# 1,3-Dipolar Activity in Cycloadditions of an Aliphatic Sulfine†,[1]

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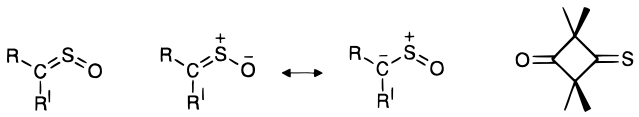
2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-oxide (**4**) combines with diaryl thioketones at room temperature furnishing spiro-1,2,4-oxadithiolanes **6** in equilibrium reactions. Compound **6a** was oxidized to the *cis-S,S*-dioxide **9**, the structure of which was established by X-ray analysis. These are the first unequivocal 1,3-cycloadditions of thione *S*-oxides (sulfines) which possess an allyl anion type MO; cycloadditions to the C═S bond of sulfines as dipolarophile and dienophile had been described before.

## Introduction

The first sulfine was prepared, inadvertently, by Wedekind *et al.* in 1923.[3] The systematic development of this class of organosulfur compounds was largely a fruit of the pioneering efforts of Block[4] and Zwanenburg.[5]

Many authors use the heterocumulene formula **1** for sulfines. However, most theoreticians do not regard the participation of sulfur d-orbitals as high.[6] Therefore, we prefer the thione *S*-oxide structure **2a**, due to the sulfur and oxygen bearing a net positive and a negative charge, respectively.[7] The parent sulfine, prepared by Block *et al.*,[8] has a dipole moment of 2.99 D (gas phase).



**1** **2a** **2b** **3**

The resonance hybrid **2** constitutes a 1,3-dipole;[9a] sulfines are the thio analogues of carbonyl oxides, the well-known intermediates in the ozonation of alkenes.

Zwanenburg and his group discovered the readiness with which the CS bond of sulfines participates as 2$\pi$ reactant in Diels−Alder reactions and 1,3-dipolar cycloadditions.[5] Sulfines behave as *dipolarophiles* vs diazoalkanes, nitrile ylides, nitrile imines, and nitrile oxides as well as nitrones and münchnones. However, Zwanenburg *et al.*[10] stated in 1967, "*...we have found no indications for 1,3-dipolar cycloaddition reactions of sulfines despite several attempts.*" The lack of 1,3-dipolar activity of sulfines, still in the early 1990s,[11] was less understandable since thiocarbonyl ylides are highly active 1,3-dipoles[12] and numerous 1,3-cycloadditions of thiocarbonyl imines are likewise known.[13]

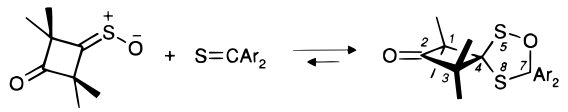
We recently presented kinetic evidence for thiones as being *superdipolarophiles.*[14−16] High rate constants of cycloadditions were attributed to low $\pi$ HOMO−LUMO separations. Calculations (MP2/6-31G*, Becke3LYP/6-31G*) for the concerted addition of the nitrone parent to thioformaldehyde resulted in *negative* activation enthalpies.[17]

We report here the first unequivocal 1,3-dipolar cycloadditions of sulfines.

## Results and Discussion

**Cycloaddition Equilibria of Sulfine 4 and Aromatic Thioketones.** 2,2,4,4-Tetramethyl-3-thioxocyclobutanone (**3**) is easily available, and its *S*-oxide **4**, described by Zwanenburg *et al.*,[18] is relatively thermostable; we found it unchanged after 4 h at 80 °C, making **4** a suitable model sulfine.

The reaction of thiobenzophenone (**5a**) and its 4,4′-dichloro derivative (**5b**) with 1.1 equiv of **4** in pentane−dichloromethane proceeded at rt in the dark; the 1,2,4-oxadithiolanes **6a** and **6b** were obtained as colorless crystals. The moderate isolated yields (62 and 55%) reflect the ease of cycloreversion. The specimens turned deep-blue at the melting point, the color of **5a** or **5b**.



**4** + S=CAr$_2$ ⇌

| | | | |
|---|---|---|---|
| **5a** | Ar = $C_6H_5$ | **6a** |
| **5b** | Ar = $C_6H_4Cl$-*p* | **6b** |
| **5c** | Ar = $C_6H_4OCH_3$-*p* | **6c** |

† Dedicated to Jürgen Sauer, Regensburg, to whom cycloaddition chemistry owes so much, on the occasion of his 65th birthday.

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(1) 1,3-Dipolar Cycloadditions. 95. For part 94, see, ref 16.

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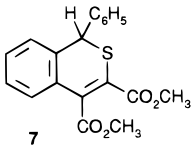
When sulfine **4** was reacted with 2 equiv of thiones **5a** or **5b** in $CDCl_3$ at rt, $^1H$ NMR analysis after 2, 9, and 70 h indicated 96−100% of the oxadithiolanes **6a** and **6b**, respectively. This allows for several conclusions: (a) the conversion of **4** to the oxadithiolanes **6** is virtually quantitative in the presence of an excess of thioketone; (b) the equilibration is complete after 2 h; (c) the equilibrium system is stable at rt.

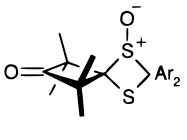
Fresh solutions of the oxadithiolanes **6a** and **6b** started to turn blue after several minutes at ambient temperature; however, the color nearly disappeared upon cooling to −20 °C. Due to the high extinction of the long-wave light absorption of **5**, the color test is overly sensitive. Only a small percentage of **6** is dissociated in solution at rt. The Diels−Alder reaction of thiobenzophenone with dimethyl acetylenedicarboxylate (DMAD) affording **7**[19] is slow but irreversible. Adduct **6a** and 2 equiv of DMAD in $CDCl_3$ were heated to 50 °C; after 6 d the $^1H$ NMR analysis established 89% of **7**, 96% of sulfine **4**, and still 4% of adduct **6a**. Thus, thiobenzophenone was removed through a small equilibrium concentration by cycloaddition to DMAD.



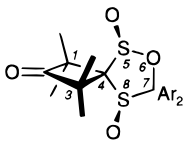

**7**

The degree of dissociation of oxadithiolane **6c** into 4,4′-dimethoxythiobenzophenone (**5c**) plus **4** is much higher than that of **6a** or **6b**. Only 76% of **6c** was found when **4** and **5a** were reacted in 1:2 ratio under the standard conditions described above for complete conversion to **6a** and **6b**. Ground state stabilization of **5c** by participation of quinonoid resonance structures influences the cycloaddition equilibrium. A value of $K_{add} = 3.3\ M^{-1}$ ($CDCl_3$, 25 °C) for **6c** was measured and corresponds to $\Delta G_{298} = 0.70$ kcal $mol^{-1}$; 41% is dissociated in 1 M oxadithiolane **6c** in $CDCl_3$.

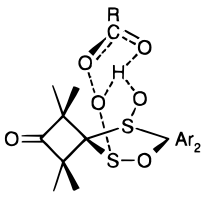
**Structure of Cycloadducts.** In accord with the $C_s$ symmetry of **6a** and **6b**, the $^1H$ NMR spectra show pairwise identical methyl groups ($\delta$ 1.25 and 1.40, $CDCl_3$); formula **8** of a 1,3-dithietane *S*-oxide would require four different $CH_3$. The $^{13}C$ NMR spectra allow a complete assignment of signals.




**8**




**9**




**10**

The $M^+$ peaks are missing in the mass spectra of **6a** and **6b**; mainly those of the thioketones were observed. Fragments coming from the sulfine part are rare, however, suggesting a fast dissociation, $M^{+\bullet} \rightarrow 5^{+\bullet} + 4$. Dichlorobenzophenone$^+$ and 4-chlorobenzoylium ion (base peak) point to another fragmentation pathway for $\mathbf{6b}^{+\bullet}$. Finally, in the MS of the thiofluorenone adduct **12**, a peak for $M^+ - 2CH_3$ was observed.

Since the thin leaflets of **6a** were not suitable for single crystal analysis, **6a** was oxidized by *m*-CPBA to a single bis-*S*-oxide **9** (82%). This makes the four methyl signals in the $^1H$ NMR spectrum of **9** nonequivalent; they spread over a wide range ($\delta$ 0.47, 1.07, 1.72, 1.90). A sultone or sulfone structure should have retained pairwise equivalence of the methyls. The IR spectrum showed a strong sulfoxide absorption at 1091 $cm^{-1}$ and a further strong S−O band at 1163 $cm^{-1}$ for the sultine group. Benzophenone radical cation and benzoylium ion constitute the most populous peaks in the MS of **9**.

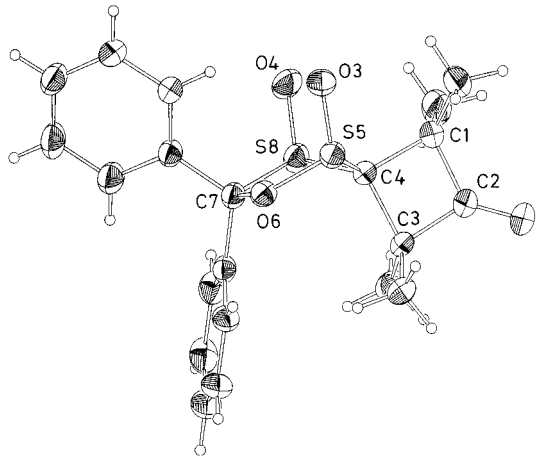



**Figure 1.** X-ray structure of the spiro-oxadithiolane *cis*-dioxide **9** (ORTEP plot).

The X-ray analysis of the monoclinic crystal revealed the *cis*-*S*,*S*-dioxide **9** in an *envelope* conformation with C4 as the flap (Figure 1). The sums of the bond angles at S5 and S8 are 311° and 310°, respectively, revealing the extent of pyramidalization. Both oxide functions are in a pseudoaxial conformation at the 5-membered ring. The folding angle of the cyclobutane ring amounts to 11.4°.

The bond length of 1.471 Å for the sulfoxide (S8−O4) is nearly identical with that of DMSO (1.477 Å), and C4−S8 with 1.823 Å compares well with 1.810 Å for C−S in DMSO.[20] The angles C4−S8−O4 (107.2°) and C7−S8−O4 (109.8°) correspond to 106.7° for DMSO. The semipolar bond S5−O3 (1.447 Å) of the sultine group is somewhat shorter than that of the sulfoxide, and the length of the single bond S5−O6 is 1.609 Å.

Why the kinetic preference for the *cis*-5,8-dioxide? After the first oxygen transfer, the sulfoxide will form a strong hydrogen bond with the second molecule of peracid. As the sketch (structure **10**) of the TS suggests, the second O transfer should take place on the same face of the 5-membered heterocycle as the first one. Sulfoxides are strong hydrogen bond acceptors; it may be recalled, that proton exchange of secondary alcohols is suppressed in DMSO, and coupling of O−H with C−H becomes observable.[21]

In 1963, it was proposed that 1,3-dipolar cycloadditions to heteromultiple bonds are guided in a direction that gives rise to two new strong carbon−heteroatom bonds rather than to C−C plus the weaker heteroatom−heteroatom bond.[22] In our case, the formation of a 1,2,4-oxadithiolane should be preferred to that of the 1,2,5-regioisomer. However, the *principle of maximum gain of* $\sigma$-bond energy[22] was later discarded in favor of the

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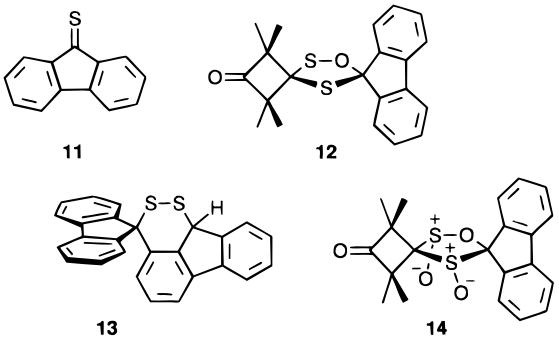
perturbation MO treatment of concerted cycloadditions.[9b,23] Thus, the structure of **6** was not *a priori* clear.

**Thiofluorenone as a Dipolarophile.** The cycloaddition of sulfine **4** to thione **11** generated the colorless needles of **12**; the $^1$H and $^{13}$C NMR spectra are in accord with a plane of symmetry in **12**. Oxidation by *m*-CPBA provided the *S,S*-dioxide **14** in analogy to the conversion of **6a** → **9**.

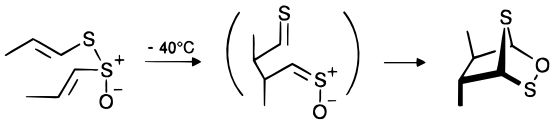


**11** **12** **13** **14**

Interestingly, the yield of **12** went through a maximum when the reaction with 1:2 stoichiometry at rt was monitored by $^1$H NMR spectroscopy: 32% of **12** after 2 h, 54% after 9 h, and 26% after 70 h. The reason is the irreversible dimerization of thiofluorenone furnishing **13**; the dimer was recognized as a Diels−Alder adduct by Schönberg *et al.*[24] After 9 h (70 h), 18% (23%) of **13** was detected; therefore, there must be further side reactions.

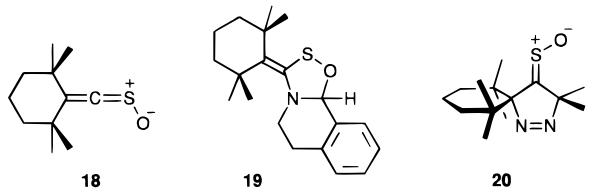
The "semiquantitative" evidence that thiofluorenone reacts slower than thiobenzophenone is surprising. In the 1,3-cycloadditions of thiobenzophenone *S*-methylide, thiofluorenone exceeded thiobenzophenone 60-fold in the rate constant.[14] In the dienophilic activity vs cyclopentadiene, thiofluorenone is 7100 times faster than thiobenzophenone.[25]

**Related Cycloadditions.** Block *et al.* obtained the *(E,E)*-thiosulfinate **15**, in the context of his masterly studies on the chemistry of onions, by oxidation of the disulfide at −60 °C. The conversion to the 2-oxa-3,7-dithiabicyclo[2.2.1]heptane derivative **17** at −40 °C was plausibly interpreted by a thio-Claisen rearrangement to afford **16** and a subsequent intramolecular 1,3-dipolar cycloaddition of the *(Z)*-sulfine function to the thioaldehyde.[26]




**15** *(E,E)* **16** *(Z)* **17**

Schaumann and Walter[27] obtained the 3-methylene-1,2,4-oxathiazolidine **19** from the thioketene *S*-oxide **18** by addition to 3,4-dihydroisoquinoline. The X-ray analysis revealed an envelope structure of the heterocycle with C-5 as the flap and an S−O bond length of 1.661 Å.[28] In comparison with sulfines, thioketene *S*-oxides reveal markedly changed bond lengths and reactivity. No longer does the C=S bond behave as a dipolarophile but the C=C does; the addition of 2-diazopropane furnished **20**.[29]



**18** **19** **20**

**Further Observations.** The dipolarophile scale for 1,3-cycloadditions of sulfine **4** is limited. No reaction was observed with DMAD, dimethyl 2,3-dicyanofumarate, *N*-sulfinylaniline, *N*-benzylidenemethylamine ($CDCl_3$, 7 d at 25 °C, some hours at 60 °C). When **4** was treated with *N*-isobutenylpyrrolidine (12 d, rt), the main product was tetramethylcyclobutane-1,3-dione.

No interaction of adamantanethione *S*-oxide with thiobenzophenone was monitored by the $^1$H NMR spectrum ($CDCl_3$) in 14 d at rt; at 80 °C, the sulfine disappeared in 2 d, and adamantanone occurred among the products.

**Kinetic or Thermodynamic Control.** Why does **4** combine with the C=S double bond but not with olefinic and acetylenic bonds? According to calculations (MP4SDTQ/6-31G*//6-31G* + ZPE) by Schleyer and Kost,[30] the CS $\pi$-bond of $H_2C$=S is 14 kcal mol$^{-1}$ weaker than the CC $\pi$-bond of ethylene. Since the $\sigma$-bond energy of C−S is likewise lower than that of C−C, even by 19 kcal mol$^{-1}$, the sulfine cycloaddition to ethylene should be more exothermic by 5 kcal mol$^{-1}$ than the addition to thioformaldehyde. The nonreactivity of CC multiple bonds toward sulfines is probably a *kinetic* phenomenon.

However, the conclusion is still shaky. Bond energies depend on adjacent groups, and sufficient group values[31] are not known for sulfur functions to calculate reliable reaction enthalpies. Furthermore, different cycloaddition entropies could change the picture. More information is required.

## Experimental Section

**General Methods and Instruments.**[16] NMR spectral data were taken in acid-free $CDCl_3$, stored over dry $K_2CO_3$; assignments were based on DEPT ($^1$H) and spectra with and without decoupling ($^{13}$C). MS evaluation of the isotope peaks helped the assignment. Melting points are uncorrected.

**2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-Oxide (4).** Thione **3**[16] was converted to **4**[18] by *m*-CPBA in ether at 0 °C; 78% of colorless crystals from pentane−$CH_2Cl_2$ 1:1, mp 48−49 °C (80%, mp 52.3−53.2 °C).[18] IR (KBr): 1069 st (st means strong) (SO), 1789 st (C=O). $^1$H NMR: $\delta$ 1.51 (s, 2 $CH_3$), 1.66 (s, 2 $CH_3$). MS (EI 70 eV, 40 °C): *m/z* (proposed ion, percent intensity) 172 ($M^+$, 23), 156 (**3**$^+$, 4%), 144 ($M^+$ − CO, $C_7H_{12}S^+$, 55; $^{13}$C calcd 4.3, found 4.4; $^{34}$S calcd 2.5, found 2.2), 140 (tetramethylcyclobutane-1,3-dione$^+$, 11), 127 ($C_7H_{11}S^+$, 25), 96 ($C_7H_{12}^+$, 100; $^{13}$C calcd 7.8, found 7.9), 86 (dimethylthioketene$^+$, 14), 81 ($C_6H_9^+$, methylpentadienyl, 80), 70 (dimethylketene$^+$,

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85). Above 100 °C, the peak of a *dimer* of **4** begins to appear and reaches a maximum at 245 °C. MS (EI, 70 eV): *m/z* 344 ($M_2^+$ 1.5; $^{13}$C calcd 0.26, found 0.28), 204 ($M_2$ − tetramethylcyclobutanedione, 2.2), 172 ($M^+$, 51; $^{13}$C calcd 4.5, found 4.4). We are dealing with a *thermal dimerization*, since $M_2^+$ did not disappear after cooling.

**1,1,3,3-Tetramethyl-7,7-diphenyl-6-oxa-5,8-dithiaspiro-[3.4]octan-2-one (6a). (A) Synthesis.** Sulfine **4** (568 mg, 3.3 mmol) and thiobenzophenone (**5a**, 595 mg, 3.0 mmol) reacted in 2 mL of $CH_2Cl_2$ and 6 mL of pentane for 12 h at rt. After evaporation of the solvent, the still blue residue was taken up in 1 mL of dichloromethane and 5 mL of ethanol, concentrated at rt, and cooled to 0 °C: colorless crystals of **6a** (690 mg, 62%); from pentane at −78 °C in thin leaflets, mp 80−81 °C (blue melt). $^1$H NMR: $\delta$ 1.25 (s, 2 $CH_3$), 1.40 (s, 2 $CH_3$), 7.2−7.6 (m, 2 $C_6H_5$). $^{13}$C NMR: $\delta$ 21.6 (q, 2 $CH_3$), 25.2 (q, 2 $CH_3$), 66.3 (s, C-1 and C-3), 82.7 (s, C-4), 111.8 (s, C-7), 127.4, 128.0, 128.3 (3 d, 6 aromatic CH), 142.9 (s, 2 aromatic $C_q$), 218.8 (s, CO). MS (EI, 70 eV, 100 °C): *m/z* 198 (**5a**$^+$, 94; $^{13}$C calcd 14, found 15), 182 (benzophenone$^+$, 5), 165 (fluorenyl$^+$, 100; $^{13}$C calcd 15, found 15), 121 ($C_6H_5C{\equiv}S^+$, 72; $^{34}$S calcd 3.2, found 3.3), 105 ($C_6H_5C{\equiv}O^+$, 10), 86 (dimethylthioketene$^+$, 8), 77 ($C_6H_5^+$, 27). Anal. Calcd for $C_{21}H_{22}O_2S_2$: C, 68.07; H, 5.99; S, 17.31. Found: C, 68.08; H, 5.99; S, 17.30.

**(B) $^1$H NMR Monitoring of Equilibrium.** The methyl singlets of **4** and **6a** can be integrated separately; 2,6-dimethylnaphthalene (s $\delta$ 2.43, 2 $CH_3$) served as a weight standard for the quantitative analysis (±5%). Sulfine **4** (0.50 mmol), thione **5a** (1.00 mmol), and a standard in 1.0 mL of $CDCl_3$ were sealed in the NMR tube. Integration of **6a** was measured as follows: 100% (2 h), 98% (9 h), 96% (70 h at rt). In a second series of tests, **4** (0.60 mmol) and **5a** (0.50 mmol) in 0.5 mL of $CDCl_3$ were reacted in the sealed NMR tube. The integration of **6a** was measured as follows: 84% (2 h at rt), 96% (9 h), 91% (70 h).

**(C) Interception by DMAD.** Oxadithiolane **6a** (78 mg, 0.21 mmol), dimethyl acetylenedicarboxylate (54 mg, 0.38 mmol), and 2,6-dimethylnaphthalene (0.079 mmol) in 0.7 mL $CDCl_3$ were reacted in the sealed NMR tube at 50 °C; the blue solution turned turquois after 6 d. The $^1$H integrals indicated 89% of **7** (s at $\delta$ 5.13, *tertiary* H), 96% of **4** (s, 1.66, 2 $CH_3$), and 4% **6a** (s, 1.40, 2 $CH_3$).

**1,1,3,3-Tetramethyl-7,7-bis(4-chlorophenyl)-6-oxa-5,8-dithiaspiro[3.4]octan-2-one (6b). (A) Synthesis.** The reaction of **4** (3.3 mmol) and **5b** (3.0 mmol), run as described above, provided 731 mg (55%) of **6b** from ethanol, mp 95−97 °C. After thick-layer chromatography (silica gel, $CH_2Cl_2$−pentane 1:1), colorless prisms crystallized from pentane at −20 °C, mp 105−106 °C. IR (KBr): 1786 st (C═O). $^1$H NMR: $\delta$ 1.25 (s, 2 $CH_3$), 1.40 (s, 2 $CH_3$), 7.26−7.41 (AA′BB′ of $C_6H_4Cl$); at $\delta$ 1.51 and 1.66, 3.4% of **4** (equilibration). $^{13}$C NMR: $\delta$ 21.5 (q, 2 $CH_3$), 25.2 (q, 2 $CH_3$), 66.2 (s, C-1 and C-3), 83.0 (s, C-4), 110.6 (s, C-7), 128.4 and 128.7 (2 d, 8 aromatic CH), 134.6 and 141.2 (2 s, 4 aromatic $C_q$), 218 (s, C═O). MS (EI, 70 eV, 90 °C): *m/z* 266 (**5b**$^+$, 60; 268 ($^{37}$Cl + $^{34}$S) calcd 42, found 42; 270 $^{37}$Cl calcd 6, found 6), 250 (4,4′-dichlorobenzophenone$^+$, 35; $^{37}$Cl calcd 22, found 23), 233 (3,6-dichlorofluorenyl$^+$, 57), 231 (65), 155 ($ClC_6H_4CS^+$, 60; $^{34}$S + $^{37}$Cl calcd 22, found 22), 139 ($ClC_6H_5C{\equiv}O^+$, 100; $^{37}$Cl calcd 32, found 34), 111 ($ClC_6H_4^+$, 38), 86 (dimethylthioketene$^+$, 29), 81 ($C_6H_9^+$, 31). If **6b** would undergo thermal dissociation before ionization, peak 172 (**4**$^+$) and its secondary ions should appear; *m/z* 172 is missing. This suggests a splitting of $M^+ \rightarrow$ **4** + **5b**$^+$. Anal. Calcd for $C_{21}H_{20}Cl_2O_2S_2$: C, 57.39; H, 4.59; S, 14.60. Found: C, 57.51; H, 4.83; S, 14.64.

**(B) $^1$H NMR Monitoring of Equilibrium.** The cycloaddition with **4**/**5b** = 1:2 (described above for **5a**) furnished 100% **6b** after 2 h at rt, 97% after 9 h, and 98% after 70 h. In the experiment with 1.2 equiv of **4**, the yields of **6b** amounted to 89% (2 h), 94% (9 h), and 89% (70 h).

**1,1,3,3-Tetramethyl-7,7-bis(4-methoxyphenyl)-6-oxa-5,8-dithiaspiro[3.4]octan-2-one (6c). (A) Synthesis.** The substantial equilibrium concentration of the reactants thwarted the isolation of pure **6c**. Column chromatography (silica gel, $CH_2Cl_2$−pentane 4:1) of the equilibrium system at −20 °C afforded a colorless fraction of **6c**. Upon evaporation of the solvent at 0 °C, the blue color of **5c** reappeared; the freshly isolated **6c** contained ca. 10% of **5c**. $^1$H NMR: $\delta$ 1.24 (s, 2 $CH_3$), 1.41 (s, 2 $CH_3$), 3.80 (s, 2 $OCH_3$), 6.84 and 7.38 (AA′XX′, $C_6H_4$).

**(B) Equilibrium Constant.** Sulfine **4** (35.5 mg), thione **5c** (71.6 mg), and 1,1,1,2-tetrachloroethane (57.5 mg, weight standard) were dissolved in $CDCl_3$ in a 2 mL volumetric flask. $^1$H NMR analysis (400 MHz) after 14 h (same integrals after 24 h) at rt indicated 0.0544 mmol of **6c** ($\delta$ 1.24, 3.80, 7.38), 0.134 mmol of **4** ($\delta$ 1.51), and 0.245 mmol of **5c** ($\delta$ 3.87, 7.7−7.85): $K_{298} = 3.3\ M^{-1}$.

**1,1,3,3-Tetramethyl-7,7-diphenyl-6-oxa-5,8-dithiaspiro-[3.4]octan-2-one 5,8-*cis*-Dioxide (9).** *m*-CPBA (345 mg, 2.0 mmol) in 5 mL of $CH_2Cl_2$ was introduced dropwise into the stirred, ice-cooled solution of **6a** (185 mg, 0.50 mmol) in 2 mL of $CH_2Cl_2$ in 5 min. After 45 min, 20 mL of $CH_2Cl_2$ were added. The resulting solution was washed with aqueous $NaHSO_3$ and then with water. The residue after evaporation gave on trituration with ethanol 165 mg (82%) of colorless **9**; after two recrystallizations from $CH_2Cl_2$−ethanol, the melting point was 159−160 °C (gas evolution, red). IR (KBr): 780 st (S−O); 1091 st, 1163 vst (S═O), 1788 vst (C═O). The range of sulfoxide absorptions is usually given as 1040−1060 $cm^{-1}$; the value here is somewhat higher. The S−O vibration of 5-membered sultines[32] was found at 1100−1135 $cm^{-1}$. $^1$H NMR: $\delta$ 0.47, 1.07, 1.72, 1.90 (4 s, 4 $CH_3$), 7.25−7.57 (m, 2 $C_6H_5$). MS (EI, 70 eV, 40 °C): *m/z* 214 ($C_{13}H_{10}OS^+$, probably diphenylsulfine, 4), 182 (benzophenone$^+$, 62; $^{13}$C calcd 9.0, found 9.5), 105 ($C_6H_5C{\equiv}O^+$, 100; $^{13}$C calcd 7.8, found 7.4), 77 ($C_6H_5^+$, 46). Anal. Calcd for $C_{21}H_{22}O_4S_2$: C, 62.66; H, 5.51; S, 15.93. Found: C, 62.68; H, 5.60; S, 15.99.

**X-ray Structure of 9.**[33] A crystal of **9** with an empirical formula of $C_{21}H_{22}O_4S_2$ (mol wt. 402.5) was found to be monoclinic with a space group of $P2_1/n$ (No. 14). Unit cell dimensions were determined to be $a = 8.870(2)$, $b = 15.530(4)$, and $c = 14.288(4)$ Å, $\beta = 95.57(2)°$, Vol = 1959 Å$^3$, $Z = 4$, $D_c = 1.365$ g/cm$^3$, $F(000) = 848$, $T = 294(1)$ K, and $\mu$(Mo K$_\alpha$) = 0.283 $mm^{-1}$. Data collection was performed on a CAD4 diffractometer with a colorless crystal (size 0.4 × 0.4 × 0.27 mm) mounted in a glass capillary. Cell constants were from 25 centered reflections using Mo Kα radiation, a graphite monochromator, $\lambda = 71.069$ pm, $\omega$ scan with profile fitting, scan width with (1.00 + 0.35 tan $\theta$)°, and a maximum measuring time of 60 s. The intensity of three standard reflections were checked after every hour. In the 2$\theta$ range of 4−46° 2963 reflections with indices $\pm h/+k/+l$ were measured; 2594 were unique and observed, and 2374 had $I > 2\sigma(I)$. The structure was solved with SHELXS-86, and the refinement was done with SHELXL-93. All nonhydrogen atoms were refined anisotropically, and hydrogens were refined with $U_i = 1.2 \times U_{eq}$ of the adjacent carbon atom. A full matrix refinement against $F^2$ was performed. Final $R_1$ and $wR_2$ values were 0.0395 and 0.1139 for 2374 reflections with $I > 2\sigma(I)$ and 248 variables. For all data, $R_1 = 0.0434$ and $wR_2 = 0.1183$ (weights: SHELXL-93). The maximum and minimum electron density of the final Fourier cycle were 0.396 and −0.281 eÅ$^{-3}$, respectively.

**1,1,3,3-Tetramethyl-2-oxo-6-oxa-5,8-dithia[3.4]octane-7-spiro-9′-fluorene (12) (A) Synthesis.** Sulfine **4** (3.3 mmol) and 3.0 mmol of thiofluorenone (**11**, freshly recrystallized, brown needles) were reacted as described for **6a**; 490 mg (44%) of **12**. Recrystallization from $CH_2Cl_2$−2-propanol at −20 °C gave thick colorless needles, mp 116−117 °C (brown). IR (KBr): 1786 st (C═O). $^1$H NMR: $\delta$ 1.47 (s, 2 $CH_3$), 1.59 (s, 2 $CH_3$), 7.2−7.8 (m, 8 aromatic CH). $^{13}$C NMR: $\delta$ 21.1 (q, 2 $CH_3$), 25.9 (q, 2 $CH_3$), 66.3 (s, C-1, C-3), 82.2 (s, C-4), 107.3 (s, C-7), 119.9, 125.6, 128.3, 130.5 (4 d, 8 aromatic CH), 139.2, 145.0

(32) Sharma, N. K.; Reinach-Hirtzbach, F. de; Durst, T. *Can. J. Chem.* **1976**, *54*, 3012.

(33) The authors have deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

(2 s, 4 aromatic $C_q$), 218.1 (C═O). MS (EI, 70 eV, 40 °C): *m/z* 328 ($M^+ - 2CH_3$. 4.0; $^{13}C$ calcd 0.85, found 1.05; $^{34}S$ calcd 0.18, found 0.17), 196 (**11**$^+$, 100; $^{13}C$ calcd 15, found 14; $^{34}S$ calcd 4.4, found 4.2), 180 (fluorenone$^+$, 5.9), 152 (biphenylene$^+$, 25; $^{13}C$ calcd 3.3, found 2.9), 96 ($C_7H_{12}^+$, 13), 86 (dimethylthioketene$^+$, 3), 81 ($C_6H_9^+$, 10). Anal. Calcd for $C_{21}H_{20}O_2S_2$: C, 68.44; H, 5.47; S, 17.40. Found: C, 68,52; H, 5.34; S, 17.40.

**(B) $^1$H NMR Monitoring of Equilibrium.** Signals were observed at $\delta$ 1.59 (**12**, 2 $CH_3$), 5.67 (**13**, *tertiary* H), and 4.43 (1,1,1,2-tetrachloroethane, weight standard). The cycloaddition reaction with **4**/**11** = 1:2 furnished 39% of **12** after 2 h at rt, 54% of **12** and 18% of **13** after 7 h, 26% of **12** and 23% of **13** after 70 h.

**Dimeric thiofluorenone (13)**;[24] mp 216−217 °C (dec, 230−232 °C [24]). $^{13}C$ NMR: $\delta$ 53.6 (d, aliphatic CH), 57.4 (s, aliphatic $C_q$). MS (EI, 70 eV, 85 °C): *m/z* 392 ($M^+$, 9.2; $^{13}C$ calcd 2.7, found 2.7), 328 ($M^+ - 2S$, 100; $^{13}C$ calcd 26, found 25), 327 (56), 326 (40), 164 (fluorenylidene$^+$, 10), 163 (18), 162 (11).

**1,1,3,3-Tetramethyl-2-oxo-6-oxa-5,8-dithia[3.4]octane-7-spiro-9′-fluorene *S,S*-Dioxide (14).** Oxidation was as described for the preparation of **9**. After purification on a silica gel column ($CH_2Cl_2$−acetone 98:2), 49% of **14** was obtained; colorless crystals, mp 169−170 °C. IR (KBr): 1083, 1165 st (S═O), 1787 st (C═O). $^1$H NMR: $\delta$ 1.57, 1.62, 1.75, 1.87 (4s, 4 $CH_3$). Anal. Calcd for $C_{21}H_{20}O_4S_2$: C, 62.92; H, 5.03. Found: C, 62.17; H, 5.13.

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