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Thiophene 1,1-Dioxide: Synthesis, Isolation, and Properties

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Oxidation of thiophene with dimethyldioxirane at −20 °C and removal of the solvent and volatile materials below −40 °C allowed the isolation of the parent thiophene 1,1-dioxide (**1**) as colorless crystals in pure form. The 1,1-dioxide **1**, which had eluded isolation for a long time despite many efforts, melted at about 6 °C and the melt solidified at room temperature because of the dimeric and trimeric products formation. The structure of **1** was fully characterized by ^{1}H- and ^{13}C NMR, IR, Raman, UV/vis, and Mass spectroscopies. The decomposition of **1** in solution provided the dimer (**7**) as the principal product along with the trimer (**9**), whereas the decomposition of a neat sample furnished **7** and **9** in comparable amounts. The half-life of **1** is dependent upon the concentration of **1**; 137 and 747 min at 25 °C in 0.12 and 0.025 M $CDCl_3$ solutions (1 M = 1 mol dm^{-3}), respectively. Kinetics of the dimerization of **1** in a dilute solution provided the activation parameters of E_a = 64.4 (±0.3) kJ mol^{-1}, $\Delta H^{\neq}$ = 62.0 (±0.3) kJ mol^{-1}, and $\Delta S^{\neq}$ = −59.8 (±1.0) J K^{-1} mol^{-1}. Attempted reactions of **1** with a series of dienophiles and dienes all failed because the dimerization of **1** is much faster than reactions with these additives. An exception is the reaction with cyclopentadiene which gave the Diels–Alder adduct in good yield. The adduct of the dimer **7** with dimethyl acetylenedicarboxylate was found to undergo a retro Diels–Alder reaction to regenerate **1**.

Thiophene 1,1-dioxides in which the lone pair electrons on the sulfur atom are substituted by two oxygen atoms are no longer aromatic. Thus they undergo a wide variety of reactions as unsaturated cyclic sulfones and hence have attracted much attention of synthetic as well as theoretical chemists. A recent exhaustive literature survey disclosed that more than three hundred papers had dealt with the chemistry of thiophene 1,1-dioxides.[1,2] Thiophene 1,1-dioxides are generally highly reactive, and only those which have more than two substituents on the thiophene ring are isolable under ordinary conditions. Although the chemistry of the parent thiophene 1,1-dioxide (**1**) had been a matter of keen interest,[3—5] it has eluded isolation and full characterization. We report here the synthesis, isolation, and properties of **1**.[6]

Previously the 1,1-dioxide **1** was generated by Hoffmann elimination of **2**[3b] or by dehydrobromination of **3** and **4**.[3a,3q—s] Evidence for the generation of **1** was provided by the formation of its [4+2] self-dimerization product and also by adduct formations with some other reagents (Chart 1).[3c,3d,3g—m,3o,3p,3t,4] It was also claimed that ^{1}H- and ^{13}C NMR[3n] and UV/vis[3b,3c] spectra of **1** were determined. The chemistry of **1** was also studied theoretically.[5]

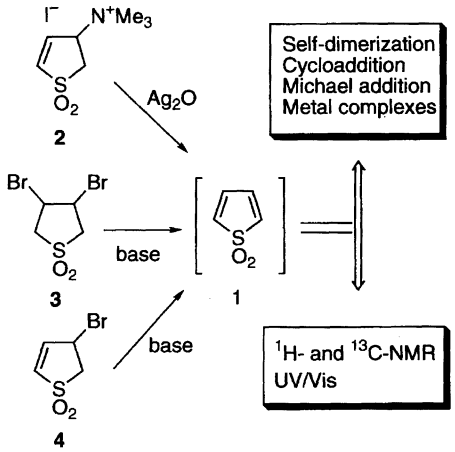
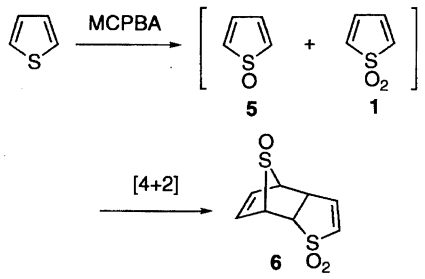


Chart 1.

Results and Discussion

Synthesis. Oxidation of thiophenes provides the most direct synthesis of thiophene 1,1-dioxides. Indeed, oxidation with peracids has most frequently provided the synthesis of thiophene 1,1-dioxides which are isolated under ordinary conditions.[1,2] Reportedly, however, the oxidation of thiophene with *m*-chloroperbenzoic acid (MCPBA) produced the sesquioxide **6**, which could be explained as the result of [4+2] cycloaddition of thiophene 1-oxide (**5**) and the 1,1-dioxide (**1**) (Scheme 1).[1e]

In the present study, dimethyldioxirane (DMD),[7] which is a strong but neutral oxidant and would be capable of oxidizing thiophene to the 1,1-dioxide **1** at low temperature, was employed with purpose of isolating **1**.[8] For this method, if the expected oxidation took place, the resulting products are only **1** and acetone formed from DMD. Even if thiophene and DMD remained unchanged, they are volatile and can be readily removed from the reaction mixture under reduced pressure. Thus, a solution of two molar amounts of DMD in acetone was added to a solution of thiophene in acetone at −18 °C, and the mixture was allowed to stand at that

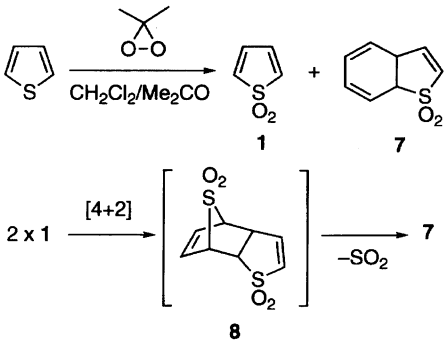


Scheme 1.

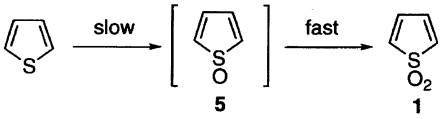
temperature for 7 h. The solvent and the volatile materials were removed below −15 °C under reduced pressure. An ^{1}H NMR spectrum analysis disclosed that the resulting crude product consisted of **1** and a dimeric product (**7**) in the molar ratio 88 : 12 (Table 1; Run 1). The dimer **7** is the product of [4+2] self-dimerization of **1**, followed by extrusion of SO_2 from the initial adduct **8**[3c] (Scheme 2). Structure proof for **1** and **7** is provided later. The oxidation, which was carried out by using three molar amounts of DMD at −20 °C for 36 h and then removing the solvent below −25 °C, yielded a mixture of **1** and **7** in the molar ratio 91 : 9 (Run 2). Finally, the reaction was carried out at −20 °C and the solvent was removed below −40 °C. This furnished the 1,1-dioxide **1** which is almost free of the dimeric product **7** (Run 3). The colorless crystals of the practically pure **1**, obtained in this way, melted at about 6 °C and the melt solidified slowly on standing because of the dimeric and trimeric products formation; the structure of the trimeric product is discussed later.

The following are concluded from the above results. Solvent removal below −40 °C is of crucial importance for isolation of **1** in pure form by suppressing the self-dimerization particularly when its solution was concentrated. It is noticeable that no product derived from the 1-oxide intermediate **5** was obtained. This suggests that, once **5** is formed, it is quickly oxidized to **1**, that is, the oxidation of **5** to **1** is much faster than the oxidation of thiophene to **5**, a process of the loss of the aromaticity of thiophene (Scheme 3). This conclusion should be generally true of oxidation of thiophenes because the oxidation usually affords thiophene 1,1-dioxides[1,2] and is seldom quenched at the 1-oxide stage.[9] The yield of **1** is nearly quantitative based on the consumed thiophene because of no formation of any by-product.

Spectroscopy. The ^{1}H NMR spectrum of **1** showed multiplets typical of an A_2B_2 pattern at δ = 6.53—6.61 and 6.75—6.83 (each 2H) (Fig. 1). The simulated spectrum, obtained by the Bruker software package PANIC with $^3J_{2,3}$ = 6.7, $^4J_{2,4}$ = 1.1, $^5J_{2,5}$ = 2.5, and $^3J_{3,4}$ = 4.0 Hz, is in good agreement with the observed one (Fig. 1).



Scheme 2.



Scheme 3.

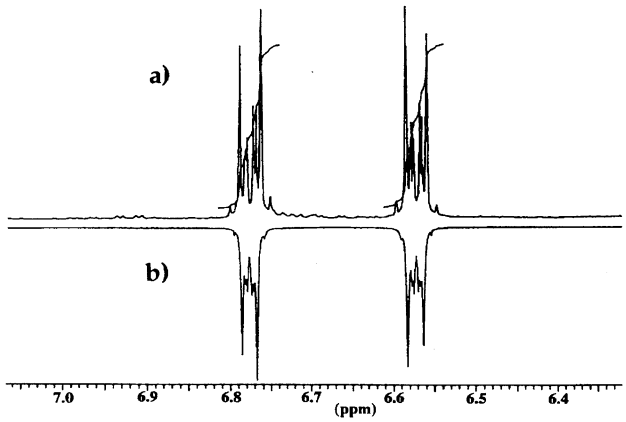
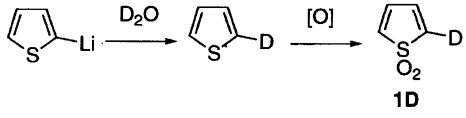


Fig. 1. ^{1}H NMR spectrum of **1** ($CDCl_3$ as solvent): a) top, observed; b) bottom, simulated.

The assignment of α- and β-hydrogen signals was made unambiguous by comparison of the spectrum of **1** and 2-deuteriothiophene 1,1-dioxide (**1D**). The latter 1,1-dioxide was prepared by oxidation of 2-deuteriothiophene which was obtained from 2-thienyllithium and D_2O (Scheme 4). In the ^{1}H NMR spectrum of **1D**, the intensity of the up-field



Scheme 4.

Table 1. Oxidation of Thiophene with Dimethyldioxirane (DMD)

Run	Reaction temperature	Reaction time	DMD (molar amounts)	Solvent-removal temperature	Molar ratio[a] **1** : **7**
1	−18 °C	2 h	2	below −15 °C	88 : 12
2	−25 °C	36 h	3	below −25 °C	91 : 9
3	−25 °C	6 h	3	below −40 °C	100 : 0[b]

a) The ratio was determined by ^{1}H NMR. b) **7** was found only in a trace amount.

multiplet is about half of that of the down-field one. Thus the up-field multiplet was assigned to the α-hydrogens and the down-field one to the β-hydrogens.

The ^{13}C NMR spectrum of **1** showed only two peaks at δ = 129.3 and 131.1 as expected from its structure (Fig. 2). The signals at δ = 131.3 and 129.3 showed the correlation with the α- and β-hydrogens in the C–H COSY NMR, and thus are assigned to the α- and β-carbons, respectively. The NMR data of **1** are summarized in Fig. 3. The previous paper reported that the ^{13}C NMR spectrum of **1**, produced by dehydrobromination of **4**, showed only one peak at δ = 129.1 due to accidental overlapping of the two signals.[3n] The same authors reported that the ^{1}H NMR spectrum of **1** showed two multiplets centered at δ = 6.38 and 6.64 which were, contrary to our assignment, assigned to the β- and α-hydrogens, respectively. The ^{13}C NMR data and the ^{1}H NMR assignment of this paper might require reconsideration.

Figure 4 shows the IR spectrum of **1**. The very strong absorptions at 1306 and 1152 cm^{-1} are assigned to ν_{SO2} asymmetric and symmetric stretching vibrations, respectively. Also in the Raman spectrum, the corresponding absorptions were observed at 1305 and 1151 cm^{-1}, respectively (Fig. 5). The absorption due to the C=C stretching vibration, which was very weak in the IR spectrum (1530 cm^{-1}), was now observed as an intense and sharp signal at 1530 cm^{-1}.

The UV/vis spectrum of **1** in $CHCl_3$ showed two absorption maxima at 245 (ε 870) and 288 nm (1070) (Fig. 6). Reportedly, **1**, generated from **2**, showed absorption maxima at 220 (ε 2010), 254 (450), and 289 nm (1230) ($CHCl_3$ as solvent),[3b] and **1**, generated from **3**, showed them at 220 (2000) and 289 nm (ε 880) (MeOH as solvent).[3f]

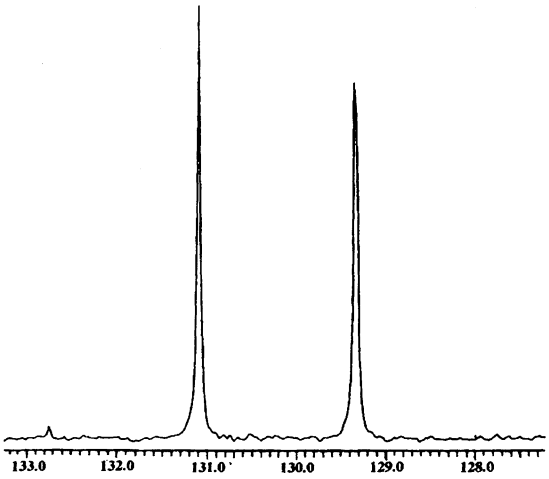


Fig. 2. ^{13}C NMR spectrum of **1** ($CDCl_3$ as solvent).

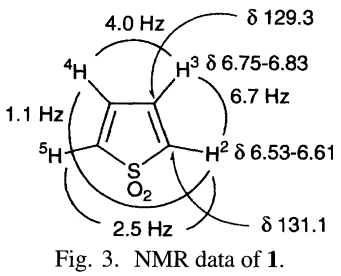


Fig. 3. NMR data of **1**.

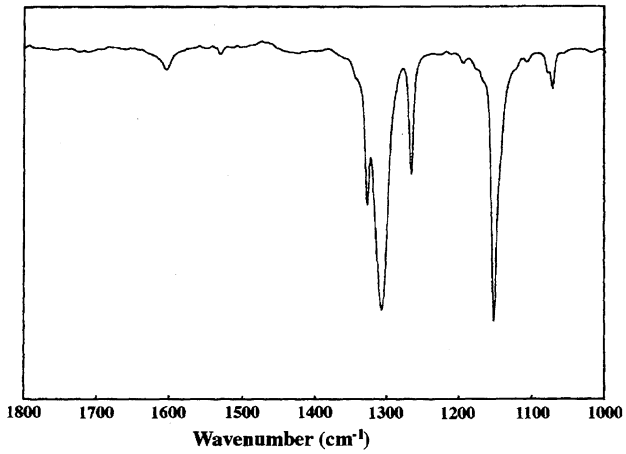


Fig. 4. FT-IR spectrum of **1** ($CDCl_3$ as solvent).

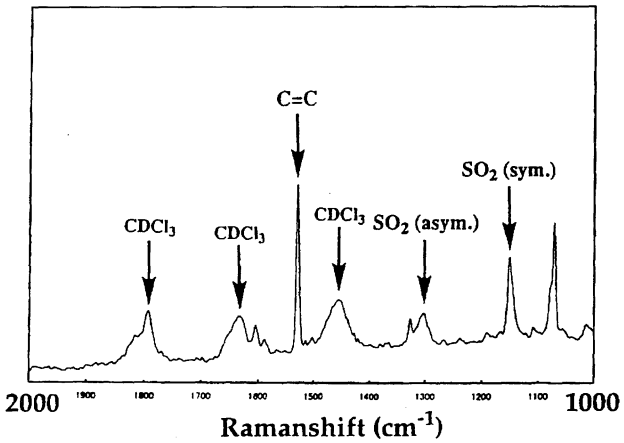


Fig. 5. FT-Raman spectrum of **1** ($CDCl_3$ as solvent).

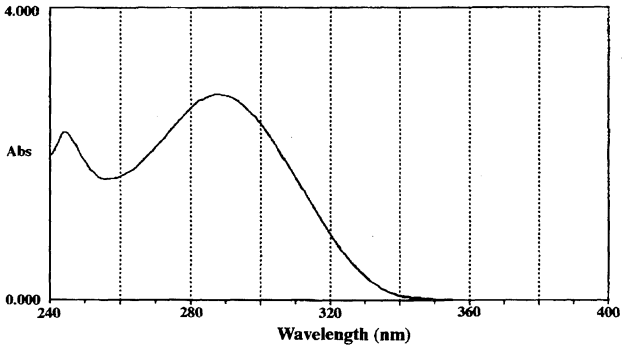
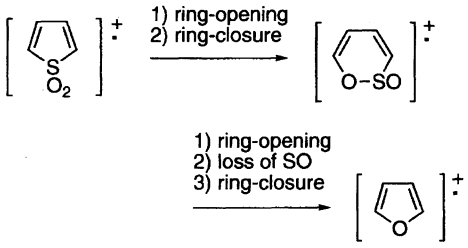


Fig. 6. UV/vis spectrum of **1** ($CDCl_3$ as solvent).

The GC/MS of **1** showed the molecular ion peak at the correct position of *m/z* 116. The most intense peak, which appeared at *m/z* 68, corresponds to the furan radical cation (Scheme 5). This fragmentation is in agreement with the frequent formation of furans by pyrolysis of thiophene 1,1-dioxides.[10] The HRMS gave the satisfactory results of, Calcd for $C_4H_4O_2S$: M, 115.9932. Found: *m/z* 115.9932.

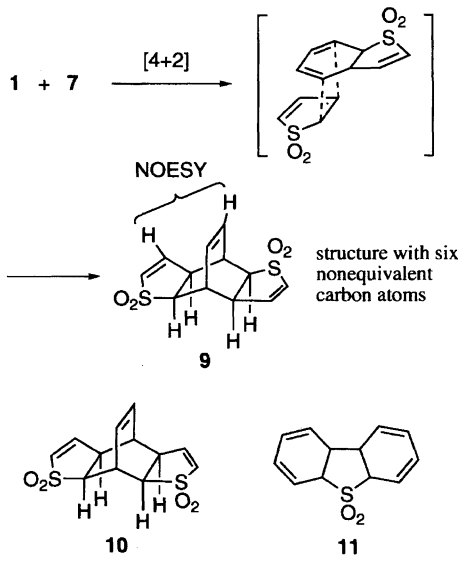
Dimerization vs. Trimerization of 1. The formation of the dimeric product **7** by decomposition of **1** was reported previously.[3c] Also claimed was the formation of a trimeric product by decomposition of **1** generated from



Scheme 5.

3 and **4**, although its exact structure has remained to be determined.[3a] Meanwhile, another paper reported that the formation of the trimetic product was not observed by ^{1}H NMR spectroscopy.[3n] We have now found that the trimeric product is truly formed in addition to **7**, when **1** was decomposed both in solution and without a solvent as described below. Structure of the trimeric product, including the stereochemistry, was determined as **9**, based on ^{13}C NMR and NOESY NMR spectra analyses (Scheme 6). The formation of **9** would be best explained by head-to-tail [4+2] cycloaddition of **1** and **7** in the *endo* mode, as was true in most Diels–Alder reactions. The trimer **9** showed only six peaks in the ^{13}C NMR spectrum, thus ruling out the isomeric structure **10**, which should exhibit eight peaks. The *endo* stereochemistry of **9** was confirmed by NOESY NMR experiments where the hydrogens of the central double bond and the β-hydrogens of the five-membered rings showed correlation to each other. The transition state leading to **10** in the head-to-head fashion should be unfavorable because of the dipole–dipole repulsive interactions between the two SO_2 groups. Another possible trimeric product **11**, which is formed by [4+2] cycloaddition of **1** and **7** where **1** acts as a diene and **7** as a dienophile, followed by loss of SO_2, was eliminated by the results of the elemental analysis.

The followings are experimental details on the formation of **7** and **9**. Letting a 0.12 M solution (1 M = 1 mol dm^{-3}) of **1** stand at 303 K for 3 d resulted in the complete decomposition of **1** to give **7** and **9** in the ratio 1.0 : 0.22 (Table 2, Run 1). Time course of the decomposition, monitored by ^{1}H NMR, is shown in Fig. 7. Six clean multiplets due to the six olefinic hydrogens of **7** are observed after 17 h. In the spectra after 30 and 51 h, new multiplets due to the trimeric product **9** are observed. Thus the trimer **9** begins to form with accumulation of the dimer **7**. For a more concentrated 0.20 M solution, the decomposition completed for 30 h to afford **7** and **9** in the ratio 1.0 : 0.36 (Run 2). The decomposition of a neat sample completed within 10 min at 303 K to produce **7** and **9** in the ratio 1.0 : 1.5 (Run 3). The rate of the decomposition of **1** is therefore remarkably accelerated by increasing concentration of **1** with increasing yield of **9**. The combined yield of **7** and **9** is quantitative since no other product is formed as is evident from the NMR spectra (Fig. 7).



Scheme 6.

Table 2. Rate and Product Ratio Dependence on Concentration in Decomposition of **1** at 303 K

Run	Concentration of $CDCl_3$ solution of **1** (M)	Time required for decomposition of **1**	Ratio of the yield **7**	**9**
1	0.12	3 d	1.0	0.22
2	0.20	30 h	1.0	0.36
3	Neat	< 10 min	1.0	1.5

Half-Life and Kinetics of the Decomposition of 1. Kinetics of the decomposition of **1** was determined by ^{1}H NMR spectroscopy at 298 K in $CDCl_3$. The decomposition obeyed the second order kinetics in **1** at the early stage. Table 3 summarizes the rate constants and the half-lives. The half-life of **1** is 137 min in a 0.12 M solution, while it is as long as 747 min in a dilute solution of 0.025 M. The previous studies reported that **1** survived for several days[3b] or for one day[3n] without self-dimerization in dilute solutions. Therefore, the present results, along with the previous ones, lead to the conclusion that **1** is thermodynamically rather stable, whereas it is kinetically reactive and dimerizes (trimerizes) quickly in concentrated solutions.

Next, kinetics of the decomposition of **1** was determined at 303, 308, 313, and 318 K, using a dilute $CDCl_3$ solution of 0.024 M where trimerization is neglected at the early stage of the reaction (Fig. 8). The rate constants are second order in **1** and are 1.65×10^{-3}, 2.49×10^{-3}, 3.78×10^{-3}, and 5.21×10^{-3} M^{-1} s^{-1} at 303, 308, 313, and 318 K, respectively. The Arrhenius plot (R^2 = 0.999) of the rate constants provided E_a of 64.4 ($\pm$0.3) kJ mol^{-1} and the Eyring plot (R^2 = 0.999) furnished $\Delta H^{\neq}$ of 62.0 ($\pm$0.3) kJ mol^{-1} and $\Delta S^{\neq}$ of -59.8 ($\pm$1.0) J K^{-1} mol^{-1}. The E_a value of the dimerization of cyclopentadiene was reported to be 68.5 kJ mol^{-1} both in benzene and ethanol[11] which is 4.1 kJ mol^{-1} larger than that of **1**. The relatively large negative value of $\Delta S^{\neq}$ reveals that the [4+2] dimerization of **1** takes place in a concerted Diels–Alder mode and the extrusion of SO_2 from the intermediate **8** is sufficiently fast and is not involved in the rate-determining step. The HOMO-LUMO energy gaps of **1** and cyclopentadiene, estimated by CNDO/2 calculations, are 13.03 and 15.61 eV, respectively.[3l] Although the above

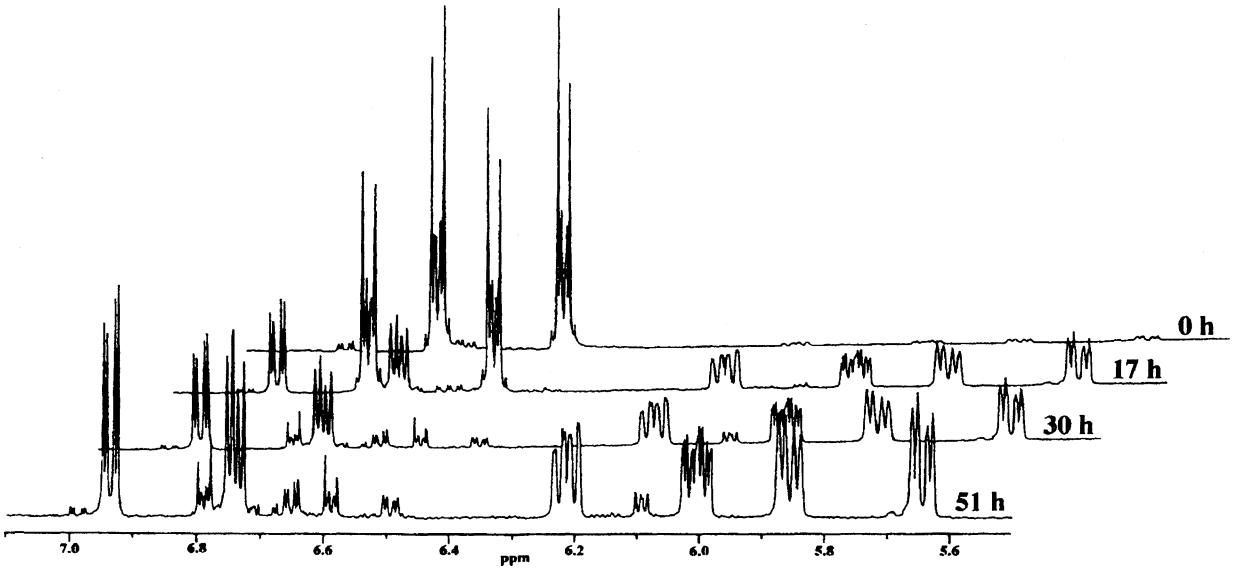


Fig. 7. Time course ^{1}H NMR spectrum of **1** (0.12 M $CDCl_3$ solution) at 298 K: from the top, after 0, 17, 30, 51 h, respectively.

Table 3. Rate Constant of the Decomposition and Half-Life of **1** in $CDCl_3$ at 298 K (^{1}H NMR Spectroscopy)

Concentration (M)	Rate constants k (M^{-1} s^{-1})	Half-lives (min)
0.12	9.48×10^{-4}	137
0.047	9.44×10^{-4}	371
0.025	8.94×10^{-4}	747

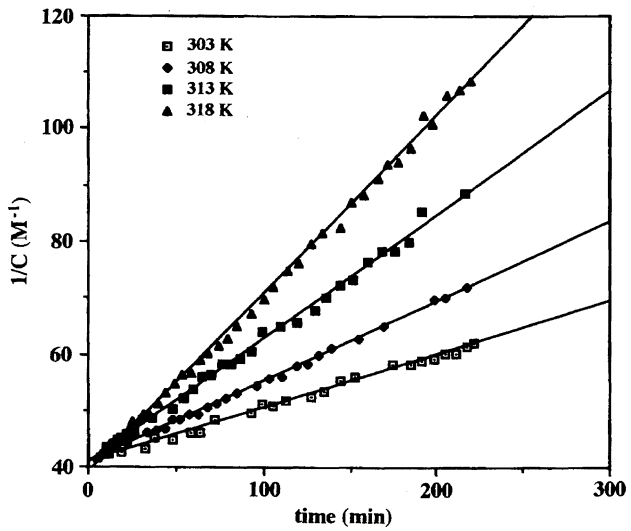
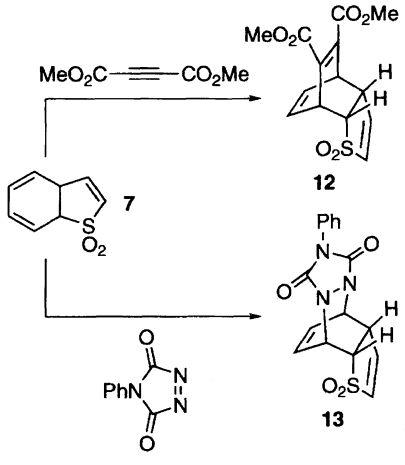


Fig. 8. Second order kinetics of the dimerization of **1** for a 0.024 M $CDCl_3$ solution at 303, 308, 313, and 318 K.

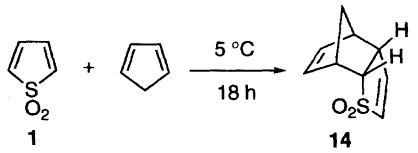
calculations provide a criterion to explain the easier dimerization of **1**, the HOMO-LUMO energy gaps, estimated by AM1 calculations, are comparable (9.61 and 9.56 eV for **1** and cyclopentadiene, respectively).[5g]

Reactions of 1. Reportedly **1** acted as a dienophile or a diene towards 2π-, 4π-, and 6π-components such as diethyl acetylenedicarboxylate,[3d] cyclooctyne,[3m] 1-bromo-2-chlorocyclopropene,[3t] indene,[3d] 1,2-bis(methylene)cyclohexane,[3d] and 6-(dimethylamino)fulvene.[3g,3h] We therefore examined the reactions of **1** with dienophiles in the beginning. Unexpectedly, **1** failed to react with electron-deficient dienophiles, dimethyl acetylenedicarboxylate (DMAD), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD), and *p*-benzoquinone, angle-strained alkenes, norbornene and acenaphthylene, and an electron-rich alkyne, bis(diethylamine)acetylene. In the cases of DMAD and PTAD, compounds **12** and **13**, which correspond to the Diels–Alder adducts of the dimer **7** with DMAD and PTAD, were obtained in good yields (Scheme 7). The stereochemistry of **12** was determined by NOESY experiments, while that given for **13** is tentative. In the other cases, the sole product was the dimer **7**, indicating that the dimerization of **1** is much faster than reactions with these dienophiles. This may in turn suggest that satisfactory chemical trapping of **1** requires its generation in situ in low concentration.

Examined next was trapping with dienes. Cyclopentadiene is the only compound that was able to react with **1**. The reaction afforded a good yield of the [4+2] adduct **14**, whose *endo* stereochemistry was determined by NOESY ex-



Scheme 7.

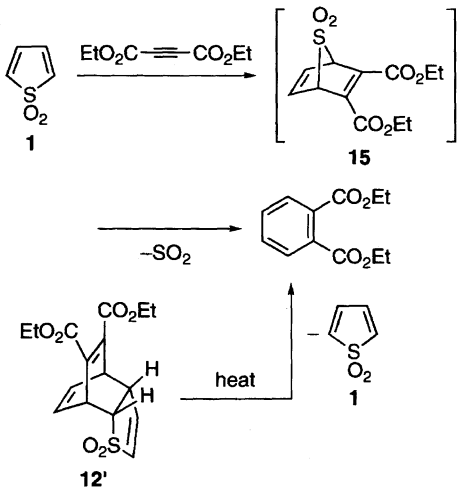


Scheme 8.

periments (Scheme 8). 2,3-Dimethyl-1,3-butadiene, though used in large excess, failed to react with **1**; the dimer **7** was the sole product again.

Generation of 1 by Thermolysis of the Adduct 12. It was reported that diethyl acetylenedicarboxylate could trap **1** to give diethyl phthalate, which was formed by elimination of SO_2 from the initial adduct (**15**) (Scheme 9).[3d] In our case, however, **1** failed to react with DMAD, but reacted with the dimer **7** to form **12** in good yield. The formation of diethyl phthalate might be alternatively explained by the retro Diels–Alder reaction of the adduct **12′** which was produced from **7** and diethyl acetylenedicarboxylate. We therefore investigated the thermolysis of **12**.

Heating of **12** in boiling 1,2-dichloroethane for 44 h provided dimethyl phthalate and **7** in 95 and 85% yields, respectively, thus suggesting the efficient formation of **1** by the expected retro Diels–Alder reaction. We then investigated



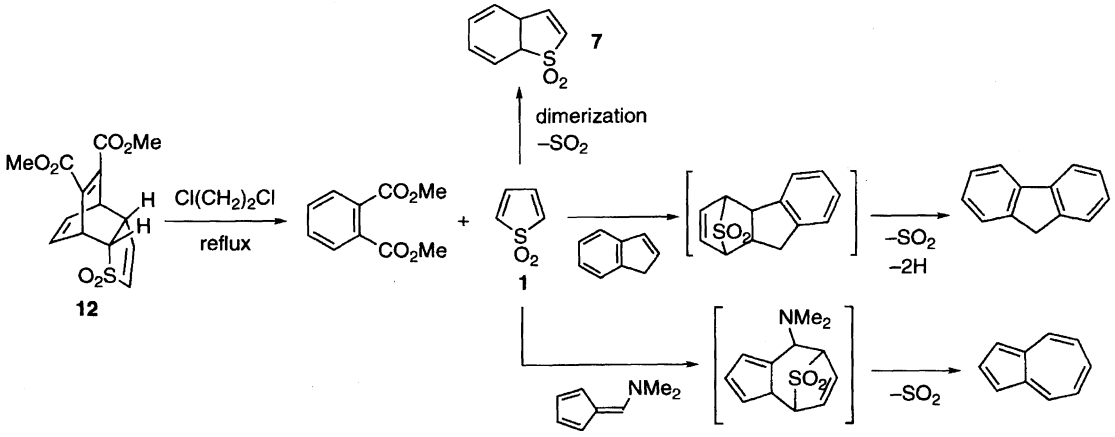
Scheme 9.

the thermolysis of **12** in the presence of a series of trapping agents. The decomposition in the presence of indene gave fluorene in 12% yield, along with **7** (63%) and dimethyl phthalate (80%) (Scheme 10). The formation of fluorene is explained as the result of [4+2] cycloaddition of **1** and indene, followed by loss of SO_2 and air oxidation.[3d] The decomposition in the presence of 6-(dimethylamino)fulvene furnished azulene in 31% yield. The formation of azulene is also explained by [6+4] cycloaddition of **1** and the fulvene and then elimination of SO_2 and dimethylamine from the initial adduct.[3g,3h] However, acenaphthylene, norbornene, 2, 3-dimethyl-1,3-butadiene, and *p*-benzoquinone all failed to react with **1**. The decomposition in the presence of PTAD gave dimethyl phthalate and **13** (adduct of **7** with PTAD) in 68 and 52% yields, respectively, with recovery of **12** in 32% yield.

Therefore, although the previous papers claimed that **1**, generated in situ, could be trapped with a series of substrates,[3] these results, particularly the real intermediacy of **1** in these reactions, might require reconsideration, keeping the present results in mind.

Experimental

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H- and ^{13}C NMR spectra were determined on a Bruker AM400, a Bruker ARX400, a Bruker AC300P, or a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard (400, 300, and 200 MHz for ^{1}H 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 spectrometer. Raman spectra were determined on a Perkin Elmer System 2000 FT-Raman spectrometer. UV/vis spectra were determined on a Shimadzu UV-160A or a JASCO V-560 spectrophotometer. Mass 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 was 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), respectively. Dimethyldioxirane (DMD) was prepared by the literature method as an acetone solution and DMD concentration was determined by



Scheme 10.

titrimetry (oxidation of thioanisole to its sulfoxide derivative) prior to use. The purity of every sample of thiophene 1,1-dioxide (**1**), used for spectroscopic analyses and kinetics studies, was determined by ^{1}H NMR prior to use.[7] The melting point of **1** (about 6 °C) was determined in a room kept at −20 °C.

Preparation of Thiophene 1,1-Dioxide (1). A Typical Procedure. A mixture of thiophene (58 mg, 0.69 mmol) and molecular sieves 4A (ca. 200 mg) in acetone (5 ml) was cooled at −25 °C (molecular sieves was used to be freed of contaminating water which is otherwise difficult to remove at the workup stage). A solution of DMD (2.0 mmol) in acetone, cooled at −20 °C, was then added to the mixture through a piece of Teflon® tubing. The resulting mixture was stirred for 36 h at −20 °C and then cooled below −40 °C. The solvent and the volatile materials were removed thoroughly in vacuo below −40 °C (several hours might be required) to furnish colorless crystals of **1**, mp about 6 °C. The yield of **1** is about 20—30% based on the thiophene used, but quantitative based on the thiophene consumed. Spectroscopic properties of **1** have already given in the text.

Formation of Dimer 7 and Trimer 9 by Decomposition of 1. Thiophene (58 mg, 0.69 mmol) was oxidized by DMD according to the same procedure as described above. The resulting **1** was warmed and kept at 25 °C for 10 min. Purification of the resulting mixture by silica-gel column chromatography gave 4 mg (8%) of **7** and 7 mg (12%) of **9**. The combined yield (**7**+**9**, 20%) must be nearly quantitative based on **1** since the yield of **1** from thiophene is estimated to be about 20—30%.

7: Mp 92—93 °C (from CH_2Cl_2/hexane) (lit,[3c] mp 90.0—91.5 °C); ^{1}H NMR (200 MHz) δ = 3.97—4.19 (m, 2H), 5.64 (d/d, J = 9.5/2.9 Hz, 1H), 5.88 (d/d, J = 9.5/3/4 Hz, 1H), 5.92—6.09 (m, 1H), 6.21 (d/d, J = 6.7/5.5 Hz, 1H), 6.74 (d/d, J = 6.7/3.0 Hz, 1H), 6.94 (d/d, J = 6.7/1.7 Hz, 1H); ^{13}C NMR (50 MHz) δ = 39.2, 58.3, 115.8, 122.1, 122.6, 126.7, 132.4, 139.6; IR (KBr) 1132, 1284, 1313, 1600, 3076 cm^{-1}; MS (EI) m/z 168 (M^+), 120, 103, 78. Found: C, 57.00; H, 4.78%. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79%.

9: Mp > 245 °C (decomp); ^{1}H NMR (400 MHz) δ = 3.41—3.57 (m, 6H), 6.10 (d/d, J = 4.4/3.2 Hz, 2H), 6.50 (d/d, J = 6.7/2.4 Hz, 2H), 6.66 (d/d, J = 6.7/2.4 Hz, 2H); ^{13}C NMR (100.6 MHz) δ = 34.7, 45.5, 60.3, 129.0, 134.4, 138.9; IR (KBr) 1126, 1290, 1320, 1606, 3093 cm^{-1}; MS (EI) m/z 284 (M^+), 220, 165, 78. Found: C, 50.68; H, 4.22%. Calcd for $C_{12}H_{12}O_4S_2$: C, 50.69; H, 4.25%.

The 1,1-dioxide **1** is thermally unstable and cannot be weighed at room temperature. Therefore, the decomposition study of **1** in $CDCl_3$ solution (Table 2) was examined in the following way. A fixed amount of *t*-butylbenzene (internal standard) and **1** (obtained below −40 °C) were dissolved in $CDCl_3$. The solution was made to a constant volume. An aliquot was analyzed by ^{1}H NMR to determine the concentration of **1**. The whole solution was then kept at 25 °C in a thermostat. The progress of the reaction was monitored by ^{1}H NMR. In this way, for example, a 0.12 M $CDCl_3$ solution of **1** was determined to give **7** and **9** in the ratio 1.0 : 0.22.

The sample solutions used for kinetic determination were also prepared in the same way.

Reactions of 1 with Dienophiles. With Dimethyl Acetylenedicarboxylate (DMAD). The 1,1-dioxide **1** was prepared from 63 mg (0.75 mmol) of thiophene in acetone and was allowed to react with a large excess of DMD (1.0 g, 7.4 mmol) at room temperature for 24 h. Purification of the mixture by silica-gel column chromatography gave 26 mg (23% yield based on the thiophene) of **12**: Mp 141—142 °C (decomp) (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz) δ = 3.48 (d/d, J = 7.8/2.7 Hz, 1H), 3.53—3.59 (m, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 4.20—4.26 (m, 1H), 4.56—4.62 (m, 1H), 6.31—6.37 (m, 1H), 6.49 (d/d, J = 6.0/2.4 Hz, 1H), 6.52—6.58 (m, 2H); ^{13}C NMR (100.6 MHz) δ = 40.3, 42.4, 49.2, 52.61, 52.62, 61.8, 131.9, 132.5, 135.2, 139.2, 142.0, 143.5, 164.8, 165.1; IR (KBr) 1136, 1252, 1281, 1322, 1720, 1742, 2975, 3060 cm^{-1}; MS (EI) m/z 310 (M^+), 214, 163. Found: C, 54.27; H, 4.47%. Calcd for $C_{14}H_{14}O_6S$: C, 54.12; H, 4.55%.

With 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD). The reaction of **1** (prepared from 0.70 mmol of thiophene) with PTAD (2.1 mmol) was carried out in a manner similar to that with DMAD. The mixture was purified by alumina column chromatography to give 17 mg (15% yield based on the thiophene) of **13**; Mp > 278 °C (decomp) (from acetone); ^{1}H NMR (300 MHz) δ = 3.91—4.02 (m, 2H), 5.15—5.24 (m, 1H), 5.44—5.53 (m, 1H), 6.30—6.39 (m, 1H), 6.53—6.67 (m, 1H), 6.73 (d/d, J = 10.9/2.5 Hz, 1H), 7.38—7.54 (m, 5H); ^{13}C NMR (100.6 MHz) δ = 44.0, 49.6, 52.1, 56.2, 126.3, 128.3, 128.9, 129.1, 129.3, 131.1, 134.5, 139.0, 155.3, 156.6; MS (EI) 343 (M^+), 279, 227. Found: C, 56.19; H, 3.70; N, 12.03%. Calcd for $C_{16}H_{13}N_3O_4S$: C, 55.97; H, 3.82; 12.24%.

Although reactions of **1** with *p*-benzoquinone, acenaphthylene, norbornene, and bis(dimethylamino)acetylene were carried out in similar manners, no adduct with **1** was obtained.

Reactions of 1 with Dienes. With Cyclopentadiene. The reaction of **1** (prepared from 0.57 mmol of thiophene) with cyclopentadiene (3.7 mmol) was carried out in a manner similar to that with DMAD. The mixture was purified by alumina column chromatography to give 25 mg (25% yield based on the thiophene) of **14**; Mp 107—108 °C (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz) δ = 1.59 (d, J = 9.2 Hz, 1H), 1.79 (d, J = 9.2 Hz, 1H), 3.09—3.15 (m, 1H), 3.39—3.46 (m, 1H), 3.69 (d/d, J = 7.0/4.3 Hz, 1H), 3.72—3.79 (m, 1H), 5.97 (d/d, J = 5.5/2.9 Hz, 1H), 6.32 (d/d, J = 5.5/2.9 Hz, 1H), 6.37 (d/d, J = 6.6/1.8 Hz, 1H), 6.44 (d/d, J = 6.6/2.6 Hz, 1H); ^{13}C NMR (50 MHz) δ = 45.3, 45.4, 50.5, 51.3, 62.9, 132.9, 133.9, 134.7, 140.6; IR (KBr) 1101, 1119, 1132, 1283, 1331, 1590, 3064 cm^{-1}; MS (EI) m/z 182 (M^+), 133, 117. Found: C, 59.41; H, 5.58%. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53%.

An attempted reaction of **1** with 2,3-dmethyl-1,3-butadiene gave only **7** (11% yield based on the thiophene) as the product isolated.

Trapping of 1 Generated by Thermolysis of 12. With Indene. A mixture of 53 mg (0.17 mmol) of **12** and 38 mg (0.34 mmol) of indene in 10 ml of 1,2-dichloroethane was heated at reflux for 44 h. The mixture was evaporated and the residue was purified by silica-gel column chromatography (AcOEt/hexane = 1/1) to give 2 mg (12%) of flurorene, mp 113—114 °C (mp of a commercial product, Tokyo Kasei, 115 °C), 9 mg (65%) of **7**, 3 mg (6%) of **12**, and 26 mg (80%) of dimethyl phthalate.

With 6-(Dimethylamino)fulvene. A mixture of 50 mg (0.16 mmol) of **12** and 39 mg (0.32 mmol) of 6-(dimethylamino)fulvene in 13 ml of 1,2-dichloroethane was heated at reflux for 44 h. The mixture was evaporated and the residue was purified by alumina column chromatography (AcOEt/hexane = 1/2) to give 6 mg (31%) of azulene, mp 93—94 °C (mp of a commercial product, Tokyo Kasei, 100 °C), and 29 mg (94%) of dimethyl phthalate.

Attempted trapping of **1** with acenaphthylene, norbornene, *p*-benzoquinone, and 2,3-dimethyl-1,3-butadiene all failed in adduct formation. For example, heating a mixture of **12** (0.09 mmol) and acenaphthylene (0.26 mmol) in 1,2-dichloroethane (8 ml) at reflux for 40 h gave only **7** (85%) and dimethyl phthalate (95%).

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