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## Synthesis of 2,5-Disubstituted Thienosultines and Their Thermal Reactions with Dienophiles and Nucleophiles

Wen-Dar Liu, Chih-Chin Chi, I-Feng Pai, An-Tai Wu, and Wen-Sheng Chung\*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, ROC

wschung@cc.nctu.edu.tw

Received December 3, 2001

The 2,5-disubstituted thienosultines (5,7-disubstituted 1,4-dihydro-1H- $3\lambda^4$ -thieno[3,4-d][2,3]oxathiin-3-oxides) **5a**–**d** were prepared from the corresponding dichlorides **4a**–**d** with the commercially available Rongalite (sodium formaldehyde sulfoxylate) in 17–60% yields. When heated in the presence of electron-poor dienophiles, sultines **5a**–**d** underwent elimination of SO<sub>2</sub>, and the resulting non-Kekulé biradicals **7a**–**d** were intercepted as the 1:1 adducts **8**–**12** in good to excellent yields. The pyrolysis of sultines and sulfolenes with different concentrations of dienophiles revealed that either a preequilibrium between starting reagents and biradical species or Diels–Alder and retro-Diels–Alder reaction mechanisms may be involved; however, more work is necessary to establish the proposed mechanisms. Reaction of sultine **5b** with *n*BuLi was found to undergo a nucleophilic ring-opening reaction to give sulfinyl alcohol **17** after H<sub>2</sub>O workup. When sultine **5a** was heated in benzene in a sealed tube in the presence of methanol, methanol- $d_4$ , or 2-mercaptoethanol, the respective 1:1 trapping adducts **19–21** as well as the rearranged sulfolene **6a** were isolated in similar amounts. The isolation of adducts **19–21** may be explained by the involvement of either biradical or ionic intermediates during the pyrolysis.

#### Introduction

The study of heterocyclic fused *o*-quinodimethane (*o*-QDM, **1**) has received considerable current interest,<sup>1</sup> and many methods have been developed for the generation of *o*-QDM; for example, azo compounds, sulfolenes, ben-



zocyclobutenes, and dihalides are popular precursors. Although azo compounds are popular for the generation of *o*-QDMs because of their clean thermal and photochemical reactions, they are notorious for their thermal instability in thieno- and pyrrolo-fused diazenes.<sup>2b,c</sup> On the contrary, sulfolenes are so stable that harsh reaction conditions, such as flash vacuum pyrolysis or hightemperature pyrolysis, are usually required.<sup>1c,d,g</sup> Benzo-

10.1021/jo011122s CCC: 22.00 @ 2002 American Chemical Society Published on Web 12/04/2002

cyclobutenes are also useful precursors, but they often come from other precursors;<sup>1h,i</sup> therefore, an extra step in synthesis is usually required. Dihalides are useful in thermal reactions; however, they usually require the addition of other catalysts<sup>1a,e,i</sup> to enhance the reactivity. We choose sultines<sup>3–5</sup> as precursors for *o*-QDM because they are usually stable above room temperature and yet react thermally at milder conditions than sulfolenes.

Pioneering studies on benzosultine and derivatives as *o*-QDM precursors had been explored by Durst et. al in the last two decades,<sup>4</sup> but further development of other sultines was hampered by their tedious synthesis. The successful application of Rongalite in the conversion of

<sup>(1)</sup> For reviews of *o*-quinodimethanes, benzocyclobutenes, and related chemistry, see: (a) Segura, J. L.; Martín, N. *Chem. Rev.* **1999**, *99*, 3199. (b) Collier, S. J.; Storr, R. C. In *Progress in Heterocyclic Chemistry*; Gribble, G. W., Gilchrist, T. L., Eds.; Pergamon: New York, 1998; Vol. 10, pp 25–48. (c) Ando, K.; Kankake, M.; Suzuki, T.; Takayama, H. *Tetrahedron* **1995**, *51*, 129. (d) Chou, T.-S. *Rev. Heteroatom Chem.* **1993**, *8*, 65. (e) Martín, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237. (f) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (g) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (h) Kametani, T. *Pure Appl. Chem.* **1979**, *51*, 747. (i) Oppolzer, W. *Synthesis* **1978**, 793; *Heterocycles* **1980**, *14*, 1615.

<sup>(2) (</sup>a) Berson, J. A. *Acc. Chem. Res.* **1997**, *30*, 238. (b) In a study by Lu et al. the thiophene diazene was unstable below -10 °C: Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 265. (c) The azo precursor was reported to be stable only below -20 °C by Bush et al.: Bush, L. C.; Heath, R. B.; Berson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 9830.

<sup>(3) (</sup>a) Wu, A.-T.; Liu, W.-D.; Chung, W.-S. *J. Chin. Chem. Soc.* **2002**, 49, 77. (b) Liu, J.-H.; Wu, A.-T.; Huang, M.-H.; Wu, C.-W.; Chung, W.-S. *J. Org. Chem.* **2000**, 65, 3395. (c) Chung, W.-S.; Liu, J.-H. *Chem. Commun.* **1997**, 205. (d) Chung, W.-S.; Lin, W.-J.; Liu, W.-D.; Chen, L.-G. *J. Chem. Soc., Chem. Commun.* **1995**, 2537.

<sup>(4)</sup> For some earlier works on sultines, see: (a) King, J. F.; Rathore, R. *Tetrahedron Lett.* **1989**, *30*, 2763. (b) Durst, T.; Charlton, J. L.; Mount, D. B. *Can. J. Chem.* **1986**, *64*, 246. (c) Charlton, J. L.; Durst, T. *Tetrahedron Lett.* **1984**, *25*, 5287. (d) Jung, F.; Molin, M.; Van Den Elzen, R.; Durst, T. *J. Am. Chem. Soc.* **1974**, *96*, 935. (e) Connolly, T. J.; Durst, T. *Tetrahedron Lett.* **1997**, *38*, 1337. (f) Sharma, N. K.; De Reinach-Hirtzbach, F.; Durst, T. *Can. J. Chem.* **1976**, *54*, 3012. (g) Roversi, E.; Monnat, F.; Schenk, K.; Vogel, P.; Braña, P.; Sordo, J. A. *Chem. – Eur. J.* **2000**, *6*, 1858 and earlier references therein. (h) Megevand, S.; Moore, J.; Schenk, K.; Vogel, P. *Tetrahedron Lett.* **2001**, *42*, 673.

<sup>(5)</sup> For a review of sultines, see: Dittmer, D. C.; Hoey, M. D. *The Chemistry of Sulphinic Acids, Esters, and Their Derivatives*; Wiley: Chichester, U.K., 1990; pp 239–273.

#### SCHEME 1<sup>a</sup>



<sup>*a*</sup> Reagents and conditions: (a) *n*BuLi, THF, 0 °C, 3 h; ZnCl<sub>2</sub>, rt, 2 h; (b) PhBr, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, 55 °C, 24 h; (c) *n*BuLi, THF, 0 °C, 3 h; CH<sub>3</sub>I, 0 °C  $\rightarrow$  rt, 24 h.

dihalides to sultines by Hoey and Dittmer<sup>5,6</sup> makes it a convenient precursor for *o*-QDM. Although the application of sulfolenes and sultines as *o*-QDM precursors has been popular, important questions remain to be answered concerning their differences in reactivity and reaction mechanisms. In their pyrolysis studies of sulfolenes with alkenes, Takayama et al. reported<sup>1c,7</sup> that Diels–Alder reaction occurred first on the aromatic moiety, followed by SO<sub>2</sub> extrusion, then a second Diels–Alder reaction to give 1:2 cycloadducts, and finally a retro-Diels–Alder reaction to give the 1:1 fused adducts (vide infra).

We have been interested in the application of heterocyclic fused *o*-QDM in Diels–Alder reactions,<sup>3</sup> and in this work  $\alpha, \alpha'$ -disubstituted thienosultines are synthesized to find out whether sultines react through the mechanism proposed by Takayama for sulfolenes or through a biradical mechanism similar to those of diazenes.<sup>2</sup> On one hand, the bulky  $\alpha, \alpha'$ -disubstituents on thienosultines may have two functions: (1) they hinder the direct addition of dienophiles to  $\alpha$ -positions of thiophene, and (2) the phenyl group(s) may stabilize the thus formed non-Kekulé biradicals. Therefore, if the 1:1 fused adducts are still formed with the bulky substituents, the biradical mechanism may be involved. Furthermore, concentration-dependent trapping studies on the pyrolysis of sulfolenes and sultines are carried out in the hope to differentiate their reaction mechanisms on the basis of whether their rate-determining steps are unimolecular or bimolecular reactions. We herein report our exploration of the scope of thienosultine derivatives and their thermal reaction with various dienophiles and nucleophiles.

#### **Results and Discussion**

The syntheses of 2,5-disubstituted thienosultines 5a-d are shown in Schemes 1 and 2. 2,5-Dimethylthiophene (**3a**) and 2,5-dichlorothiophene (**3b**) are commercially





available. Butyllithium treatment of 2-phenylthiophene (2)<sup>8a</sup> followed by methylation led to 2-methyl-5-phenylthiophene (3c) in 97% yield. 2,5-Diphenylthiophene (3d) was prepared by a known method using a palladium catalyst.<sup>8b</sup> 2,5-Disubstituted 3,4-bis(chloromethyl)thiophenes **4a**-**d** were prepared by chloromethylation of the corresponding 2,5-disubstituted thiophenes 3a-d adapted according to the procedures developed by Wynberg et al. in the synthesis of the corresponding sulfones **6**.<sup>9a,b</sup> The key step in the synthesis of sultines 5a-d is the use of Rongalite (sodium formaldehyde sulfoxylate) with the corresponding dichlorides **4a**-**d**. Unfortunately, the yields for the preparation of these sultines are relatively poor compared to that of ca. 70% for the preparation of benzosultine,<sup>5,6</sup> and there is room for further improvement of the thienosultine synthesis.

The <sup>1</sup>H NMR spectra of sultines 5a-d deserve some comments because they show two characteristic AB quartets of the 1,4-hydrogens near oxathiin-3-oxide functional groups. It has been reported that hydrogens on the carbon  $\alpha$  to the oxygen of an oxathiin-3-oxide (sultine) have chemical shifts of 4.9-5.6 ppm, whereas hydrogens on the carbon  $\alpha$  to the sulfinyl of an oxathiin-3-oxide have chemical shifts of 3.5–4.7 ppm.<sup>3–4,11b</sup> The four  $\alpha$ -hydrogens of sulfolenes **6a**-**d** have chemical shifts in the range of 4.1–4.4 ppm and appear as singlets (except those for 6c, for which two singlets were observed) due to symmetry and lack of a nearby chiral center. In the five thienosultines we have studied, the chemical shifts of hydrogens in sultines **5a**-**d** fell into two regions, 3.6-4.4 and 4.9–5.5 ppm (see the Experimental Section), which are in good agreement with the above description. The magnitude of the geminal coupling constant of the hydrogens  $\alpha$  to the oxygen,  $J_{cd}$ , is usually smaller than that of hydrogens  $\alpha$  to the sulfinyl group of a sultine (i.e.,  $J_{ab}$ ). The former are in the range of 13.6–14.9 Hz, whereas the latter are in the range of 15.3-16.0 Hz (see Table 1). The assignments of thienosultine <sup>1</sup>H NMR chemical shifts are based on previous assignments by Pirkle on benzosultines<sup>11b</sup> and the known propensity of

<sup>(6) (</sup>a) Hoey, M. D.; Dittmer, D. C. J. Org. Chem. 1991, 56, 1947.
(b) Jarvis, W. F.; Hoey, M. D.; Finocchio, A. L.; Dittmer, D. C. J. Org. Chem. 1988, 53, 5750.

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<sup>(8) (</sup>a) Rossi, R.; Carpita, A.; Ciafalo, M.; Lippolis, V. *Tetrahedron* **1991**, *47*, 8443. (b) Campaigne, E.; Foye, W. *J. Org. Chem.* **1952**, *17*, 1405.

<sup>(9) (</sup>a) Wynberg, H.; Zwanenburg, D. J. *J. Org. Chem.* **1964**, *29*, 1919.
(b) Zwanenburg, D. J.; Wynberg, H. *J. Org. Chem.* **1969**, *34*, 333. (c) Winn, M.; Bordwell, F. G. *J. Org. Chem.* **1967**, *32*, 1610.

| Sultine   | Ha        | H <sub>b</sub> | $J_{ab}{}^{a}$ | H <sub>c</sub> | H <sub>d</sub> | $J_{cd}{}^{a}$ | Ref          |
|---|-----------|----------------|----------------|----------------|----------------|----------------|--------------|
| Hd Hc<br>O<br>S<br>Hb Ha  | 3.50      | 4.31           | 15.3           | 4.88           | 5.23 -         | 13.6           | 11b          |
| Hd Hc<br>R N S<br>R N Hb Ha                                       | 3.80-3.85 | 4.63–4.71      | 15.4–15.6      | 5.19–5.21      | 5.50–5.55      | 13.7–14.1      | 3b           |
| $R = H, CI, Ph$ $CH_{3}^{Hd}, Hc$ $S = O$ $CH_{3}_{Hb} Ha O$ $5a$ | 3.58      | 3.88           | 15.3           | 4.93           | 5.16           | 14.1           | this<br>work |
| CI Hd, Hc<br>S, S, S, CI<br>Hb, Ha<br>5b                          | 3.66      | 3.73           | 16.0           | 4.94           | 5.08           | 14.9           | this<br>work |
| Ph Hd Hc<br>S S<br>CH <sub>3Hb</sub> Ha                           | 3.79      | 4.15           | 15.5           | 5.05           | 5.26           | 14.0           | this<br>work |
| CH <sub>3</sub> <sup>Hd</sup> Hc<br>S<br>Ph Hb Ha                 | 3.60      | 4.05           | 15.6           | 5.03           | 5.44           | 14.1           | this<br>work |
| SC<br>Ph Hd Hc<br>S<br>Ph Hb Ha<br>Ph Hb Ha                       | 3.80      | 4.36           | 15.6           | 5.16           | 5.49           | 14.0           | this<br>work |

 TABLE 1.
 Characteristic Hydrogen Chemical Shifts and Geminal Coupling Constants of Thienosultines 5a-d and Other

 Heterocyclic Sultines

<sup>a</sup> Estimated accuracy for coupling constants is ca. ±0.2 Hz. All measurements were done in CDCl<sub>3</sub> in a 300 MHz NMR spectrometer.

protons cis to a sulfinyl oxygen to be deshielded; therefore,  $H_b$  is downfield shifted from  $H_a$  and  $H_d$  is downfield shifted from  $H_{\rm c}.^{11d}$ 

Sealed tube reaction of sultines **5a**-**d** in benzene alone gave the corresponding sulfolenes 6a-d in excellent yields (83-94%). The Diels-Alder reactions of sultines 5a-d and sulfolenes 6a-d with typical electron-poor dienophiles are presented in Scheme 3 and Table 2. For example, when heated in benzene (sealed tube, 180 °C, 24 h) in the presence of 3 equiv of *N*-phenylmaleimide, dimethyl fumarate, fumaronitrile, dimethyl acetylenedicarboxylate, or diethyl fumarate, the sultines **5a**-**d** all underwent extrusion of SO<sub>2</sub>, and the resulting non-Kekulé biradicals 7a-d were intercepted as the 1:1 fused adducts 8-12 in 37-91% yields (entries 1-3, 5-7, 9-12, and 14-17 of Table 2). In each case, small to substantial amounts of sulfolenes 6a-d were also formed depending on the power of the dienophiles; that is, stronger dienophiles led to higher yields of fused adducts and less sulfolenes. It is important to note that sulfolenes 6a-d did not react with any of these dienophiles under the same reaction conditions (entries 4, 8, 13, and 18 of Table 2). The low reactivity of sulfolenes 6a-d is in sharp contrast with the high reactivity of sultines 5a-d but is consistent with those reported by Takayama,<sup>1c,7a-c</sup> Chou,<sup>7d,e</sup> and Wynberg<sup>9</sup> in their early attempts. Furthermore, it is interesting to observe the great similarity of our results with sultines and those with diazenes reported by Berson et al.<sup>2,10</sup> For example, in the trapping experiments of thiophene biradical **7e** (X = Y = H) derived from a diazene precursor,<sup>10</sup> the sole adducts formed (85–100%) had the fused structure (such as **8**) but not the bridged structure **13** (see Scheme 4).

The pyrolysis results of these sultines may be explained by at least three possible reaction mechanisms. The most likely pathway is the formation of non-Kekulé biradicals 7a-d, followed by the Diels-Alder reaction with a dienophile to form either bridged adducts **13** or fused adducts **8–12** (pathway A, Scheme 3). This mechanism resembles those proposed for thieno- or furano-

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#### SCHEME 3



 TABLE 2.
 Sealed Tube Reactions of 2,5-Disubstituted

 Thienosultines 5a-d and Sulfolenes 6a-d with Various
 Dienophiles (3 equiv) in Benzene<sup>a</sup>

| entry | diene     | dienophile                         | products<br>(yield, %)           | total<br>yield, % |
|-------|-----------|------------------------------------|----------------------------------|-------------------|
| 1     | 5a        | N-phenylmaleimide                  | <b>6a</b> (6) + <b>8a</b> (91)   | 97                |
| 2     | 5a        | dimethyl fumarate                  | <b>6a</b> (49) + <b>9a</b> (40)  | 89                |
| 3     | 5a        | fumaronitrile                      | <b>6a</b> (46) + <b>10a</b> (43) | 89                |
| 4     | 6a        | various dienophiles <sup>b</sup>   | no reaction                      | 0                 |
| 5     | 5b        | <i>N</i> -phenylmaleimide          | <b>6b</b> (7) + <b>8b</b> (65)   | 72                |
| 6     | 5b        | dimethyl fumarate                  | <b>6b</b> (4) + <b>9b</b> (64)   | 68                |
| 7     | 5b        | fumaronitrile                      | <b>6b</b> (16) + <b>10b</b> (77) | 93                |
| 8     | 6b        | various dienophiles <sup>b</sup>   | no reaction                      | 0                 |
| 9     | <b>5c</b> | <i>N</i> -phenylmaleimide          | <b>6c</b> (16) + <b>8c</b> (76)  | 92                |
| 10    | <b>5c</b> | fumaronitrile                      | <b>6c</b> (13) + <b>10c</b> (75) | 88                |
| 11    | 5c        | dimethyl<br>acetylenedicarboxylate | <b>6c</b> (47) + <b>11c</b> (37) | 84                |
| 12    | 5c        | diethyl fumarate                   | <b>6c</b> (23) + <b>12c</b> (69) | 92                |
| 13    | 6c        | various dienophiles <sup>b</sup>   | no reaction                      | 0                 |
| 14    | 5d        | <i>N</i> -phenylmaleimide          | <b>6d</b> (6) + <b>8d</b> (82)   | 88                |
| 15    | 5d        | dimethyl fumarate                  | 6d (12) + 9d (79)                | 91                |
| 16    | 5d        | fumaronitrile                      | 6d(21) + 10d(75)                 | 96                |
| 17    | 5d        | diethyl fumarate                   | <b>6d</b> (30) + <b>12d</b> (67) | 97                |
| 18    | 6d        | various dienophiles <sup>b</sup>   | no reaction                      | 0                 |

<sup>&</sup>lt;sup>*a*</sup> All reactions were carried out in benzene solution in a sealed tube at 180 °C for 24 h. <sup>*b*</sup> All the dienophiles used in the table were tested for sulfolenes 6a-d.

diazenes.<sup>2,10</sup> Alternatively, sultines may undergo a onebond (carbon–oxygen bond) cleavage to form alkyl sulfinyl biradicals of the type 7'a-d. The biradicals 7'a-d may then undergo either an intramolecular rearrangement to form sulfolenes **6a**–d or an intermolecular trapping by olefins to form after losing SO<sub>2</sub> the 1:1 fused adducts SCHEME 4



(pathway B, Scheme 3). The third possible reaction mechanism of thienosultines 5a-d is to undergo a Diels– Alder reaction on the aromatic moieties first followed by instantaneous SO<sub>2</sub> elimination to give bridged adducts **13**. Compounds **13** further react with another dienophile to give the 1:2 adducts **15**, and finally a retro-Diels–Alder reaction of **15** would occur to form fused adducts **8–12** (Scheme 4). The latter mechanism was proposed by Takayama to explain results with furano- and pyrrolosulfolenes.<sup>1c,7</sup>

In the mechanisms involving biradical intermediates (pathways A and B in Scheme 3), the rate will be dependent only on the sultine concentration if the dienophile concentration is kept high and a steady-state approximation of the biradical concentration is satisfied. However, if the dienophile concentration is low, the rate of reaction will be dependent not only on the concentration of sultines but also on the concentration of dienophiles.<sup>11e</sup> Alternatively, if a Diels-Alder reaction occurs first on the aromatic part of sultine and it happens to be the rate-determining step, the reaction would be second order and first order with respect to both the sultine and the dienophile. In the latter mechanism, the higher the dienophile concentration the faster products are formed and the faster starting sultines (or sulfolenes) are consumed. Because thienosulfolenes 6a-d required a much higher temperature to react with dienophiles, we used furanosulfolene  $16^{3d}$  instead and thienosultine 5afor concentration-dependent kinetic studies.



Concentration-dependent studies on the thermolysis of thienosultine **5a** (150 °C, 5 h) and furanosulfolene **16** (120 °C, 2 h) are shown in Figure 1. In the thermolysis of **5a**, the yield of sulfolene **6a** gradually decreased from 23% to ca. 2% when the concentration of fumaronitrile in-

<sup>(11) (</sup>a) Andersen, K. K.; Foley, J.; Perkins, R.; Gaffield, W.; Papanikalaou, N. *J. Am. Chem. Soc.* **1964**, *86*, 5637. (b) Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1832. (c) Harpp, D. N.; Vines, S. M.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* **1976**, *41*, 3987. (d) Alternatively, one may envision that the lone pair electrons on sulfur of a sulfinyl group could act to shield a proton cis-vicinal to it. (e) For an excellent monograph on the kinetics of reactions involving intermediates, see: Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 1.

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**SCHEME 5** 

**FIGURE 1.** Product distributions of the sealed tube reactions of sultine **5a** and sulfolene **16** with various concentrations of fumaronitrile: (a) 2,5-dimethylthienosultine **5a** (16.5 mM in toluene), reacted at 150 °C for 5 h, where closed circles indicate the yield (%) of sulfolene **6a**, open triangles indicate the yield (%) of cycloadduct, and open squares indicate the yield (%) of the recovered sultine; (b) furanosulfolene **16** (15.8 mM in benzene), reacted at 120 °C for 2 h, where open circles indicate the yield (%) of recovered sulfolene and open triangles indicate the yield (%) of cycloadduct formed. All the reactions were stopped far before completion.

creased from 0 to 0.25 M (Figure 1a). Concurrently, the percentage yield of cycloadduct 10a increased when the concentration of fumaronitrile increased. The results may be rationalized easily if diradical intermediates are invoked; that is, a competitive trapping of biradicals 7 by SO<sub>2</sub> or dienophile determines the relative amount of sulfolene 6a and cycloadduct 10a. A similar explanation may be applied in the Diels-Alder and retro-Diels-Alder reaction mechanism (Scheme 4), where a competitive trapping of reactive diene 13 by dienophile or SO<sub>2</sub> determines the relative product ratios. The consumption rate of furanosulfolene 16 is shown to be concentration dependent on both the sulfolene and fumaronitrile (Figure 1b). That is, higher dienophile (or sulfolene) concentration led to faster consumption of sulfolene and faster formation of cycloadducts. It would certainly be desirable to differentiate the above mechanisms; however, more accurate kinetic data are necessary for such an analysis.

Such an analysis would require direct spectroscopic measurement as has been elegantly demonstrated in the pyrolysis of a diazene.<sup>10f</sup> However, we lack a proper thermostated optical cell for the in situ monitoring of high-temperature kinetics. Although laser flash spectroscopy and matrix isolation would also provide valuable information about the transient species, they are related to photochemical and photophysical properties of these sultines and may not be related to the thermolysis results discussed here. Clearly more work is necessary to establish these proposed mechanisms.

It has long been known that the reaction of an optically active reagent on sulfinate esters (sultines) will lead to sulfoxides of high optical purity, the so-called Andersen synthesis.<sup>11a</sup> These reactions are stereospecific and proceed with inversion at sulfur.<sup>11b</sup> Nucleophilic ring opening of heterocyclic fused sultines, however, has rarely been reported. Some of the few reported reactions of sultines with Grignard reagents as well as organocopper-lithium reagents<sup>11c</sup> were mainly with aliphatic sultines. Reaction of sultine **5b** with *n*BuLi gave the sulfinyl alcohol **17** after workup by H<sub>2</sub>O; however, it gave a deuterated sulfinyl alcohol, 18, as the main product if worked up by  $D_2O$ (Scheme 5). Careful inspection of the <sup>1</sup>H NMR spectrum of 18 revealed that deuterium appeared only on the α-sulfinyl carbon, and no sign of deuterium scrambling in other carbons was found. The isolation of 18 as the major product indicated that neighboring alkoxide might have undergone a H abstraction from the  $\alpha$ -carbon of the sulfinyl group, giving hydroxyl and sulfinyl anion groups. The sulfinyl anion group eventually abstracts either a H from H<sub>2</sub>O or a deuterium from D<sub>2</sub>O to form **18** as the finally observed product. Although yields for the nucleophilic attack of cyclic sulfinate esters (sultines) by *n*BuLi are low (33–47%), they are comparable to the yields reported (40–70%) for aliphatic sultines.<sup>11a–c</sup>

Sulfolenes are well-known to undergo alkylation readily at their  $\alpha$ -sulfonyl position upon deprotonation with *n*BuLi followed by methyl iodide and ethyl, butyl, and benzyl bromides, respectively.<sup>7</sup> By contrast, sultines undergo a nucleophilic attack if treated with a strong base such as a Grignard reagent or *n*BuLi; therefore, the synthesis of  $\alpha$ -derivatives of sultines will not be straightforward. Reminiscences of the work done by Durst indicated that sulfinyl alcohols **17** and **18** (so-called  $\delta$ -hydroxy sulfoxides)<sup>4d,f</sup> may be useful intermediates in the synthesis of sultines.

To learn more about sultine chemistry and to determine the nature of the reactive intermediates, we further explored the reaction of sultine **5a** with radical trapping reagents such as methanol, 1,4-cyclohexadiene, and 2-mercaptoethanol.<sup>12-14</sup> In the presence of 2-mercaptoethanol in a sealed tube reaction in benzene, sultine 5a underwent SO<sub>2</sub> extrusion and gave a radical (or ionic) trapping product, 19, as well as the rearranged sulfolene 6a in a ca. 2:3 ratio, with a total yield of 50%. Similar trapping of the reactive intermediates by methanol gave 20 and sulfolene 6a in a ca. 1:1 ratio. The abstractions of a hydrogen and a methoxy group in product 20 were confirmed by a methanol- $d_4$  trapping experiment, where the disappearance of a methyl ether signal and a decrease of the 3-methyl signal from an integration of three to two protons were observed in <sup>1</sup>H NMR spectra of adduct **21**. Although the formation of adducts **19–21** may be explained by a biradical trapping mechanism, alternatively, it may also be explained by ionic intermediates similar to those used by Myers in their trapping of  $\alpha$ , 3-dehydrotoluene.<sup>13,14</sup> The trapping of the reactive intermediate, resulting from the pyrolysis of sultine 5a, by 1,4-cyclohexadiene was found to be inefficient even though it has been frequently used in the trapping of biradicals. The results implied that the biradicals might have been formed; however, they were either retrapped by  $SO_2$  (7ad) or underwent intramolecular rearrangement (through 7'a-d) to give only sulfolene 6a in 86% yield. Alternatively, the latter results may favor the nucleophilic displacement by methanol or mercaptoethanol on the O-carbon atom to yield a sulfinic acid, which after losing SO<sub>2</sub> gives the observed products.<sup>15</sup>

In conclusion, we have synthesized 2,5-disubstituted thienosultines **5a**-**d** and studied their thermal reactions

with electron-poor alkenes, alkynes, radical trapping agents, and nucleophiles. When heated in the presence of electron-poor dienophiles, sultines 5a-d underwent elimination of SO<sub>2</sub>, and the resulting biradicals (7a-d or 7'a-d, Scheme 3) were intercepted as the 1:1 adducts 8-12 in good to excellent yields. In each case, small to substantial amounts of sulfolenes **6a-d** were also formed. When sultine **5a** was heated in benzene in a sealed tube in the presence of methanol or 2-mercaptoethanol, the respective trapping adducts **19–21** as well as the rearranged sulfolene 6a were isolated. Reaction of sultine 5b with *n*BuLi was found to undergo a nucleophilic ringopening reaction to give sulfoxide alcohol 17 after H<sub>2</sub>O workup. Sulfoxide alcohols can be further transformed into other sultine derivatives.<sup>4d,f</sup> Concentration-dependent trapping of sultines and sulfolenes through thermolysis revealed that different reaction mechanisms may be involved. We are in the process of studying the photochemistry and transient absorption spectroscopy of these and other heterocyclic fused sultines,<sup>3</sup> and the results will be reported in due course.

### **Experimental Section**

General Procedures. Melting points were determined on a melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded at 300 MHz, 13C and DEPT NMR spectra were recorded at 75.4 MHz, and the chemical shifts are reported in parts per million ( $\delta$ ) relative to that of CDCl<sub>3</sub> ( $\delta$  = 7.25 ppm for proton, and  $\delta$  = 77.00 ppm for carbon) or tetramethylsilane as internal standard. Coupling constants are reported in hertz (Hz). High-resolution mass spectra were recorded on a spectrometer of the instrument center of either National Tsing-Hua University or National Chung-Hsin University. C, H, and N combustion analyses were determined, and all analyzed compounds are within  $\pm 0.4\%$  of the theoretical value unless otherwise indicated. Column chromatography was performed on silica gel of 70-230 or 230-400 mesh. The preparation of **2** followed a literature<sup>8a</sup> procedure. The synthesis of dihalides 4a and 4b followed a literature procedure.<sup>9b,c</sup>

**Data for 2-Phenylthiophene (2):** 98% yield; white solid; mp 31–32 °C (lit.<sup>8a</sup> mp 36 °C); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 7.03–7.05 (1H, m), 7.23–7.37 (5H, m), 7.58–7.61 (2H, m); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  123.03 (CH), 124.75 (CH), 125.90 (CH), 127.41 (CH), 127.96 (CH), 128.84 (CH), 134.35 (C<sub>q</sub>), 144.38 (C<sub>q</sub>).

Synthesis of 2-Methyl-5-phenylthiophene (3c). To a solution of 2 (4.36 g, 27.26 mmol) in THF (60 mL) at 0 °C was slowly added *n*-butyllithium (2.5 M in hexane, 30 mmol) via syringe under nitrogen. After the solution was stirred for 3 h, methyl iodide (8.1 g, 54 mmol) in THF (4 mL) was added dropwise with vigorous stirring. The reaction mixture was gradually warmed to ambient temperature and stirred overnight. The solution was poured into 50 mL of ice-water, the two layers were separated, and the aqueous layer was extracted with ether (3  $\times$  50 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated. Flash column chromatography on silica gel (hexane) gave 4.6 g (26 mmol, 97%) of **3c** as a white solid: mp 39–41 °C; <sup>1</sup>H NMR  $\delta$ 2.47 (3H, s), 6.70-6.69 (1H, m), 7.07-7.08 (1H, m), 7.21-7.55 (5H, m); <sup>13</sup>C NMR & 15.45 (CH<sub>3</sub>), 122.85 (CH), 125.47 (CH), 126.16 (CH), 126.96 (CH), 128.78 (CH), 134.68 (Cq), 139.48 (Cq), 141.96 (C<sub>q</sub>).

**Synthesis of 2,5-Diphenylthiophene (3d).** A hexane solution of *n*-butyllithium (34.3 mmol) was added via syringe to a stirred solution of 2-phenylthiophene (5.0 g, 31.2 mmol) in anhydride THF (50 mL) at 0 °C under nitrogen. The mixture was stirred at this temperature for 3 h, and then transferred via syringe to a stirred solution of zinc chloride (4.68 g, 34.3 mmol) in 20 mL of anhydride THF at room temperature. The

<sup>(12)</sup> For examples of radical trapping by thiols, see: (a) Ottenheijm, H. C. J. *J. Org. Chem.* **1981**, *46*, 5408. (b) Tome, A. C.; Cavaleiro, J. A. S.; Storr, R. C. *Tetrahedron* **1996**, *52*, 1723.

<sup>(13)</sup> For efficient trapping of biradical intermediates using 1,4cyclohexadiene, see: (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. J. Am. Chem. Soc. **1989**, 111, 8057. (b) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. J. Am. Chem. Soc. **1992**, 114, 9369.

E. Y. J. Am. Chem. Soc. **1992**, 114, 9369. (14) Storr et al. reported<sup>12b</sup> a similar observation of conjugate addition of thiol nucleophiles on the pyrimidin-4-ones generated from the corresponding sulfolene with  $SO_2$  extrusion.

<sup>(15)</sup> We thank one of the reviewers for the suggestion of this mechanism.

solution was stirred at ambient temperature for another 2 h and then added via syringe to an oven-dried 250 mL roundbottom flask containing tetrakis(triphenylphosphine)palladium (108 mg, 0.0936 mmol) and bromobenzene (5.0 g, 31.2 mmol) in 20 mL of dry THF. The reaction mixture was then slowly heated to 55 °C and kept at this temperature for 24 h. Dilute hydrochloric acid (0.1 N, 30 mL) was added to the cooled reaction mixture. The layers were separated, and the aqueous layer was extracted with  $CH_2Cl_2$  (3  $\times$  30 mL). The organic layers were combined, washed with saturated sodium bicarbonate solution (30 mL) and water (3  $\times$  30 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated. Recrystallization in hot 2-propanol gave 3.4 g (14.4 mmol, 46%) of 3d as a pale yellow powder: mp 149–150 °C (lit.<sup>8b</sup> mp 149–150 °C); <sup>1</sup>H NMR  $\delta$ 7.26–7.66 (12H, m); <sup>13</sup>C NMR  $\delta$  123.97 (CH), 125.60 (CH), 127.50 (CH), 128.90 (CH), 134.27 (Cq), 143.58 (Cq); MS (EI) m/z 237 (M<sup>+</sup> + 1, 58), 236 (M<sup>+</sup>, 100), 202 (8).

General Procedure for the Synthesis of 2,5-Disubstituted 3,4-Bis(chloromethyl)thiophenes 4a-d.9c The procedure for 4c is given as an example. Compound 3c (5.0 g, 28.7 mmol) was dissolved in carbon disulfide (10 mL), and chloromethyl methyl ether (7.3 g, 86 mmol) was added. The solution was cooled to 0 °C. A solution of tin tetrachloride (11.3 g, 43.05 mmol) in 10 mL of carbon disulfide was added dropwise via an additional funnel under nitrogen. The mixture turned dark green upon addition. The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature for 2 h. The heterogeneous dark green mixture was poured into ice-water (20 mL), and CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added. After the mixture was stirred for 10 min, the layers were separated and the organic layer was washed with water (20 mL) and dried over MgSO<sub>4</sub>. The solvent was distilled off in vacuo to yield 3.7 g (1.37 mmol, 48%) of 4c as a viscous green oil. Product 4c decomposed after chromatography on silica gel; therefore, crude product was used without further purification. The isolated yields based on starting materials **3a**-**c** are as follows: 4a, 41%; 4b, 69%; 4c, 48%; 4d, 64%.

**Data for 3,4-Bis(chloromethyl)-2,5-dimethylthiophene** (4a): white solid; mp 59–61 °C; <sup>1</sup>H NMR  $\delta$  2.40 (6H, s), 4.60 (4H, s); <sup>13</sup>C NMR  $\delta$  12.75 (CH<sub>3</sub>), 37.23 (CH<sub>2</sub>), 131.95 (C<sub>q</sub>), 135.91 (C<sub>q</sub>). Anal. Calcd for C<sub>8</sub>H<sub>10</sub>Cl<sub>2</sub>S: C, 45.95; H, 4.82. Found: C, 46.00; H, 4.85.

**Data for 2,5-Dichloro-3,4-bis(chloromethyl)thiophene (4b):** white solid; mp 38–39 °C (lit.<sup>9b</sup> mp 41–42 °C); <sup>1</sup>H NMR  $\delta$  4.63 (4H, s); <sup>13</sup>C NMR  $\delta$  35.66 (CH<sub>2</sub>), 126.94 (C<sub>q</sub>), 132.88 (C<sub>q</sub>). Anal. Calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>4</sub>S: C, 28.83; H, 1.61. Found: C, 29.05; H, 1.62.

Data for 3,4-Bis(chloromethyl)-2-methyl-5-phenyl-thiophene (4c):<sup>2b</sup> viscous green oil; <sup>1</sup>H NMR  $\delta$  2.48 (3H, s), 4.63 (2H, s), 4.69 (2H, s), 7.36–7.52 (5H, m); <sup>13</sup>C NMR  $\delta$  12.96 (CH<sub>3</sub>), 37.12 (CH<sub>2</sub>), 38.55 (CH<sub>2</sub>), 128.21 (CH), 128.83 (CH), 129.02 (CH), 131.63 (C<sub>q</sub>), 132.89 (C<sub>q</sub>), 133.07 (C<sub>q</sub>), 138.92 (C<sub>q</sub>), 140.49 (C<sub>q</sub>); MS (EI) *m*/*z* 272 (M<sup>+</sup> + 2, 17), 271 (M<sup>+</sup> + 1, 30), 270 (M<sup>+</sup>, 25), 269 (36), 234 (64), 185 (100).

**Data for 3,4-Bis(chloromethyl)-2,5-diphenylthiophene** (4d): white solid; 64% yield; mp 108.1–108.7 °C; <sup>1</sup>H NMR  $\delta$  4.76 (4H, s), 7.42–7.61 (10H, m); <sup>13</sup>C NMR  $\delta$  38.45 (CH<sub>2</sub>), 128.55 (CH), 128.94 (CH), 129.08 (CH), 132.50 (C<sub>q</sub>), 132.58 (C<sub>q</sub>), 143.22 (C<sub>q</sub>); MS (EI) *m*/*z* 336 (M<sup>+</sup> + 3, 4), 335 (M<sup>+</sup> + 2, 7), 334 (M<sup>+</sup> + 1, 27), 333 (M<sup>+</sup>, 17), 332 (42), 298 (20), 297 (47), 248 (100), 247 (62), 129 (69). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>S: C, 64.87; H, 4.23. Found: C, 64.70; H, 4.62.

General Procedure for the Synthesis of 5,7-Disubstituted 1,4-Dihydro-1*H*- $3\lambda^4$ -thieno[3,4-*d*][2,3]oxathiin-3oxides (Sultines) 5a-d. A solution of 4a-d (0.30 g for 4a, 1.43 mmol), Rongalite (0.44 g, 2.86 mmol), and TBAB (0.69 g, 2.15 mmol) in DMF (50 mL) was stirred at room temperature for 2 h. The mixture was diluted with H<sub>2</sub>O (40 mL) and extracted three times (3 × 20 mL) with ether. The organic layer was dried over MgSO<sub>4</sub>, concentrated, and purified by column chromatography (25–5:1 hexane/ethyl acetate) to give 0.14 g (0.67 mmol, 47%) of 5a. Corresponding yields for other substituents are as follows: 60% for **5b**, 17% for **5c** and **5c'** (as a 1:1 mixture), and 25% for **5d**.

**Data for 5,7-Dimethyl-1,4-dihydro-1***H***·3** $\lambda$ **<sup>4</sup>-thieno[3,4-***d*]**[2,3]oxathiin-3-oxide (Sultine 5a):** white solid; mp 70–71 °C; <sup>1</sup>H NMR  $\delta$  2.27 (6H, s), 3.58 (1H, A'B', J = 15.3 Hz), 3.88 (1H, A'B', J = 15.6 Hz), 4.93 (1H, AB, J = 14.1 Hz), 5.16 (1H, AB, J = 14.1 Hz); <sup>13</sup>C NMR  $\delta$  12.11 (2 CH<sub>3</sub>), 50.92 (CH<sub>2</sub>), 58.73 (CH<sub>2</sub>), 119.13 (C<sub>q</sub>), 125.40 (C<sub>q</sub>), 128.72 (C<sub>q</sub>), 133.15 (C<sub>q</sub>); MS (EI) *m*/*z* 202 (M<sup>+</sup>, 6.0), 138 (M<sup>+</sup> – SO<sub>2</sub>, 100); HRMS *m*/*z* calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub> 202.0122, found 202.0116. Anal. Calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>: C, 47.50; H, 4.98. Found: C, 47.29; H, 5.06.

**Data for 5,7-Dichloro-1,4-dihydro-1***H***·3** $\lambda$ **<sup>4</sup>-thieno[3,4-***d***]-<b>[2,3]oxathiin-3-oxide (Sultine 5b):** white solid; mp 86–87 °C; <sup>1</sup>H NMR  $\delta$  3.66 (1H, A'B', J = 16.0 Hz), 3.73 (1H, A'B', J = 16.1 Hz), 4.94 (1H, AB, J = 14.9 Hz), 5.08 (1H, AB, J = 14.9 Hz); <sup>13</sup>C NMR  $\delta$  49.50 (CH<sub>2</sub>), 57.04 (CH<sub>2</sub>), 120.44 (C<sub>q</sub>), 121.23 (C<sub>q</sub>), 125.51 (C<sub>q</sub>), 126.36 (C<sub>q</sub>); MS (EI) *m*/*z* 242 (M<sup>+</sup>, 11.4), 178 (M<sup>+</sup> – SO<sub>2</sub>, 100); HRMS *m*/*z* calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 241.9030, found 241.9024. Anal. Calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 29.64; H, 1.66. Found: C, 29.66; H, 1.94.

**Data for 7-Methyl-5-phenyl-1,4-dihydro-1***H***3** $\lambda^4$ **-thieno-[3,4-***d***]<b>[2,3]oxathiin-3-oxide (Sultine 5c):** pale yellow solid; mp 91–92 °C; <sup>1</sup>H NMR  $\delta$  2.41 (3H, s), 3.79 (1H, A'B', J=15.5 Hz), 4.15 (1H, A'B', J=15.5 Hz), 5.05 (1H, AB, J=14.0 Hz), 5.26 (1H, AB, J=14.0 Hz), 7.35–7.45 (5H, m); <sup>13</sup>C NMR  $\delta$  12.71 (CH<sub>3</sub>), 51.59 (CH<sub>2</sub>), 58.81 (CH<sub>2</sub>), 121.02 (C<sub>q</sub>), 126.42 (C<sub>q</sub>), 127.79 (CH), 128.40 (CH), 128.94 (CH), 133.00 (C<sub>q</sub>), 135.01 (C<sub>q</sub>), 136.02 (C<sub>q</sub>); MS (EI) *m*/*z* 264 (M<sup>+</sup>, 5), 200 (M<sup>+</sup> – SO<sub>2</sub>, 96), 119 (96), 185 (M<sup>+</sup> – SO<sub>2</sub> – CH<sub>3</sub>, 100); HRMS *m*/*z* calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: C, 59.07; H, 4.58. Found: C, 59.32; H, 4.71.

**Data for 5-Methyl-7-phenyl-1,4-dihydro-1***H***3** $\lambda$ <sup>4</sup>**-thieno-[3,4-***d***]<b>[2,3]oxathiin-3-oxide (Sultime 5c'):** pale yellow solid; mp 95–97 °C; <sup>1</sup>H NMR  $\delta$  2.37 (3H, s), 3.60 (1H, A'B', *J* = 15.6 Hz), 4.05 (1H, A'B', *J* = 15.6 Hz), 5.03 (1H, AB, *J* = 14.1 Hz), 5.44 (1H, AB, *J* = 14.1 Hz), 7.29–7.46 (5H, m); <sup>13</sup>C NMR  $\delta$  12.59 (CH<sub>3</sub>), 51.54 (CH<sub>2</sub>), 58.75 (CH<sub>2</sub>), 121.04 (C<sub>q</sub>), 126.42 (C<sub>q</sub>), 127.71 (CH), 128.33 (CH), 128.86 (CH), 132.96 (C<sub>q</sub>), 134.93 (C<sub>q</sub>), 135.91 (C<sub>q</sub>); MS (EI) *m*/*z* 264 (M<sup>+</sup>, 6), 200 (M<sup>+</sup> – SO<sub>2</sub>, 78), 199 (100), 185 (75).

**Data for 5,7-Diphenyl-1,4-dihydro-1***H***·3** $\lambda^4$ **-thieno[3,4-***d*]**[2,3]oxathiin-3-oxide (Sultine 5d):** clear crystal after recrystallization from a solvent of CH<sub>2</sub>Cl<sub>2</sub> and hexane; mp 176–177 °C; <sup>1</sup>H NMR  $\delta$  3.80 (1H, A'B', J=15.6 Hz), 4.36 (1H, A'B', J=15.6 Hz), 5.16 (1H, AB, J=14.0 Hz), 5.49 (1H, AB, J=14.0 Hz), 7.37–7.49 (10H, m); <sup>13</sup>C NMR  $\delta$  53.22 (CH<sub>2</sub>), 59.43 (CH<sub>2</sub>), 121.22 (C<sub>q</sub>), 127.78 (C<sub>q</sub>), 128.24 (CH), 128.31 (CH), 128.66 (CH), 128.95 (CH), 129.00 (CH), 129.05 (CH), 132.59 (C<sub>q</sub>), 132.67 (C<sub>q</sub>), 137.87 (C<sub>q</sub>), 140.95 (C<sub>q</sub>); MS (EI) *m*/*z* 326 (M<sup>+</sup>, 1.5), 262 (34), 261 (100), 228 (28); HRMS *m*/*z* calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 66.23; H, 4.32. Found: C, 66.18; H, 4.39.

**General Procedure for the Trapping Experiments of 2,5-Dimethylthienosultine 5a with Dienophiles Such as N-Phenylmaleimide, Dimethyl Fumarate, and Fumaronitrile.** A solution of 2,5-dimethylthienosultine **5a** (50 mg, 0.25 mmol), with or without the respective dienophiles (0.74 mmol), in benzene (3 mL) was kept in a sealed tube at 180 °C for 24 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 16:1 to 4:1) as the eluent. Sulfolene **6a** was obtained in 90% yield (no quencher). For the trapping by dienophiles, the respective yields are as follows: *N*phenylmaleimide, 6% **6a** and 91% **8a**; dimethyl fumarate, 49% **6a** and 40% **9a**; fumaronitrile, 46% **6a** and 43% **10a**.

**Data for 4,6-Dimethyl-1,3-dihydro-1***H***-**2 $\lambda$ <sup>6</sup>**-thieno[3,4***c*]**thiophene-2,2-dione (6a):** white solid; mp 187–188 °C; <sup>1</sup>H NMR  $\delta$  2.34 (6H, s), 4.11 (4H, s); <sup>13</sup>C NMR  $\delta$  13.54 (CH<sub>3</sub>), 54.71 (CH<sub>2</sub>), 126.59 (C<sub>q</sub>), 133.57 (C<sub>q</sub>); MS (EI) *m*/*z* 202 (M<sup>+</sup>, 21.7), 138 (M<sup>+</sup> – SO<sub>2</sub>, 100); HRMS *m*/*z* calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub> 202.0122, found 202.0119. Anal. Calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub>: C, 47.50; H, 4.98. Found: C, 47.29; H, 5.06.

Data for 1,3-Dimethyl-6-phenyl-4a,5,6,7,7a,8-hexahydro-4*H*-thieno[3,4-f]isoindole-5,7-dione (8a): white solid; mp 149–151 °C; <sup>1</sup>H NMR  $\delta$  2.20 (6H, s), 2.57–2.63 (2H, m), 3.12–3.18 (2H, m), 3.20–3.30 (2H, m), 6.82–6.86 (2H, m), 7.24–7.33 (3H, m); <sup>13</sup>C NMR  $\delta$  12.14 (CH<sub>3</sub>), 24.47 (CH<sub>2</sub>), 40.23 (CH), 126.38 (CH), 128.51 (CH), 129.01 (CH), 129.24 (C<sub>q</sub>), 130.64 (C<sub>q</sub>), 131.78 (C<sub>q</sub>), 178.77 (C<sub>q</sub>); MS (EI) *m*/*z* 311 (M<sup>+</sup>, 100), 163 (60); HRMS *m*/*z* calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>S 311.0980, found 311.0984.

**Data for Dimethyl (5***R*\*,6*R*\*)-1,3-Dimethyl-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5,6-dicarboxylate (9a): white solid; mp 106–108 °C; <sup>1</sup>H NMR  $\delta$  2.17 (6H, s), 2.21–2.48 (2H, m), 2.84–2.97 (4H, m), 3.66 (6H, s); <sup>13</sup>C NMR  $\delta$  12.46 (CH<sub>3</sub>), 27.70 (CH<sub>2</sub>), 42.68 (CH), 50.00 (CH<sub>3</sub>), 128.37 (C<sub>q</sub>), 130.58 (C<sub>q</sub>), 175.13 (C<sub>q</sub>); MS (EI) *m*/*z* 282 (M<sup>+</sup>, 71.0), 222 (67), 163 (100); HRMS *m*/*z* calcd for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>S 282.0926, found 282.0921. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>S: C, 59.55; H, 6.43. Found: C, 59.19; H, 6.38.

**Data for (5***R*\*,6*R*\*)-1,3-Dimethyl-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5,6-dicarbonitrile (10a): white solid; mp 214–215 °C; <sup>1</sup>H NMR  $\delta$  2.92 (6H, s), 2.87–2.95 (2H, m), 3.11– 3.27 (4H, m); <sup>13</sup>C NMR  $\delta$  12.58 (CH<sub>3</sub>), 26.74 (CH<sub>2</sub>), 28.87 (CH<sub>3</sub>), 118.55 (C<sub>q</sub>), 126.30 (C<sub>q</sub>), 130.58 (C<sub>q</sub>); MS (EI) *m*/*z* 216 (M<sup>+</sup>, 21.7), 138 (100); HRMS *m*/*z* calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S 216.0727, found 216.0722.

**General Procedure for the Trapping Experiments of 2,5-Dichlorothienosultine 5b with Dienophiles Such as N-Phenylmaleimide, Dimethyl Fumarate, and Fumaronitrile.** A solution of 2,5-dichlorothienosultine **5b** (50 mg, 0.21 mmol), with or without the respective dienophiles (0.62 mmol), in benzene (3 mL) was kept in a sealed tube at 180 °C for 24 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using 25:1 hexane/ethyl acetate as the eluent. Sulfolene **6b** was obtained in 95% yield (no quencher). For the trapping by dienophiles, the respective yields are as follows: *N*-phenylmaleimide, 7% **6b** and 65% **8b**; dimethyl fumarate, 4% **6b** and 64% **9b**; fumaronitrile, 16% **6b** and 77% **10b**.

**Data for 4,6-Dichloro-1,3-dihydro-1***H***2** $\lambda^6$ **-thieno[3,4-c]-thiophene-2,2-dione (6b):** white solid; mp 157–160 °C; <sup>1</sup>H NMR  $\delta$  4.22 (4H, s); <sup>13</sup>C NMR  $\delta$  55.09 (CH<sub>2</sub>), 123.07 (C<sub>q</sub>), 128.05 (C<sub>q</sub>); MS (EI) *m*/*z* 242 (M<sup>+</sup>, 18.5), 178 (M<sup>+</sup> – SO<sub>2</sub>, 100); HRMS *m*/*z* calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 241.9030, found 241.9039. Anal. Calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 29.64; H, 1.66. Found: C, 29.66; H, 1.94.

Data for 1,3-Dichloro-6-phenyl-4a,5,6,7,7a,8-hexahydro-4*H*-thieno[3,4-f]isoindole-5,7-dione (8b): white solid; mp 195–196 °C; <sup>1</sup>H NMR  $\delta$  2.77–2.85 (2H, m), 3.31–3.46 (4H, m), 7.06–7.09 (2H, m), 7.36–7.45 (3H, m); <sup>13</sup>C NMR  $\delta$  24.06 (CH<sub>2</sub>), 39.24 (CH), 121.26 (C<sub>q</sub>), 126.18 (CH), 128.69 (CH), 129.10 (CH), 131.49 (C<sub>q</sub>), 131.84 (C<sub>q</sub>), 177.52 (C<sub>q</sub>); MS (EI) *m/z* 351 (M<sup>+</sup>, 100), 169 (52), 134 (47); HRMS *m/z* calcd for C<sub>16</sub>H<sub>11</sub>-SO<sub>2</sub>Cl<sub>2</sub>N 350.9987, found 350.9887. Anal. Calcd for C<sub>16</sub>H<sub>11</sub>SO<sub>2</sub>-Cl<sub>2</sub>N: C, 54.56; H, 3.15; N, 3.98. Found: C, 54.57; H, 3.54; N, 4.09.

**Data for Dimethyl (5***R*\*,6*R*\*)-1,3-Dichloro-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5,6-dicarboxylate (9b): white solid; mp 88–89 °C; <sup>1</sup>H NMR  $\delta$  2.52–2.71 (2H, m), 2.93–3.15 (4H, m), 3.75 (6H, s); <sup>13</sup>C NMR  $\delta$  26.77 (CH<sub>2</sub>), 41.57 (CH), 52.23 (CH<sub>3</sub>), 120.56 (C<sub>q</sub>), 131.81 (C<sub>q</sub>), 174.03 (C<sub>q</sub>); MS (EI) *m/z* 322 (M<sup>+</sup>, 55.1), 262 (100), 203 (99), 168 (74); HRMS *m/z* calcd for C<sub>12</sub>H<sub>12</sub>SO<sub>4</sub>Cl<sub>2</sub> 321.9833, found 321.9828. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>-SO<sub>4</sub>Cl<sub>2</sub>: C, 44.60; H, 3.74. Found: C, 44.65; H, 3.89.

**Data for (5***R***\*,6***R***\*)-1,3-Dichloro-4,5,6,7-tetrahydrobenzo[***c***]thiophene-5,6-dicarbonitrile (10b): white solid; mp 192–194 °C; <sup>1</sup>H NMR \delta 3.00–3.21 (4H, m), 3.35–3.39 (2H, m); <sup>13</sup>C NMR \delta 25.84 (CH<sub>2</sub>), 27.86 (CH), 117.53 (C<sub>q</sub>), 123.02 (C<sub>q</sub>), 127.72 (C<sub>q</sub>); MS (EI)** *m***/***z* **256 (M<sup>+</sup>, 85.4), 178 (100); HRMS** *m***/***z* **calcd for C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>S 255.9629, found 255.9633.** 

General Procedure for the Trapping Experiments of 2-Methyl-5-phenylthienosultine 5c with Dienophiles Such as *N*-Phenylmaleimide, Fumaronitrile, Dimethyl Acet**ylenedicarboxylate, and Diethyl Fumarate.** A solution of 2-methyl-5-phenylthienosultine **5c** (50 mg, 0.189 mmol), with or without the respective dienophiles (0.567 mmol), in toluene (3 mL) was kept in a sealed tube at 180 °C for 24 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 6:1 to 4:1) as the eluent. Sulfolene **6c** was obtained in 98% yield (no quencher). For the trapping by dienophiles, the respective yields are as follows: *N*-phenylmaleimide, 16% **6c** and 76% **8c**; fumaronitrile, 13% **6c** and 75% **10c**; dimethyl acetylenedicarboxylate, 47% **6c** and 37% **11c**; diethyl fumarate, 23% **6c** and 69% **12c**.

**Data for 4-Methyl-6-phenyl-1,3-dihydro-1***H*-2λ<sup>6</sup>-thieno-[**3,4**-*c*]thiophene-2,2-dione (**6***c*): clear crystal; mp 197–198 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); <sup>1</sup>H NMR δ 2.44 (3H, s), 4.17 (2H, s), 4.38 (2H, s), 7.44–7.32 (5H, m); <sup>13</sup>C NMR δ 13.89 (CH<sub>3</sub>), 53.89 (CH<sub>2</sub>), 56.21 (CH<sub>2</sub>), 125.69 (C<sub>q</sub>), 126.88 (CH), 127.98 (CH), 128.37 (C<sub>q</sub>), 129.13 (CH), 132.94 (C<sub>q</sub>), 133.78 (C<sub>q</sub>), 136.67 (C<sub>q</sub>); MS (EI) *m*/*z* 265 (M<sup>+</sup> + 1, 3), 264 (M<sup>+</sup>, 25), 200 (M<sup>+</sup> – SO<sub>2</sub>, 100), 199 (80), 185 (M<sup>+</sup> – SO<sub>2</sub> – CH<sub>3</sub>, 64), 184 (53); HRMS *m*/*z* calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub> 264.0279, found 264.0278. Anal. Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: C, 59.07; H, 4.58. Found: C, 59.13; H, 4.67.

Data for 1-Methyl-3,6-diphenyl-4a,5,6,7,7a,8-hexahydro-4*H*-thieno[3,4-f]isoindole-5,7-dione (8c): yellow oil; <sup>1</sup>H NMR  $\delta$  2.38 (3H, s), 2.76–2.88 (2H, m), 3.29–3.58 (4H, m), 6.95–6.98 (2H, m), 7.29–7.42 (8H, m); <sup>13</sup>C NMR  $\delta$  12.37 (CH<sub>3</sub>), 24.32 (CH<sub>2</sub>), 24.94 (CH<sub>2</sub>), 40.11 (CH), 126.33 (CH), 12.76 (CH), 128.60 (CH), 128.68 (CH), 129.04 (CH), 130.46 (C<sub>q</sub>), 131.77 (C<sub>q</sub>), 131.95 (C<sub>q</sub>), 132.30 (C<sub>q</sub>), 133.60 (C<sub>q</sub>), 134.89 (C<sub>q</sub>), 178.54 (C<sub>q</sub>), 178.63 (C<sub>q</sub>); MS (EI) *m*/*z* 374 (M<sup>+</sup> + 1, 18), 373 (M<sup>+</sup>, 100), 225 (40), 187 (14); HRMS *m*/*z* calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>S 373.1137, found 373.1136.

Data for (5*R*\*,6*R*\*)-1-Methyl-3-phenyl-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5,6-dicarbonitrile (10c): pale yellow solid; mp 158.2–160.0 °C; <sup>1</sup>H NMR  $\delta$  2.37 (3H, s), 2.97– 3.40 (6H, m), 7.26–7.45 (5H, m); <sup>13</sup>C NMR  $\delta$  12.87 (CH<sub>3</sub>), 26.81 (CH<sub>2</sub>), 28.10 (CH<sub>2</sub>), 28.76 (CH), 29.03 (CH), 118.32 (C<sub>q</sub>), 118.55 (C<sub>q</sub>), 126.40 (C<sub>q</sub>), 127.39 (C<sub>q</sub>), 127.63 (CH), 128.44 (CH), 128.82 (CH), 133.38 (C<sub>q</sub>), 133.68 (C<sub>q</sub>), 135.75 (C<sub>q</sub>); MS (EI) *m*/*z* 278 (M<sup>+</sup>, 100), 199 (57), 185 (45), 165 (26); HRMS *m*/*z* calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>S 278.0879, found 278.0871.

**Data for Dimethyl 1-Methyl-3-phenyl-4,7-dihydroben**zo[*c*]thiophene-5,6-dicarboxylate (11c): yellow solid; mp 101–102 °C; <sup>1</sup>H NMR  $\delta$  2.40 (3H, s), 3.54–3.75 (4H, m), 3.79 (3H, s), 3.83 (3H, s), 7.28–7.45 (5H, m); <sup>13</sup>C NMR  $\delta$  12.95 (CH<sub>3</sub>), 27.25 (CH<sub>2</sub>), 29.00 (CH<sub>2</sub>), 52.42 (CH<sub>3</sub>), 127.12 (CH), 128.41 (CH), 128.71 (CH), 129.80 (C<sub>q</sub>), 131.78 (C<sub>q</sub>), 131.93 (C<sub>q</sub>), 133.84 (C<sub>q</sub>), 134.23 (C<sub>q</sub>), 168.19 (C<sub>q</sub>), 168.71 (C<sub>q</sub>); MS (EI) *m/z* 342 (M<sup>+</sup>, 77), 310 (100), 309 (65), 282 (34), 251 (44), 224 (87); HRMS *m/z* calcd for C<sub>19</sub>H<sub>18</sub>O<sub>4</sub>S 342.0926, found 342.0929.

**Data for Diethyl (5***R*\*,6*R*\*)-1-Methyl-3-phenyl-4,5,6,7tetrahydrobenzo[c]thiophene-5,6-dicarboxylate (12c): pale yellow solid; mp 72–73 °C; <sup>1</sup>H NMR  $\delta$  1.19–1.32 (6H, m), 2.34 (3H, s), 2.83–3.18 (6H, m), 4.10–4.23 (4H, m), 7.27–7.40 (5H, m); <sup>13</sup>C NMR  $\delta$  12.82 (CH<sub>3</sub>), 14.09 (CH<sub>3</sub>), 14.15 (CH<sub>3</sub>), 27.70 (CH<sub>2</sub>), 29.41 (CH<sub>2</sub>), 42.70 (CH), 43.08 (CH), 60.82 (CH<sub>2</sub>), 126.93 (CH), 128.37 (CH), 128.57 (CH), 130.93 (C<sub>q</sub>), 131.65 (C<sub>q</sub>), 131.87 (C<sub>q</sub>), 133.48 (C<sub>q</sub>), 134.29 (C<sub>q</sub>), 174.56 (C<sub>q</sub>), 174.63 (C<sub>q</sub>); MS (EI) *m*/*z* 372 (M<sup>+</sup>, 46), 327 (11), 298 (20), 225 (100); HRMS *m*/*z* calcd for C<sub>21</sub>H<sub>24</sub>O<sub>4</sub>S 372.1395, found 372.1395.

**General Procedure for the Trapping Experiments of 2,5-Diphenylthienosultine 5d with Dienophiles Such as N-Phenylmaleimide, Dimethyl Fumarate, Fumaronitrile, and Diethyl Fumarate.** A solution of 2,5-diphenylthienosultine **5d** (50 mg, 0.153 mmol), with or without the respective dienophiles (0.459 mmol), in toluene (3 mL) was kept in a sealed tube at 180 °C for 24 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 10:1 to 6:1) as the eluent. Sulfolene **6d** was obtained in 94% yield (no quencher). For the trapping by dienophiles, the respective yields are as follows: *N*-phenylmaleimide, 6% **6d**  and 82% 8d; dimethyl fumarate, 21% 6d and 75% 9d; fumaronitrile, 12% 6d and 79% 10d; diethyl fumarate, 30% 6d and 67% 12d.

**Data for 4,6-Diphenyl-1,3-dihydro-1***H*-2 $\lambda^6$ -thieno[3,4c]thiophene-2,2-dione (6d): white solid; mp 214–215 °C; <sup>1</sup>H NMR  $\delta$  4.41 (4H, s), 7.35–7.46 (10H, m); <sup>13</sup>C NMR  $\delta$  55.29 (CH<sub>2</sub>), 127.10 (CH), 127.23 (C<sub>q</sub>), 128.40 (CH), 129.22 (CH), 132.58 (C<sub>q</sub>), 138.44 (C<sub>q</sub>); MS (EI) *m*/*z* 326 (M<sup>+</sup>, 9), 262 (M<sup>+</sup> – SO<sub>2</sub>, 16), 261 (100), 228 (20); HRMS *m*/*z* calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub> 326.0436, found 326.0434. Anal. Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 66.23; H, 4.32. Found: C, 66.01; H, 4.44.

Data for 1,3,6-Triphenyl-4a,5,6,7,7a,8-hexahydro-4*H*thieno[3,4-f]isoindole-5,7-dione (8d): white solid; mp 214– 217 °C; <sup>1</sup>H NMR  $\delta$  2.87–2.96 (2H, m), 3.47–3.49 (2H, m), 3.59–3.64 (2H, dd, J= 14.7, 6 Hz), 6.99–7.02 (2H, m), 7.34– 7.52 (13H, m); <sup>13</sup>C NMR  $\delta$  24.91 (CH<sub>2</sub>), 40.16 (CH), 126.42 (CH), 127.75 (CH), 128.74 (CH), 128.88 (CH), 129.24 (CH), 131.55 (C<sub>q</sub>), 131.77 (C<sub>q</sub>), 133.32 (C<sub>q</sub>), 137.85 (C<sub>q</sub>), 178.58 (C<sub>q</sub>); MS (EI) *m*/*z* 436 (M<sup>+</sup> + 1, 11), 435 (M<sup>+</sup>, 100), 287 (16), 286 (20), 261 (13); HRMS *m*/*z* calcd for C<sub>28</sub>H<sub>21</sub>NO<sub>2</sub>S 435.1294, found 435.1285. Anal. Calcd for C<sub>28</sub>H<sub>21</sub>NO<sub>2</sub>S: C, 77.22; H, 4.86; N, 3.22. Found: C, 77.20; H, 5.04; N, 3.41.

**Data for Dimethyl (5***R*\*,6*R*\*)-1,3-Diphenyl-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5,6-dicarboxylate (9d): white solid; mp 184–185 °C; <sup>1</sup>H NMR  $\delta$  2.90–3.05 (4H, m), 3.24– 3.30 (2H, m), 3.71 (6H, s), 7.29–7.49 (10H, m); <sup>13</sup>C NMR  $\delta$ 29.14 (CH<sub>2</sub>), 42.79 (CH), 52.08 (CH<sub>3</sub>), 127.42 (CH), 128.52 (CH), 128.66 (CH), 131.57 (C<sub>q</sub>), 133.88 (C<sub>q</sub>), 136.52 (C<sub>q</sub>), 174.89 (C<sub>q</sub>); MS (EI) *m*/*z* 406 (M<sup>+</sup>, 34), 346 (10), 287 (100), 252 (34); HRMS *m*/*z* calcd for C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>S 406.1240, found 406.1243. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>S: C, 70.91; H, 5.45. Found: C, 71.10; H, 5.49.

**Data for (5***R*\*,**6***R*\*)-**1,3-Diphenyl-4,5,6,7-tetrahydrobenzo[***c***]thiophene-5,6-dicarbonitrile (10d):** due to the severe overlap of **10d** with **6d** in column chromatography, we obtained only proton NMR data,  $\delta$  3.19–3.48 (6H, m), 7.36– 7.49 (10H, m).

**Data for Diethyl (5***R*,6*R***)-1,3-Diphenyl-4,5,6,7-tetrahydrobenzo[***c***]thiophene-5,6-dicarboxylate (12d): white solid; mp 145–146 °C; <sup>1</sup>H NMR \delta 1.25 (6H, t, J = 7.1 Hz), 2.90– 3.04 (4H, m), 3.24–3.29 (2H, dd, J = 15, 2.7 Hz), 4.17 (4H, q, J = 7.1 Hz), 7.32–7.49 (10H, m); <sup>13</sup>C NMR \delta 14.07 (CH<sub>3</sub>), 29.16 (CH<sub>2</sub>), 42.95 (CH), 60.85 (CH<sub>2</sub>), 127.38 (CH), 128.52 (CH), 128.65 (CH), 131.74 (C<sub>q</sub>), 133.95 (C<sub>q</sub>), 136.45 (C<sub>q</sub>), 174.43 (C<sub>q</sub>); MS (EI)** *m***/***z* **435 (M<sup>+</sup> + 1, 9), 434 (M<sup>+</sup>, 59), 287 (100), 286 (79), 253 (46); HRMS** *m***/***z* **calcd for C<sub>26</sub>H<sub>26</sub>O<sub>4</sub>S 434.1553, found 434.1553. Anal. Calcd for C<sub>26</sub>H<sub>26</sub>O<sub>4</sub>S: C, 71.86; H, 6.03. Found: C, 72.07, H, 6.14.** 

**Reaction of 5b with** *n***-BuLi Followed by Quenching** with  $H_2O$  or  $D_2O$  To Give Products 17 and 18. To a 25 mL two-necked bottle were added 100 mg (0.42 mmol) of 5b and 5 mL of dry THF. The solution was cooled to -78 °C, 248  $\mu$ L (0.62 mmol) of *n*BuLi was added via syringe, and the resulting solution was stirred at this temperature for 1 h. It was then stirred at 0 °C for 1 h and at rt for another 1 h. The solution was quenched with either brine (1 mL) or  $D_2O$  (1 mL) in an ice bath, and the product was extracted with ethyl ether (3 × 5 mL). The combined organic extracts were washed with water (2 × 5 mL) and brine (5 mL) and then dried with MgSO<sub>4</sub>. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (4:1) as the eluent to yield 42 mg (0.14 mmol) of 17 or 60 mg (0.20 mmol) of 18.

**Data for 4-[(Butylsulfinyl)methyl]-2,5-dichloro-3-thienylmethanol (17):** 33% yield; white solid; mp 85–86 °C; <sup>1</sup>H NMR  $\delta$  0.98 (3H, t, J = 7.5 Hz), 1.46–1.60 (2H, m); 1.73–1.84 (2H, m); 2.47 (2H, t, J = 7.2 Hz), 3.94, 4.10 (2H, AB, J = 14.0 Hz), 4.49 (2H, d, J = 6.9 Hz), 4.70 (1H, t, J = 6.6 Hz); <sup>13</sup>C NMR  $\delta$  13.63 (CH<sub>3</sub>), 21.99 (CH<sub>2</sub>), 24.55 (CH<sub>2</sub>), 48.59 (CH<sub>2</sub>), 51.07 (CH<sub>2</sub>), 55.50 (CH<sub>2</sub>), 125.80 (C<sub>q</sub>), 126.18 (C<sub>q</sub>), 127.06 (C<sub>q</sub>), 138.68 (C<sub>q</sub>); MS (EI) *m*/*z* 301 (M<sup>+</sup> + 1, 7), 117 (100); HRMS *m*/*z* calcd for C<sub>10</sub>H<sub>14</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> 299.9812, found 299.9804;  $R_f$  = 0.1 (hexane:ethyl acetate = 4:1).

**Data for 4-[(Butylsulfinyl)methyl-***d*<sub>1</sub>**]-**2,5-**dichloro-3thienylmethanol (18):** 47% yield; white solid; mp 88–90 °C; <sup>1</sup>H NMR  $\delta$  0.95 (3H, t, J = 7.2 Hz), 1.54–1.55 (2H, m); 1.73– 1.83 (2H, m); 2.74 (2H, t, J = 7.8 Hz), 3.96, 4.08 (1H, AB, J = 13.8 Hz), 4.47 (2H, d, J = 6.6 Hz), 4.70 (1H, t, J = 6.6 Hz); <sup>13</sup>C NMR  $\delta$  13.63 (CH<sub>3</sub>), 21.99 (CH<sub>2</sub>), 24.55 (CH<sub>2</sub>), 48.39 (t, C–D), 51.13 (CH<sub>2</sub>), 55.56 (CH<sub>2</sub>), 125.83 (C<sub>q</sub>), 126.15 (C<sub>q</sub>), 127.09 (C<sub>q</sub>), 138.71 (C<sub>q</sub>); MS (EI) *m*/*z* 302 (M<sup>+</sup> + 1, 4), 117 (100); *R*<sub>f</sub> = 0.1 (hexane:ethyl acetate = 4:1).

General Procedure for the Trapping Experiments of 2,5-Dimethylthienosultine 5a by Radical Trapping Agents Such as 2-Mercaptoethanol, Methanol, Methanol- $d_4$ , and 1,4-Cyclohexadiene. A solution of 5a (50 mg, 0.25 mmol) with the respective radical trapping agents (each 1 mL except 0.5 mL for 1,4-cyclohexadiene) in benzene (2 mL) was kept in a sealed tube at 180 °C for 24 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 16:1 to 1:1) as the eluent. The trapping yields are as follows: 21% 19 and 30% 6a by 2-mercaptoethanol, 19% 20 and 20% 6a by methanol, 37% 21 and 26% 6a by methanol- $d_4$ , and 86% sulfolene 6a by 1,4-cyclohexadiene.

**Data for 2-[(2,4,5-Trimethyl-3-thienyl)methyl]sulfanyl-1-ethanol (19):** colorless liquid; <sup>1</sup>H NMR  $\delta$  2.14 (3H, s), 2.28 (3H, s), 2.35 (3H, s), 2.69 (2H, t, J = 5.7 Hz); 3.60 (2H, s), 3.68–3.88 (2H, br s); <sup>13</sup>C NMR  $\delta$  12.43 (CH<sub>3</sub>), 13.05 (CH<sub>3</sub>), 13.16 (CH<sub>3</sub>), 27.79 (CH<sub>2</sub>), 34.93 (CH<sub>2</sub>), 60.45 (CH<sub>2</sub>), 129.21 (C<sub>q</sub>), 131.28 (C<sub>q</sub>), 132.27 (C<sub>q</sub>); MS (EI) m/z 216 (M<sup>+</sup>, 10), 139 (100); HRMS m/z calcd for C<sub>10</sub>H<sub>16</sub>OS<sub>2</sub> 216.0643, found 216.0639.

**Data for 3-(Methoxymethyl)-2,4,5-trimethylthiophene** (20): colorless liquid; <sup>1</sup>H NMR  $\delta$  2.07 (3H, s), 2.27 (3H, s), 2.38 (3H, s), 3.33 (3H, s), 4.27 (2H, s); <sup>13</sup>C NMR  $\delta$  12.10 (CH<sub>3</sub>), 12.80 (CH<sub>3</sub>), 12.89 (CH<sub>3</sub>), 57.56 (CH<sub>3</sub>), 66.27 (CH<sub>2</sub>) 128.74 (C<sub>q</sub>), 132.93 (C<sub>q</sub>), 133.49 (C<sub>q</sub>), 133.58 (C<sub>q</sub>); MS (EI) *m*/*z* 170 (M<sup>+</sup>, 1), 138 (100); HRMS *m*/*z* calcd for C<sub>9</sub>H<sub>14</sub>OS 170.0765, found 170.0763.

**Data for 3-(Methoxy-***d*<sub>3</sub>**-methyl)-2,5-dimethyl-4-methyl***d*<sub>1</sub>**-thiophene (21):** colorless liquid; <sup>1</sup>H NMR  $\delta$  2.05 (2 H, t, *J* = 2.1 Hz), 2.27 (3H, s), 2.38 (3H, s), 4.26 (2H, s); <sup>13</sup>C NMR  $\delta$  11.88 (t, *J*<sub>CD</sub> = 20 Hz, CH<sub>2</sub>D), 12.84 (CH<sub>3</sub>), 12.93 (CH<sub>3</sub>), 66.19 (CH<sub>2</sub>) 128.78 (C<sub>q</sub>), 132.91 (C<sub>q</sub>), 133.53 (C<sub>q</sub>); MS (EI) *m/z* 174 (M<sup>+</sup>, 23), 139 (60), 84 (100); HRMS *m/z* calcd for C<sub>9</sub>H<sub>10</sub>D<sub>4</sub>OS 174.1017, found 170.1017.

Procedure for the Concentration-Dependent Trapping of Thienosultine 5a and Furanosulfolene 16 by Fumaronitrile. Stock solutions of 5a and 16 were first prepared by adding 60 mg (0.30 mmol) of 5a to 18 mL of toluene or 45 mg (0.28 mmol) of 16 to 18 mL of benzene. The stock solution was then equally divided into six thick-walled tubes, and each contained a 3 mL solution of 5a (16.5 mM) in toluene or 16 (15.8 mM) in benzene. Tubes a and b were without fumaronitrile, and tubes c-f were with different amounts of fumaronitrile: (c) 4 mg (0.05 mmol, 16.7 mM), (d) 20 mg (0.26 mmol), (e) 40 mg (0.51 mmol), (f) 60 mg (0.77 mmol). After three cycles of freeze-pump-thaw, these tubes were sealed under vacuum, all reacted at the same time in an oil bath thermostated at (1) 150  $\pm$  2 °C, 5 h for 5a, and (2)  $120 \pm 2$  °C, 2 h for **16**, and then cooled to room temperature. The solvent of these tubes was removed by rotary evaporation, and to each of them was added 1 mL of CDCl<sub>3</sub> with 50 mM *N*-phenylmaleimide as internal standard for <sup>1</sup>H NMR analysis. The data shown in Figure 1 are the average of at least two runs.

**Acknowledgment.** We thank the National Science Council of the Republic of China for financial support (Grant No. NSC89-2113-M-009-026).

**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C (or DEPT) NMR spectra for compounds **8a**, **8c**, **10a**–**d**, **11c**, **12c**, and **17–21**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO011122S