 74, 1952, 920.