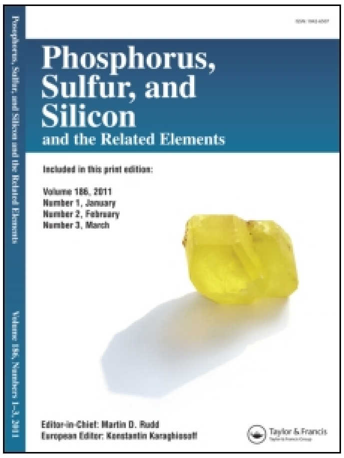

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HETEROCYCLIC THIONE S-IMIDES AND S-OXIDES. PREPARATION FROM THIONES

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HETEROCYCLIC THIONE S-IMIDES AND S-OXIDES. PREPARATION FROM THIONES

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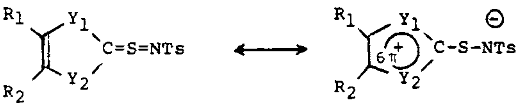
Some six-membered heterocyclic thione S-imides and the corresponding thione S-oxides (sulfines) were prepared from the corresponding thiones. Their stability is briefly discussed.

INTRODUCTION

Ylidenesulfimides (thione S-imides, **1**) belong to a novel class of thiocumulenes[1] and are isoelectronic nitrogen analogues of thione S-oxides (sulfines).[2] However, only a few examples of preparing **1** have hitherto been reported.[3-11] The stability of **1** depends on the electronic nature of the ligands (X_2C, NY) ("push-pull,"[12] "pull-pull,"[4,8]) and/or sterically hindered systems[5-7] with respect to the CSN function. Previously, we reported the synthesis of some new five-membered heterocyclic thione S-imides (**2**) which are also stabilized by effective charge delocalization of π-electrons in the push-pull substituted system.[10]

$$X_2C = S = NY \qquad (1)$$

1



2 (Y_1, Y_2 = S, NMe)

As a continuation of this work, we now report the preparation of some six-membered heterocyclic thione S-imides having similar structures. For a comparison of the stability of the thione S-imides (**5**, **7**) with the corresponding thione S-oxides (sulfines), we also attempted the preparation of the sulfines (**12**, **13**).

RESULTS AND DISCUSSION

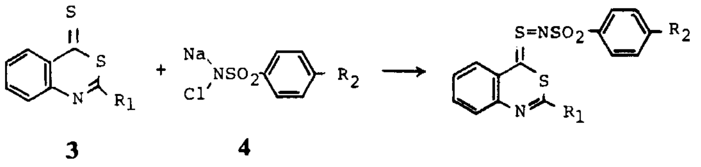
2-Substituted 3,1-benzothiazine-4-thiones (**3**) readily reacted with chloramine-T or -B (**4**) at a temperature of −15°C in methanol to give 2-substituted 3,1-benzothia-

TABLE I

3,1-Benzothiazine-4-thione S-imides (**5**)

	R_1	R_2	Yield %	Mp °C/dec	IR/cm^{-1} νCSN
5a	Ph	Me	85	112	925
5b	Ph	H	82	145	930
5c	*p*-Tol	Me	87	144	930
5d	*p*-Tol	H	61	138	920
5e	Et	Me	46	104	930

zine-4-thione S-imides (**5**) in fairly good yields (Table I).[13] The IR spectra showed typical strong absorptions of νCSN at 920–930 cm^{-1} and of νSO_2 at about 1300, 1150, and 1090 cm^{-1}. The structure was further confirmed by means of mass spectroscopy and elemental analyses (see Experimental).[14]



(3)

	R_1
a	Ph
b	p-Tol
c	Et

	R_2
a	Me
b	H

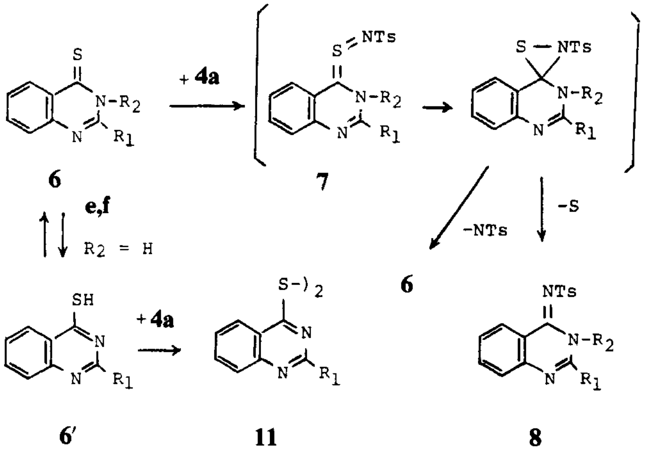
SCHEME 1

On the other hand, similar treatment of 3H-quinazoline-4-thione (**6**) with chloramine-T (**4a**) afforded thione (**6**), *N*-tosyl-3H-quinazoline-4-imine (**8**), 3H-quinazolinone (**9**), and *p*-toluenesulfonamide (**10**) in place of the expected thione S-imide (**7**). The products, **9** and **10**, most likely arose from **7** or **8** by hydrolysis. Therefore, the reaction was reexamined under anhydrous conditions.

When an equimolar amount of anhydrous chloramine-T (**4a**) in a small amount of dry methanol and acetone was added to thione (**6**) in dry dichloromethane and acetone at −15°C, most of the thione was consumed and the solution turned red. This suggested the formation of thione S-imide **7**. However, the imide could not be isolated in a pure form. Red color of the solution gradually faded and the starting thione (**6**) and imine (**8**) were formed (Table II). The reaction pathways to produce **6** and **8** are rationally explained by thiaziridine ring formation *via* **7**.[11a] Thus, the present results strongly suggest the formation of unstable **7**. In the reaction of thiones **6e, f, 4** oxidized the enethiol form **6′e, f** to give disulfides (**11**).[15]

The reaction of *N*-methylacridine-9-thione with **4a** also gave *N*-methylacridine-9-(*N*-tosyl)imine.[16]

Oxidation of thiones **3** and **6** with mCPBA (*m*-chloroperbenzoic acid) gave thione S-oxides (sulfines) **12** and **13**, respectively (Table III). The sulfines **12** and **13** did not



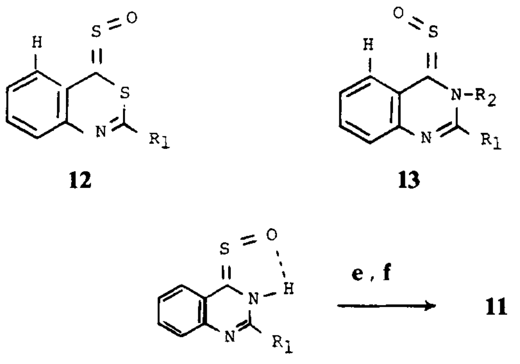
(4)

SCHEME 2

TABLE II

Reaction of 3H-quinazoline-4-thiones (**6**) with chloramine-T (**4a**)

	R_1	R_2	Product yield, %	Mp/°C **8**/**11**
a	Me	Ph	**6**, 42 **8**, 30	227–229
b	Me	*p*-Tol	**6**, 46 **8**, 29	202–204
c	Ph	Ph	**6**, 47 **8**, 21	273–274
d	Ph	*p*-Tol	**6**, 32 **8**, 43	238–240
e	Me	H	**11**, 34	156–160
f	Ph	H	**11**, 84	232–235



(5)

SCHEME 3

TABLE III

3,1-Benzothiazine-4-thione S-oxides (**12**) and 3H-quinazoline-4-thione S-oxides (**13**)

	R_1	R_2	Yield %	Mp °C/dec	IR/cm^{-1} νCSO
12a	Ph	—	80	168	1070
12b	*p*-Tol	—	83	142	1075
13a	Me	Ph	22	107	1010
13b	Me	*p*-Tol	55	118	1005
13c	Ph	Ph	41	115	1000
13d	Ph	*p*-Tol	51	195	1000
11e	Me	H	51	160	—
11f	Ph	H	50	235	—

TABLE IV

^{1}H- and ^{13}C-NMR spectral data (chemical shift) of sulfines **12a**, **13d** and thiones **3a**, **6d**

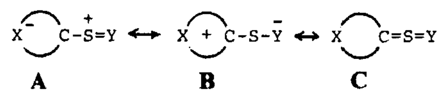
	δ peri-H	δ other Ar—H	δ C(2)	δ C(4)
3a	8.66 (1 H)	8.05–7.43 (8 H)	162.7	210.4
12a	—	7.16–8.08 (9 H)	156.7	186.2
			Δ6.0	Δ24.2
6d	8.76 (1 H)	6.90–7.77 (12 H)	154.6	190.3
13d	9.89 (1 H)	6.88–7.72 (12 H)	152.9	187.8
			Δ1.7	Δ2.7

decompose on standing at room temperature except **13e, f**.[17] Thus, the sulfines **12**, **13** ($R_2 \neq$ H) seem to be more stable than the corresponding thione S-imides (**5**, **7**). The sulfines **13e, f** are unstable and decompose into disulfides **11e, f** during isolation. This disulfide formation may be explained by the tautomerization to sulfenic acids.[18]

A comparative study of ^{1}H-NMR spectra of the sulfines (**12**, **13**) with the parent thiones (**3**, **6**) suggest the *E*, *Z*-configuration of the sulfines with respect to the bent CSO moiety.[20] Among thirteen aromatic protons in sulfine **13d**, only the peri-position proton showed a large lower-field shift (δ 9.89) as compared with those of the remaining protons (δ 6.88–7.72). This suggests that the peri-H is in the anisotropic deshielding cone of the S=O π-system; namely, the sulfines **13** should have *Z*(sym)-configuration. On the other hand, the sulfines **12** are considered to have the *E*-configuration because the same phenomenon was not observed (Table IV).

In the ^{13}C-NMR spectra, chemical shifts of C(2) and C(4) of the hetero ring in **12a** and **13d** absorbed at higher field by 6.0, 1.7 and by 24.2, 2.7 ppm than those of the thiones (**3a**, **3d**), respectively. This observation suggests that the resonance structure **A** (induced by the electron-withdrawing effect of the hetero atom (X) in the hetero ring)[19] is no less important than the "push-pull" structure **B**.[19e] Such effective delocalization of π-electrons on the cumulated system would stabilize these thiocumulenes.

X: hetero atom(s)
Y: O, NR



(6)

EXPERIMENTAL

All melting points are uncorrected. IR spectra were determined on a Hitachi Model 260-10 spectrometer. Mass spectra were recorded on a Hitachi double-focusing mass spectrometer RMU-7M operating at an ionizing potential of 70 eV. NMR spectra were measured on a JEOL JNM-FX 100 spectrometer using TMS as an internal standard.

Reaction of 3,1-benzothiazine-4-thione (**3**) *with chloramine-T* (**4a**) *or -B* (**4b**). An ethanol solution (30 ml) of **4** (11 mmol) was added dropwise to a partially suspended thione solution (10 ml) in ethanol (30 ml) with stirring at − 15–0°C. After 30 min precipitated product was filtered, washed with cold water and ethanol, dried in vacuo, and recrystallized (except **5e**) from dichloromethane-ether below 0°C to give **5** as red needles.

5a: IR (KBr) 1300, 1145, 1090 cm^{-1} (SO_2), 925 cm^{-1} (CSN); MS *m/e* 392 (2%, M^+ —S), 255 (100, $\mathbf{3a}^+$). Anal. Calcd for $C_{21}H_{16}O_2N_2S_3$: C, 59.41; H, 3.80; N, 6.60; S, 22.65. Found: C, 59.64; H, 3.79; N, 6.81; S, 22.34.

5b: IR (KBr) 1300, 1150, 1090 cm^{-1} (SO_2), 930 cm^{-1} (CSN); MS *m/e* 378 (6, M^+ —S), 255 (100, $\mathbf{3a}^+$). Anal. Calcd for $C_{20}H_{14}O_2N_2S_3$: C, 58.52; H, 3.44; N, 6.82; S, 23.43. Found: C, 58.90; H, 3.53; N, 6.58; S, 23.36.

5c: IR (KBr) 1300, 1145, 1090 cm^{-1} (SO_2), 930 cm^{-1} (CSN); MS *m/e* 406 (11, M^+ —S), 269 (100, $\mathbf{3b}^+$). Anal. Calcd for $C_{22}H_{18}O_2N_2S_3$: C, 60.25; H, 4.14; N, 6.39; S, 21.93. Found: C, 60.61; H, 4.05; N. 6.53; S, 21.63.

5d: IR (KBr) 1300, 1145, 1090 cm^{-1} (SO_2), 920 cm^{-1} (CSN); MS *m/e* 392 (10, M^+ —S), 269 (100, $\mathbf{3b}^+$). Anal. Calcd for $C_{21}H_{16}O_2N_2S_3$: C, 59.41; H, 3.80; N, 6.60; S, 22.65. Found: C, 59.69; H, 3.87; N, 6.45; S, 22.53.

5e: IR (KBr) 1305, 1150, 1095 cm^{-1} (SO_2), 930 cm^{-1} (CSN); MS *m/e* 344 (4, M^+ —S), 207 (100, $\mathbf{3c}^+$). Anal. Calcd for $C_{17}H_{16}O_2N_2S_3$: C, 54.26; H, 4.29; N, 7.44; S, 25.56. Found: C, 54.36; H, 4.30; N, 7.40; S. 25.51.

Reaction of 3H-quinazoline-4-thione (**6**) *with chloramine-T* (**4a**). A solution of **4a** in anhydrous methanol (2 ml) and acetone (3 ml) was added to a solution of thione (**6**, 3 mmol) in dry dichloromethane (15 ml) and acetone (10 ml) with stirring at − 15°C. After 1 h, the reaction mixture was kept at room temperature for 15 min, and separated by column chromatography (silica gel, dichloromethane-benzene, and dichloromethane). Thione **6** was first eluted. The second fraction gave **8**, which was washed with ether and recrystallized from benzene–hexane.

8a: IR (KBr) 1530 cm^{-1} (C = NTs); MS *m/e* 389 (9, M^+), 325 (40, M^+ —SO_2), 234 (100, M^+ —Ts); ^{1}H-NMR ($CDCl_3$) δ9.14 (d, J = 8.0 Hz, 1 H), 6.90–7.90 (m, 12 H), 2.32 (s, 3 H), 2.28 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 21.3 (q, CH_3 (Ts)), 24.8 (q, CH_3), 117.6–147.8, 153.1 (s, C-2), 155.6 (s, C-4). Anal. Calcd for $C_{22}H_{19}O_2N_3S$: C, 67.85; H, 4.87; N, 10.79. Found: C, 67.80; H, 4.82; N, 10.77.

8b: IR (KBr) 1540 cm^{-1} (C = NTs); MS *m/e* (1, M^+), 339 (31, M^+ —SO_2), 248 (100, M^+ —Ts); ^{1}H-NMR ($CDCl_3$) δ9.11 (d, J = 8.0 Hz, 1 H), 6.86–7.91 (m, 11 H), 2.44 (s, 3 H), 2.32 (s, 3 H), 2.28 (s, 3 H); ^{13}C-NMR ($CDCl_3$ δ 21.2 (q, CH_3(*p*-Tol)), 21.3 (q, CH_3 (Ts)), 24.8 (q, CH_3), 117.7–141.1, 153.5 (s, C-2), 155.6 (s, C-4). Anal. Calcd for $C_{23}H_{21}N_3O_2S$: C, 68.47; H, 5.25; N, 10.42. Found: C, 68.51; H, 5.30; N, 10.39.

8c IR (KBr) 1545 cm^{-1} (C = NTs); MS *m/e* 387 (29, M^+ —SO_2), 296 (100, M^+ —Ts); ^{1}H-NMR ($CDCl_3$) δ 9.22 (d, J = 8.0 Hz, 1 H), 6.80–7.92 (m, 17 H), 2.30 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 21.3 (q, CH_3(Ts)), 117.9–147.8, 154.3 (s, C-2), 155.8 (s, C-4). Anal. Calcd for $C_{27}H_{21}N_3O_2S$: C, 71.06; H, 4.82; N, 9.56. Found: C, 71.11; H, 4.80; N, 9.55.

8d: IR (KBr) 1525 cm^{-1} (C = NTs); MS *m/e* 465 (1, M^+), 401 (22, M^+ —SO_2), 310 (100, M^+ —Ts); ^{1}H-NMR ($CDCl_3$) δ9.18 (d, J = 8.0 Hz, 1 H), 6.80–7.84 (m, 16 H), 2.28 (s, 3 H), 2.26 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 21.0 (q, CH_3(*p*-Tol)), 21.3 (q, CH_3(Ts)), 117.9–147.7, 154.4 (s, C-2), 155.8 (s, C-4). Anal. Calcd for $C_{28}H_{23}N_3O_2S$: C, 72.24; H, 4.98; N, 9.03. Found: C, 72.33; H, 5.01; N, 9.15.

11e: MS *m/e* 350 (34, M^+), 176 (6, $M^+/2$), 143 (100, $M^+/2$ —S).

11f: MS *m/e* 474 (17, M^+), 238 (27, $M^+/2$), 205 (100, $M^+/2$ —S).

Reaction of thiones (**3, 6**) *with mCPBA*. A solution of mCPBA (85%, 3.1 mmol) in dichloromethane (20 ml) was added dropwise to a solution of thione (3 mmol) in dichloromethane (15 ml) with stirring at − 15°C until most of the thione was consumed. Then, the reaction mixture was washed with chilled aq. $NaHCO_3$ and the organic layer was dried over $MgSO_4$. Evaporation of the solvent and short-column chromatography (silica gel, dichloromethane) of the residue gave sulfine (**12, 13**), which was recrystallized as orange needles from dichloromethane–ether at low temperature.

12a: MS *m/e* 271 (68, M^+), 255 (100, M^+ —O), 223 (69, M^+ —SO). ^{1}H-NMR ($CDCl_3$) δ 7.16–8.08 (m, 9 H); ^{13}C-NMR ($CDCl_3$) δ 156.7 (s, C-2), 186.2 (s, C-4). Anal. Calcd for $C_{14}H_9ONS_2$: C, 61.99; H, 3.34; N, 5.16. Found: C, 62.29; H, 3.34; N, 5.16.

12b: MS *m/e* 285 (100, M^+), 269 (23, M^+ —O), 237 (88, M^+ —SO). ^{1}H-NMR ($CDCl_3$) δ 21.5 (q, CH_3(*p*-Tol)), 156.5 (s, C-2), 186.4 (s, C-4). Anal. Calcd for $C_{15}H_{11}ONS_2$: C, 63.16; H, 3.89; N, 4.91. Found: C, 63.31; H, 3.90; N, 5.00.

13a: MS *m/e* 268 (49, M^+), 252 (82, M^+ —O), 236 (100, M^+ —S); ^{1}H-NMR ($CDCl_3$) δ 9.82 (d, J = 8.0 Hz, 1 H), 7.16–7.72 (m, 8 H), 2.05 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 22.5 (q, CH_3), 151.4 (s, C-2), 187.1 (s, C-4). Anal. Calcd for $C_{15}H_{12}ON_2S$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.11; H, 4.61; N, 10.35.

13b: MS *m/e* 282 (9, M^+), 266 (91, M^+ —O), 250 (100, M^+ —S); ^{1}H-NMR ($CDCl_3$) δ 9.82 (d, J = 8.0 Hz, 1 H), 7.02–7.70 (m, 7 H), 2.43 (s, 3 H), 2.06 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 21.3 (q, CH_3(*p*-Tol)), 22.5 (q, CH_3). 151.7 (s, C-2), 187.3 (s, C-4). Anal. Calcd for $C_{16}H_{14}ON_2S$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.25; H, 5.06; N, 9.90.

13c: MS *m/e* 330 (3, M^+), 312 (32, M^+ —O), 297 (100, M^+ —SH); ^{1}H-NMR ($CDCl_3$) δ 9.92 (d, J = 8.0 Hz, 1 H), 7.02–7.79 (m, 13 H); ^{13}C-NMR ($CDCl_3$) δ 152.8 (s, C-2), 187.7 (s, C-4). Anal. Calcd for $C_{20}H_{14}ON_2S$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.77; H, 4.49; N, 8.41.

13d: MS *m/e* 344 (w, M^+), 328 (26, M^+ —O), 312 (63, M^+ —S); ^{1}H-NMR ($CDCl_3$) δ 9.89 (d, J = 8.0 Hz, 1 H), 6.88–7.72 (m, 12 H), 2.27 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 21.3 (q, CH_3(*p*-tol)), 152.9 (s, C-2), 187.8 (s, C-4). Anal. Calcd for $C_{21}H_{16}ON_2S$: C, 73.24; H, 4.68; N, 8.14. Found: C, 73.50; H, 4.72; N, 8.11.

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REFERENCES AND NOTES

1. Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 1 (1978).
2. For an excellent review, see "The Chemistry of Sulfines," B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **101**, 1 (1982); "New Sulfine Chemistry," E. Block, Org. Sulfur Chem., 9th Int. Sym., 15 (1981), R. Kh. Friedlina and E. Skosova (Eds.), Pergamon Press, **1981**.
3. S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972).
4. E. M. Burgess and H. R. Penton, Jr., *J. Org. Chem.*, **39**, 2885 (1974); *J. Am. Chem. Soc.*, **95**, 279 (1973).
5. S. Holm, J. A. Boerma, N. H. Nilson and A. Senning, *Chem. Ber.*, **109**, 1069 (1976).
6. I. Crossland, *Acta Chem. Scand.*, **B 31**, 890 (1977).
7. A. Tangerman and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **98**, 127 (1979); *idem*, *Tetrahedron Lett.*, 259 (1977).
8. T. Saito and S. Motoki, *J. Org. Chem.*, **42**, 3922 (1977).
9. (a) G.-J. Wentrup and F. Boberg, *Justus Liebigs Ann. Chem.*, 387 (1978); (b) F. Borberg, U. Puttins and G.-J. Wentrup, *ibid.*, 689 (1979).
10. A. Koide, T. Saito, M. Kawasaki and S. Motoki, *Synthesis*, 486 (1981).
11. (a) S. Tamagaki, K. Sasaki and S. Oae, *Bull. Chem. Soc. Jpn.*, **46**, 2608 (1973); *idem*, *ibid.*, **47**, 3084 (1974); *idem*, *ibid.*, **48**, 2983, 2985, 2987 (1975); (b) T. Saito and S. Motoki, *Chem. Lett.*, 591 (1978); *idem*, *J. Org. Chem.*, **44**, 2493 (1979); T. Saito, I. Oikawa and S. Motoki, *Bull. Chem. Soc. Jpn.*, **53**, 1023 (1980); *idem*, *ibid.*, 2582 (1980); T. Saito, T. Musashi and S. Motoki, *ibid.*, **53**, 3377 (1980); (c) M. A. Perez and G. Kresze, *Justus Liebigs Ann. Chem.*, 1050 (1981).
12. Refs. 3, 9, and 10.
13. With aliphatic thiones or unhindered aromatic thiones, chloramine-T gave no stable thione S-imide but its degradation products: M. M. Capbell and D. M. Evgenios, *J. Chem. Soc., Perkin I*, 2866 (1973), and ref. 7.
14. Although geometrical isomerism for **5** may be present,[7] conclusive evidence for its configuration could not be obtained because clear NMR spectra could not be given due to the poor solubility of **5** into a solvent and to the instability in a solution.
15. F. Ogura, H. Yamaguchi, T. Otsubo and H. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 641 (1982).
16. Colorless crystals; mp. 265–268°C; MS *m/e* 362 (94, M^+), 298 (100, M^+ —SO_2), 207 (73, M^+ —Ts).
17. The results are contrast with those reported by Walter *et al.* They found that the oxidation of **6** with H_2O_2 also gave **13**, but only the sulfines having hydrogen at the 3-position (R_2 = H) were isolated. On the basis of these data, they pointed out that this hydrogen atom was a prerequisite for the stabilization by internal hydrogen bonding with the oxygen atom in a CSO moiety.

18. E. Block, R. E. Penn and L. K. Revelle, *J. Am. Chem. Soc.*, **101**, 2200 (1979). We thank a referee for the advice on disulfide formation from sulfines.
19. (a) B. Zwanenburg and J. Strating, *Quart. Rep. Sulf. Chem.*, 79 (1970), and references cited therein; (b) W. Walter, J. Voss and J. Curts, *Justus Liebigs Ann. Chem.*, **695**, 77, 87 (1966); W. Walter and G. Randau, *ibid.*, **681**, 55 (1965); (c) S. Tamagaki, K. Hotta and S. Kozuka, *Chem. Lett.*, 691 (1980); (d) A. Miguel and G. Kresze, *Justus Liebigs Ann. Chem.*, 1510 (1981); (e) H. Behringer and E. Meinetsberger, *Phosphorus and Sulfur*, **12**, 115 (1981); (f) E. Schaumann, H. Behr, G. Adiwijaja, A. Tangerman, B. H. M. Lammerrink and B. Zwanenburg, *Tetrahedron*, **37**, 219 (1981); (g) R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin I*, 2401 (1979); (h) T. J. Adley, A. K. M. Anisuzzman and L. N. Owen, *J. Chem. Soc., (C)*, 807 (1967).
20. B. Zwanenburg, L. Thijs and A. Tangerman, *Tetrahedron*, **27**, 1731 (1971).