Thioaldehyde S-Oxide (Monosubstituted Sulfines) from Thioacylsilane S-Oxides. Synthesis and Fluorine- and Acid-Induced Z/E Isomerization. 2[1]

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Aromatic and aliphatic, not enethiolizable, thioaldehyde S-oxides (monosubstituted sulfines) are obtained from stereospecific fluorodesilylation of the corresponding thioacylsilane S-oxides with retention of configuration. A detailed investigation on the mechanism of the desilylation, as well as of the acid and fluoride ion induced Z/E interconversion has been performed.

Thioketone S-oxides (disubstituted sulfines) are reactive heterocumulenic compounds that are not accessible via a variety of methods.[2a-d] In contrast, little information is available on the less stable thioaldehyde S-oxides (monosubstituted sulfines). Literature refers to the synthesis of alkanethial S-oxide from the reaction of the corresponding sulfinyl chlorides with 1 equiv of triethylamine.[3] This method has not been used much for the monoaryl sulfines, since the corresponding arylmethanesulfinyl chlorides are not easily available. In fact, only the isolation of 2-methoxynaphthalene-1-thiocarbaldehyde S-oxide and the in situ formation of thiobenzaldehyde S-oxide were reported.[4-6] In the last two cases the stereochemical assignment about the C=S double bond was not done.

In connection with our studies on the chemistry of compounds containing the Si-C-S[7a] unit, we designed[7b] a procedure for the synthesis of thioacylsilane S-oxides. A preliminary investigation[1] of their reactivity showed that fluorodesilylation could be used to obtain the corresponding thioaldehyde S-oxides. The present paper deals with the stereochemistry of the fluorodesilylation of some thioacylsilane S-oxides (Scheme I).

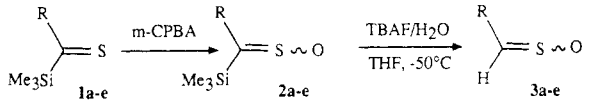
Furthermore, details of the thermal stability of the monosubstituted sulfines, thus obtained, and their acid- or base-induced Z/E interconversion will be presented. These studies provide useful information on their reactivity. For instance, a yet unexplained loss of stereospecificity was observed by us in the Diels-Alder reactions of **3a** and **3b** with 2,3-dimethylbuta-1,3-diene.[1,8] In contrast, the stereochemistry of unsymmetrically disubstituted sulfines is retained in the cycloadducts when they are reacted with dienes.[9]

Results and Discussion

(A) Synthesis and Configurational Assignment of the Thioacylsilane S-Oxides 2a-e. The oxidation of the aromatic thioacylsilanes **1a-d** into the corresponding thioacylsilane S-oxides **2a-d** could be easily performed by controlled oxidation with *m*-chloroperbenzoic acid. By contrast, among the aliphatic ones, only the not-enethiolizable *tert*-butyl trimethylsilyl thioketone **1e** was transformed into the corresponding S-oxide **2e**, whereas the methyl trimethylsilyl thioketone could not be oxidized, due to a concurrent enethiolization[10] (Table I).

All of the thioacylsilanes were available in high purity (>95%) with the exception of the thermally labile compound **1c** (60% pure), where partial oligomerization could not be avoided during its preparation or attempted purification. The oxidation to the S-oxides **2a-c** is stereospecific, since only their *E* isomers were obtained. In fact, the crude isolated material exhibited ^1H and ^{13}C NMR

Scheme I. Synthesis of Thioacylsilane S-Oxides 2a-e by Oxidation of the Corresponding Thioacylsilanes 1a-e with *m*-Chloroperbenzoic Acid and Their Fluorodesilylation to Monosubstituted Sulfines 3a-e



R: a = C_6H_5; b = *p*-Me-C_6H_4; c = *m*-Cl-C_6H_4; d = 2,4,6-Me_3-C_6H_2; e = Me_3C

Table I. Thioacylsilane S-Oxides 2a-e from Oxidation of Thioacylsilanes (1a-e) with *m*-Chloroperbenzoic Acid

entry	R	2 (E:Z)	yields,[a] %	purity,[b] %
a	C_6H_5	(E)	65	E (90)
b	*p*-Me-C_6H_4	(E)	85	E (95)
c	*m*-Cl-C_6H_4	(E)	82[c]	–
d	2,4,6-$Me_3C_6H_2$	(66:33)	92	E[d] (55); Z[e] (45)
e	Me_3C	(60:40)	80	Z (100)

[a] On the crude reaction mixture. [b] After chromatography. [c] 45% purity. [d] As a *E*-**2d**/*Z*-**3d** mixture. [e] As a *Z*-**2d**/*Z*-**3d** mixture.

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Table II. Thioaldehyde *S*-Oxides 3a–e by Fluorodesilylation of Thioacylsilane *S*-Oxides 2a–e

entry	R	reagent *E*:*Z*	product *E*:*Z*	yields,[a] %	purity[b] (*E*:*Z*)
a	C_6H_5	*E*	1:99	75.0	85.0 (1:99)
b	p-Me-C_6H_4	*E*	1:99	85.0	90.0 (1:99)
c	m-Cl-C_6H_4	*E*[c]	1:99	63.0	64.0 (1:99)
d	2,4,6-$Me_3C_6H_2$	*E*[d]	5:95[e]	90.0	95.0 (*Z*)
d	2,4,6-$Me_3C_6H_2$	*Z*[f]	5:95[e]	90.0	95.0 (*Z*)
d	2,4,6-$Me_3C_6H_2$	66:33	5:95[e]	90.0	95.0 (*Z*)
e	Me_3C	*E*	23:77	69.0	-
e	Me_3C	60:40	30:70	44.0	-

[a] On the crude reaction mixture. [b] After chromatography. [c] As a 45% pure. [d] As a *E*-**2d**:*Z*-**3d** = 55:45 mixture. [e] Before the quenching. [f] As a *Z*-**2**:*Z*-**3d** = 50:50 mixture.

Table III. Relevant ^{1}H NMR (C*H*SO) and ^{13}C NMR (*C*HSO) Data in $CDCl_3$ (C_6D_6) of Sulfines 3a–e

entry	^{1}H NMR, δ $CDCl_3$ (C_6D_6)	^{1}H NMR, δ $\delta(CDCl_3) - \delta(C_6D_6)$	^{13}C NMR, δ ($CDCl_3$)
Z-**3a**	8.30 (7.55)	0.75	166.7
E-**3a**	9.65		
Z-**3b**	8.33 (7.39)	0.90	166.7
E-**3b**	9.61 (9.07)	0.54	
Z-**3c**	8.31 (7.25)	1.06	166.4
E-**3c**	9.61		
Z-**3d**	8.58 (7.71)	0.87	169.0
E-**3d**	10.27 (9.75)	0.52	182.0
Z-**3e**	7.65		
E-**3e**	9.14		

spectra typical of a single isomer. On the other hand, a 2:1 and a 1.5:1 *E*/*Z* mixture was found for **2d** and **2e**,[11] respectively. The *E*/*Z* stereochemistry of sulfines was established by means of LIS measurements.[7b,10,12] ASIS studies confirmed the proposed assignments (see the Experimental Section). Flash chromatography on Florisil allowed the purification of compounds *E*-**2a** and *E*-**2b**, which were obtained in a 90–95% purity (Table I). Attempts to purify compound *E*-**2c** failed. Only a small amount of the sulfine was obtained, together with variable mixtures of the protodesilylated derivative *Z*-**3c** and degradation products, such as *m*-chlorobenzaldehyde and stilbenes. Only thick-layer chromatography allowed the separation of the two isomers of **2d**, but both were isolated along with considerable amounts (ca. 50%) of *Z*-**3d**. Attempts to separate *Z*- and *E*-**2e** failed; only the *E* isomer was recovered.

(B) Synthesis of Sulfines 3a–e by TBAF-Induced Desilylation of Thioacylsilane *S*-Oxides 2a–e. The desilylation to compounds **3a–e** was performed with an equimolar amount of tetrabutylammonium fluoride (TBAF) in THF/H_2O at −50 °C. After 15 min the reaction was quenched with water. Overall yields are collected in Table II.

Analysis by ^{1}H NMR spectroscopy (200 MHz) (Table III) of the crude reaction mixtures revealed the presence of two singlets for the C*H*SO protons, attributed to the *Z* and *E* isomers. The major isomer absorbed in the range of 7.65–8.58 ppm ($CDCl_3$), while the minor absorbed at lower field, in the range of 9.15–9.65 ppm (Table III).

We assigned the *Z* stereochemistry to the major isomer on the basis of the deshielding effect exerted by the CSO moiety on their ortho aromatic protons (0.6–0.7 ppm), as it has been found for aromatic unsymmetrically disubstituted sulfines.[13a] Moreover, the CHSO protons of both *E* and *Z* derivatives absorbed very close to values reported for the aliphatic monosubstituted sulfines.[3] A further proof was obtained by ASIS effect[13b] measured on compound **3b**. The CHSO signal of the *Z* derivative was shifted upfield more than that of the *E* (see Table III). The progress of desilylation of sulfines *E*-**2a–c** was monitored at −50 °C by ^{1}H NMR spectroscopy. The reaction was completed in ca. 10 min after the reagents were mixed. The integration gave an *E*/*Z* distribution of 1:99. Both isomers persisted after the workup of the reaction mixtures, their distribution being unaltered with time. This result indicates that the fluorodesilylation of **2a–c** is stereospecific, the retention being the structural relationship between the *Z*-thioaldehyde *S*-oxides and the parent *E*-silylated sulfines. In contrast, loss of stereochemical integrity was found during the desilylation of the mesityl- and *tert*-butylsulfines **2d** and **2e**, respectively. In fact, when a mixture of *E*/*Z*-**2d** = 66:33 was desilylated, the ^{1}H NMR spectrum, recorded before the quenching with water was accomplished, showed the presence of both of the corresponding *E*- and *Z*-sulfines **3d**. The pertinent resonances were present at δ 10.27 and at 8.58 ppm, attributed to the CHSO protons of *E*- and *Z*-**3d**, respectively. Integration gave an *E*/*Z* distribution of 5:95. The sulfine *Z*-**3d** was recovered in 90% yield after quenching of the reaction mixture, while the *E* isomer disappeared very quickly.[14]

E/*Z*-Sulfines **2e** behave similarly. In fact, an *E*/*Z* ca. 1:3 ratio (Table II) was found for the corresponding sulfine **3e**, when either *E*-**2e** or a *E*/*Z*-**2e** = 60:40 mixture was used. Interestingly, this distribution is similar to that observed by Block[3] in the dehydrohalogenation of the sulfinyl chlorides.[15] The spectroscopic features of *E*- and *Z*-**3e** are consistent with the literature data.

(C) Stability and *Z*/*E* Interconversion of Sulfines 3a–e. The monosubstituted sulfines **3a–c** were thermally labile even when left in inert atmosphere. $CDCl_3$ solutions (2–3 mmol) of compounds **3a–c** decomposed in a few days at 25 °C. Phenylsulfine (**3a**) gave *trans*-stilbene as the major product, together with minor amounts of its cis isomer. The ^{1}H NMR spectrum of the crude mixture revealed the presence of other minor resonances, which were attributed to the same compounds found by Trippet.[6] A similar behavior was observed for the sulfine **3b**. On the other hand, the mesitylsulfine *Z*-**3d** was indefinitely stable at room temperature, once isolated; decomposition, leading to the corresponding *trans*-stilbene and traces of its cis

(11) The *E*/*Z* isomer distribution in the crude reaction mixture was found to be not rigorously the same in each experience, variations being of the order of few percent.

(12) Tangerman, A.; Zwanenburg, B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 352. Tangerman, A.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 196.

(13) (a) Zwanenburg, B.; Thijs, L.; Tangerman, A. *Tetrahedron* **1971**, *27*, 1731. (b) Tangerman, A.; Zwanenburg, B. *Tetrahedron* **1973**, *1*, 79.

(14) In an attempt to separate the 2:1 *E*/*Z* mixture of **2d** by thick-layer chromatography (see the Experimental Section) two fractions were obtained, viz. one containing *E*-**2d** admixed with ca. 50% of already desilylated material *Z*-**3d**, and one consisting of *Z*-**2d** containing ca. 50% of *Z*-**3d**. Upon desilylation of both fractions the same *Z*/*E* mixture of **3d** was obtained with the ratio of 95:5.

(15) Actually, the *Z* isomer is the major component of the *E*/*Z* mixture both for aliphatic and aromatic substituted thioaldehyde *S*-oxides. For the alkyl derivatives this preference has been interpreted by a "syn effect"[16a,b] which stabilizes the *Z* configuration through σ and π bonding interactions between the hydrogens of the alkyl group and the oxygen atom. Our results suggest that a similar stabilizing effect is present also in monoaryl sulfines **3a–c**. From a qualitative analysis, this dominance can be due to either the stabilizing attraction between the positively charged ortho-H and the negatively charged oxygen atom, active in this form, or destabilizing *S* lone pair interactions, and destabilizing steric interactions (H, H and H, S) active in the *E* form (D. Cremer, private communication). When the stabilizing effect is counterbalanced by steric ones, the relative amount of the *E* isomer will increase, as has been observed for sulfines **3d** and **3e**.

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Table IV. ^{1}H NMR Data ($CDCl_3$) for the *E*-, *Z*-C*H*SO Protons of Sulfines 3a–e in the Presence of Lewis Acids and *Z* to *E* Maximum Conversion after *t* (min)

Lewis acid (mmol)	reagent (mmol)	*Z*-CHSO, ppm	*E*-CHSO, ppm	*E*:*Z*	*t*, min
TFA (1.34)	**3b**[a] (0.17)	8.53	10.1	1:14	30
TFA (0.78)	*Z*-**3d** (0.11)	9.00	10.7	1:1.3	150
BF_3 (0.12)	*Z*-**3d** (0.12)	8.70	11.0	1:0.6	20
TFA (0.33)	**3e**[b] (0.06)	7.79	9.4	1:0.9	20
TFA (0.53)	**3c** (0.09)	8.52	9.98	1:20	15

[a] As *E*:*Z* = 1:99 mixture. [b] As *E*:*Z* = 20:80 mixture.

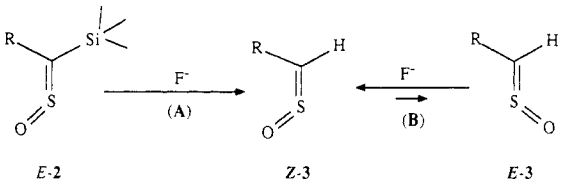
isomer, required higher temperatures (80–100 °C). Thermal induced buildup of *E*-sulfines with respect to the corresponding *Z* isomers, during the decomposition of **3a–d**, was not observed.[17] (*E*)- and (*Z*)-*tert*-butylsulfines **3e** are more labile than the aromatic ones. In fact, a 1:3 *E*/*Z* mixture decomposed completely in few hours. *E*- and *Z*-sulfines **3a–c** and *Z*-**3d** were purified by flash chromatography, the isomer distribution being unaffected during the elution. In contrast, sulfines *E*- and *Z*-**3e** decomposed entirely on a column.

In examining the question of the loss of stereospecificity during the fluorodesilylation of sulfines **2d** and **2e**, we examined whether such partial scrambling arose as a consequence of the formation of an intermediate that can lose its stereochemical integrity, or of isomerization of the products, that of the reagents being not observed in the reaction conditions. The second hypothesis was found correct after we discovered that the addition of an equimolar amount of TBAF to a solution of *Z*-**3d** caused its partial isomerization, the equilibrium being reached at an *E*/*Z* ratio of 5:95 in a few minutes at 25 °C and in ca. 4 h at −50 °C. Remarkably both isomers slowly converted into the corresponding *cis*- and *trans*-stilbenes, in the presence of TBAF, the *E*/*Z* ratio being unchanged with the time. Therefore, the desilylation, with 25% of TBAF, of pure thioacylsilane *S*-oxide *Z*-**2d**, free from its *E* isomer, was followed with time at −50 °C by ^{1}H NMR spectroscopy, in order to establish whether the minor *E*-sulfine **3d** is formed stereoselectively before its isomerization. The desired pure *Z*-**2d** was obtained by a selective decomposition of its *E* isomer, in *E*/*Z* = 60:40 mixture, by means of trifluoroacetic acid (TFA) (see the Experimental Section). The desilylation was complete in ca. 10 min, then both isomers of **3d** were present in a ratio of *E*/*Z* = 55:45. Subsequently, the *E* isomer rapidly converted into the *Z* isomer. The equilibrium ratio of *E*/*Z* = 5:95 was reached in 4 h.

(D) Catalysis by Lewis Acids. Another method of inducing *Z* to *E* interconversion of thioaldehyde *S*-oxides involves the use of Lewis acids.[18] The oxygen of the sulfines, bearing a partial negative charge, can be coordinated by Lewis acids, thus favoring the *Z* to *E* isomerization. As expected, BF_3·Et_2O or TFA shifted the resonance of the C*H*SO proton of both isomers downfield. Furthermore, a synchronous decrease of the CHSO peak of *Z* and an increase of that of *E* was noticed, until the *E*/*Z* ratio reached a maximum.

Table IV shows the variation of the *E*/*Z* distribution of some sulfines after the addition of acid and gives the time required to reach the *E*/*Z* equilibrium. On longer standing at room temperature, both sulfines decomposed to the corresponding aldehyde and sulfur. For example, the

Scheme II. Stereospecific Formation of (*Z*)-Thioaldehyde *S*-Oxides (Path A) from the Fluorodesilylation of (*E*)-Thioacylsilane *S*-Oxides, Followed by Their TBAF-Induced *Z*/*E* Equilibration (Path B)



E/*Z*-**3d** mixture decomposed in 1 week (TFA) or 1 day (BF_3·Et_2O) at 25 °C. After the relative amount of isomer *E* reached its maximum value and the acid was extracted, the ^{1}H NMR spectrum showed the CHSO signals at their original positions. Interestingly, a remarkable lability was observed for the major isomer *E*-**3d**, once the TFA or BF_3 were extracted. Its total decomposition into *trans*- and *cis*-stilbenes in 2 h was observed, no appreciable conversion into *Z*-**3d** was noticed.

Conclusions. The aim of the present investigation was the study of the stereochemistry of the fluorodesilylation of thioacylsilane *S*-oxides. In addition, a detailed investigation on the thermal stability of the reaction products, i.e. the thial *S*-oxides, and on their fluoride ion and Lewis acid induced *Z* to *E* interconversion was carried out. The informations derived from these studies gave insight in the mechanism of the fluorodesilylation. The results showed that the removal of silicon is a stereospecific process, occurring with retention of configuration, and resembles the previously found desilylation at sp^2 or sp^3 carbons[19] (Scheme II). The loss of stereospecificity, observed after the formation of thioaldehyde *S*-oxides, is due to their TBAF-induced equilibration. This has been demonstrated in the case of the sterically hindered sulfine *Z*-**3d**, which does not interconvert at 25 °C. The rate of disappearance of *E*-**3d**, in the presence of TBAF, is slower than its fluoride ion induced formation from *Z*, so that a stationary *E*/*Z* isomer distribution is always present. Removal of fluoride ions inhibit the interconversion process so that *E* disappears very quickly. Finally, the presence of traces of the *E* isomers after chromatography of compounds **3a–c**, or during their decomposition, could be explained through a slow *Z* to *E* isomerization at room temperature even in the absence of TBAF. Such interconversion, associated with the relative instability of the *E* isomers, as experimentally observed for *E*-**3d**, may be responsible for the apparently higher lability of sulfines *Z*-**3a–c** when compared with *Z*-**3d**.

Experimental Section

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 250 grating spectrometer, and absorbances are given in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were determined on a Varian EM 360 and on a Varian CFT-80 spectrometers, unless stated otherwise. Abbreviations used are s (singlet), d (doublet), t (triplet), m (multiplet), b (broad). The experiments of desilylation were performed at −50 °C, and the detection of the isomers *E*-**2a–c** were done with a Varian Gemini-200 spectrometer. Mass spectra were recorded on a Varian MAT 112 S apparatus. Flash chromatography used Merck Kieselgel 60 (230–400 mesh ASTM), while TLC used E. Merck silica gel 60 F 254. Ethyl ether, tet-

(17) Instead, buildup of the *E* isomer with respect to *Z* has been observed by Block during the thermal decomposition of an *E*/*Z* mixture of the propanethioaldehyde *S*-oxide (see ref 3).
(18) Carlsen, L.; Holm, A. *Acta Chem. Scand.* **1976**, *B30*, 277.

(19) See for example: (a) Corriu, R. P. J.; Perz, R.; Reye, C. *Tetrahedron* **1983**, *39*, 999. (b) Corriu, R. P. J.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1988**, *7*, 237. (c) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (d) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P. *J. Chem. Soc., Chem. Commun.* **1988**, 365. (e) Chan, T. H.; Lau, P. W. K.; Lee, M. P. *Tetrahedron Lett.* **1976**, 2667.

rahydrofuran, and HMPA were distilled from $LiAlH_4$, acetonitrile, and CH_2Cl_2 from phosphorus pentoxide and redistilled from powdered Drierite, petroleum ether (bp 40–70 °C), and benzene from sodium. The thioacylsilane S-oxides **2a–e** were synthesized by controlled oxidation with *m*-chloroperbenzoic acid of the corresponding thioacysilanes **1a–e**, which in turn were prepared from the corresponding acylsilanes. The synthesis of thione **1a–b** and **1e** has been already reported.[7b,10]

(3-Chlorothiobenzoyl)trimethylsilane (1c). Into a solution of the corresponding acylsilane[20] (1.0 g, 4.1 mmol) in anhydrous diethyl ether (30 mL) were bubbled hydrogen chloride and hydrogen sulfide at −20 °C. When the solution turned blue, after the disappearance of the starting acylsilane (ca. 90 min), the solution was washed under CO_2 with 5% aqueous sodium hydrogen carbonate. The thioketone was too unstable to allow its isolation and was characterized only by its UV spectrum, λ_{max} (Et_2O) = 690 nm (ϵ = 34.0, yields = 55%). Details on the molar extinction coefficient determination technique are given elsewhere.[7b]

(2,4,6-Trimethylthiobenzoyl)trimethylsilane (1d). The corresponding acylsilane[21] (1.1 g, 5.0 mmol) was thiated with an equimolar amount of Lawesson reagent (toluene, 60 mL) under reflux (150 min). Chromatography of the reaction mixture (Florisil, benzene) gave **1d** (0.80 g, 3.39 mmol, 68%): Blu oil; λ_{max} (Et_2O) = 662 nm (ϵ = 29.0); ^1H NMR ($CDCl_3$) δ 0.23 (s, 9 H, 3 Me), 1.98 (s, 6 H, 2 Me), 2.25 (s, 3 H, Me), 6.80 (s, 2 H); IR (film) 1450, 1250; mass spectrum, *m/e* 236 (M^+), 163. Anal. Calcd for $C_{13}H_{20}SSi$: C, 66.03; H, 8.53; S, 13.56. Found: C, 67.01; H, 8.45; S, 14.04.

Synthesis of Thioacylsilane *S*-Oxides 2a–e: General Procedure. An equimolar solution of *m*-chloroperbenzoic acid in diethyl ether was added at −40 °C to the ethereal solution of the thioketone under argon. After the blue color of the thione faded, the solution was washed with 5% aqueous $NaHCO_3$ and with water and then dried and concentrated under vacuo. ^1H NMR (C_6D_6) inspection of the residue gave the *E*/*Z* relative amount of the corresponding sulfines, when both isomers were present. The oxidation of **1a** into the sulfine ***E*-2a** and of **1e** into a mixture of *E*- and *Z*-**2e** is reported elsewhere[7b,10] together with their configurational assignment.

(*E*)-(4-Methylthiobenzoyl)trimethylsilane *S*-Oxide (*E*-2b). Thione **1b** (1 g, 4.8 mmol) was reacted with an equimolar amount of *m*-chloroperbenzoic acid. The ^1H and ^{13}C NMR spectra of the crude reaction mixture were typical of a single sulfine. Chromatography of the residue on Florisil (petroleum ether–ethyl ether, 9:1) yielded ***E*-2b** (0.59 g, 2.4 mmol, 55%) and ***E*-3b** (0.16 g, 1.1 mmol, 22%): ^1H NMR ($CDCl_3$) δ 0.3 (s, 9 H), 2.37 (s, 3 H), 7.3 (d, 2 H, *m*-H's, *J* = 6.0 Hz), 7.60 (d, 2 H, *o*-H's, *J* = 6.0 Hz); (C_6D_6) δ 0.08 (s, 9 H), 2.07 (s, 3 H), 8.03 (d, 2 H, *m*-H's), 9.47 (d, 2 H, *o*-H's); addition of $Yb(FOD)_3$ (0.015 g) shifted the signal at 7.6 ppm downfield much more than that at 0.3 ppm. The observed shift variations were δ 1.5 and 0.46 ppm, respectively: ^{13}C NMR ($CDCl_3$) δ −0.1 (3 Me), 21.3 (Me), 127.7 (2 CH), 129.4 (2 CH), 131.2 (C), 139.8 (C), 186.9 (CSO); IR (film) 1250, 1195, 1130 (CSO); mass spectrum, *m/e* 224 (M^+), 208, 151.

(*E*)-(3-Chlorothiobenzoyl)trimethylsilane *S*-Oxide (2c). The thione **1c** (55% of purity), obtained from 0.45 g (2.1 mmol) of the corresponding acylsilane was reacted with an equimolar amount (2.3 mmol) of the peroxy acid in ethyl ether (60 mL). ^1H and ^{13}C NMR spectra of the crude reaction mixture (0.55 g) were typical of a single silylated sulfine. From integration of the Me_3Si signal of ***E*-2b**, with respect to the aromatic multiplet, a 45% purity degree was calculated. Chromatography of the residue on Florisil afforded a mixture of ***E*-2c**, ***Z*-3c**, and *m*-chlorobenzaldehyde: ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H), 6.93–7.2 (4 H arom); ^1H NMR (C_6D_6) δ −0.05 (s, 9 H), 7.07–7.6 (m, 4 H, arom); relevant ^{13}C NMR resonance ($CDCl_3$) was at δ 186.6 (CSO of *E*); IR (film) 1255, 1195, 1128; mass spectrum, *m/e* 244 (M^+), 228, 209, 171.

(*E*)- and (*Z*)-(2,4,6-Trimethylthiobenzoyl)trimethylsilane *S*-Oxides (*E*- and *Z*-2d). The thione **1d** (0.72 g, 3.1 mmol) was reacted with an equimolar amount of the peroxy acid in diethyl ether (150 ml) for 60 min. The ^1H NMR analysis of the crude residue (0.80 g, 92%) showed the presence of *E*/*Z*-**2d** exclusively in a 66:33 ratio: ^1H NMR ($CDCl_3$) δ 0.25–0.29 (m, 9 H; Me_3Si of *E* and *Z*), 2.13–2.17 (m, 9 H, 3 Me of *E*), 2.23–2.27 (m, 9 H, 3 Me of *Z*), 6.85–6.9 (b, 2 H, *m*-H's of *E* and *Z*); ^1H NMR (C_6D_6) δ −0.04 (s, 9 H, Me_3Si of *E*), 0.23 (s, 9 H, Me_3Si of *Z*), 1.88–2.00 (m, 9 H, 3 Me of *E* and *Z*), 6.6–6.63 (b, 2 H *m*-H's of *Z*), 6.66–6.7 (b, 2 H, *m*-H's of *E*). The addition of $Yb(FOD)_3$ (0.05 g) shifted the signal of the Me_3Si of *Z* downfield more than that of the corresponding signal of *E*; the observed shift variations were δ 0.85 and 0.33 ppm, respectively. In contrast, the broad methyl signal of isomer *E* shifted downfield more than that of *Z*, the new signals were observed at δ 2.33 and 2.4 (*o*- and *p*-Me of *Z*), 2.7 and 2.77 (*p*- and *o*-Me of *E*) ppm, respectively; ^{13}C NMR ($CDCl_3$) δ −1.32 (Me_3Si of *E*), 0.11 (Me_3Si of *Z*), 20.6 (Me), 20.95 (Me), 21.5 (Me), 127.73 (C), 128.6 (2 CH), 128.8 (2 CH), 129.84 (C), 132.9 (C), 135.5 (C), 137.43 (C), 138.0 (C), 194.0 (CSO of *E*), 205.0 (CSO of *Z*); IR (film) 1255, 1270, 1130 cm^{-1}; mass spectrum, *m/e* 252 (M^+), 236. Anal. Calcd for $C_{13}H_{20}SOSi$: C, 61.87; H, 7.99; S, 12.71. Found: C, 62.35; H, 7.92; S, 13.05. Attempts to separate the isomers by thick-layer chromatography gave the following: 0.35 g (1.4 mmol) of the mixture was divided over six plates. After the elution (Silica, benzene) were obtained three portions. The first and third portion contained *Z*-**2d** and *E*-**2d**, respectively, but were contamined by substantial amounts of sulfine *Z*-**3d**. In the second portion only *Z*-**3d** was present. There was obtained 0.065 g of *E*-**2d**/*Z*-**3d** (55:45) mixture, 0.030 g of *Z*-**2d**/*Z*-**3d** (50:50), and 0.02 g of pure *Z*-**3d**. Even if contamined by *Z*-**3d**, the ^1H NMR spectrum (C_6D_6) of the first and third fraction confirmed the above assignment.

Isolation of Pure Thioacylsilane *S*-Oxide *Z*-2d by Selective Decomposition of the *E* Isomer by Means of TFA. Trifluoroacetic acid (0.57 g, 5.0 mmol) was added to an *E*/*Z* mixture of **2d** (66:34) (0.31 g, 1.25 mmol) in $CDCl_3$ (2.5 mL) under argon and left at room temperature for 8 h. The solution was diluted with CH_2Cl_2 (10 mL), and the organic layer was extracted with water. The solvent was evaporated, and the residue was treated with 5 mL of *n*-pentane at 0 °C. Filtration yielded 0.10 g (0.60 mmol, 48%) of 2,4,6-trimethylbenzoic acid. The filtrate was evaporated, and the oily residue was dissolved in C_6D_6. The ^1H NMR spectrum revealed the presence of sulfine *Z*-**2d** together with traces of 2,4,6-trimethylbenzoic acid.

Synthesis of Sulfines 3a–e: General Procedure. An equimolar amount of TBAF (1.0 M solution in THF/H_2O) was added to a THF solution (10–20 mL) of thioacylsilane *S*-oxide (2–6 mmol) at −50 °C and left under argon at this temperature for ca. 15 min. The crude mixture was then transferred into cold brine and extracted with diethyl ether. The organic layer was dried and concentrated at 0 °C in vacuo. The ^1H NMR inspection of the reaction mixture gave the *E*/*Z* ratio of the corresponding sulfines **3a–e**, when both formed. Flash chromatography (silica, petroleum ether–diethyl ether, 9:1) allowed in some cases (see below) their purification. The monitoring of the desilylation experiments with the 200-MHz NMR spectrometer were performed as follows: the thioacylsilane (0.1 mmol) was dissolved (THF-d_8, 0.6 mL) in a 5-mL NMR tube. The solution was saturated with argon and frozen in liquid nitrogen, and TBAF (30%, 1 M solution in THF) was added. The solution was partially dissolved along the wall of the tube and vigorously shaken. This granted that mixing occurs below the temperature of −50 °C.

(*E*)- and (*Z*)-Phenylmethanethial *S*-Oxides (3a). A 0.60-g portion of crude mixture was obtained from 1.0 g (4.65 mmol) of ***E*-2a**. The ^1H NMR spectrum ($CDCl_3$) revealed the presence of both isomers. Integration gave an *E*/*Z* ratio of ca. 1:99. Flash chromatography (petroleum ether–diethyl ether, 9:1) afforded *E*/*Z*-**3a** in ca. 1:99 ratio (0.48 g, 3.4 mmol, 75.0%): ^1H NMR ($CDCl_3$) δ 7.1–7.6 (m, 3 H, *m*- and *p*-H's), 8.08 (dd, 2 H, *o*-H's), 8.3 (s, 1 H, of C*H*SO of *Z*), 9.65 (s, 1 H, of C*H*SO of *E*). The addition of $Yb(FOD)_3$ (0.02 g) to 0.06 g of sulfine shifted the doublet centered at δ 8.08 ppm more downfield that the singlet at 8.33, the Δ ppm values being 1.47 and 1.12, respectively: ^{13}C NMR ($CDCl_3$) δ 128.9 (2 CH), 129.3 (2 CH), 132.0 (C), 132.9 (C), 166.7 (*C*HSO of *Z*); mass spectrum, *m/e* 138 (M^+), 137; IR (CS_2) 1110; λ_{max} (*n*-hexane) 310 nm (ϵ = 18 881).

(*E*)- and (*Z*)-(4-Methylphenyl)methanethial *S*-Oxides (3b). A 0.80-g sample of crude residue was obtained from 1.12

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g (5 mmol) of *E*-**2b**. The ^1H NMR spectrum ($CDCl_3$) revealed the presence of *E*/*Z*-**3b** in 1:99 ratio. Flash chromatography (silica, petroleum ether–diethyl ether, 9:1) gave 0.55 g (3.6 mmol, 72%, *E*/*Z* = 1:99): ^1H NMR ($CDCl_3$) δ 2.4 (s, 3 H, Me), 7.25 (d, 2 H, *m*-H's), 8.0 (d, 2 H, *o*-H's, *J* = 9.0 Hz), 8.33 (s, 1 H, C*H*SO of *Z*), 9.61 (s, 1 H, C*H*SO of *E*); ^1H NMR (C_6D_6) δ 1.89 (s, 3 H), 6.81 (d, 2 H, *m*-H's), 7.39 (s, 1 H, C*H*SO of *Z*), 7.87 (d, 2 H, *o*-H's), 9.07 (s, 1 H, C*H*SO of *E*); ^{13}C NMR ($CDCl_3$) δ 21.9 (Me), 129.5 (CH), 129.6 (CH), 129.9 (C), 142.6 (C), 166.7 (*C*HSO of *Z*); mass spectrum, *m*/*e* 152 (M^+), 151, 135; IR (film) 1110; λ_{max} (*n*-hexane) 316 nm (ε = 17 958).

(*E*)- and (*Z*)-(3-Chlorophenyl)methanethial *S*-Oxides (3c). A 0.33-g portion of crude residue was obtained from 0.52 g (2.2 mmol) of *Z*-**2c**. Its ^1H NMR spectrum revealed the presence of both *E*- and *Z*-**3c** in a 1:9 ratio. Flash chromatography (diethyl ether–petroleum ether, 1:9) gave a residue (0.25 g) of *E*/*Z*-**3c** (64%, 0.93 mmol, *E*/*Z* = 1:99). Impurities were the corresponding *cis*- and *trans*-*m*-chlorophenylstilbene and *m*-chlorobenzaldehyde: ^1H NMR ($CDCl_3$) δ 7.3–7.6 (m, 2 H), 7.9–8.1 (m, 1 H), 8.1–8.2 (m, 1 H), 8.31 (s, 1 H, C*H*SO of *Z*), 9.6 (s, 1 H, C*H*SO of *E*); ^{13}C NMR relevant resonance ($CDCl_3$) was at δ 166.4 (*C*HSO of *Z*); IR (film) 1195, 1128; mass spectrum, *m*/*e* 172 (M^+), 171, 156, 111.

(*E*)- and (*Z*)-(2,4,6-Trimethylphenyl)methanethial *S*-Oxides (3d). A 0.56-g (3.11-mmol) portion of crude *S*-oxide was obtained from 0.83 g (3.29 mmol) of *E*/*Z*-**2d** = 66:34 mixture. ^1H NMR analysis revealed the presence of *Z*-**3d** only. Flash chromatography (silica, benzene) gave *Z*-**3d** (0.47 g, 2.61 mmol, 79.4%): mp 92–93 °C (from benzene–petroleum ether); ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H, *p*-Me), 2.32 (s, 6 H, 2 *o*-Me), 6.9–6.95 (b, 2 H), 8.58 (s, 1 H of C*H*SO of *Z*); ^1H NMR (C_6D_6) δ 2.0 (s, 3 H, *p*-Me), 2.09 (s, 6 H, 2 *o*-Me), 6.55–6.6 (b, 2 H), 7.71 (s, 1 H of C*H*SO of *Z*); ^{13}C NMR ($CDCl_3$) δ 20.84 (2 Me), 21.0 (Me), 128.77 (2 CH), 129.94 (C), 137.13 (C), 140.46 (C), 168.96 (*C*HSO of *Z*); IR (CS_2) 1155, 1130; λ_{max} (Et_2O) 293 nm (ε = 12 913); mass spectrum, *m*/*e* 180 (M^+), 179. Anal. Calcd for $C_{10}H_{12}SO$: C, 66.63; H, 6.71; S, 17.79. Found: C, 66.57; H, 6.66; S, 17.83. Compound *E*-**3d** was detected in the crude mixture at room temperature before the quenching with water and still in the presence of TBAF, or generated by TBAF induced isomerization of the isomer *Z*-**3d**. The *E*/*Z* ratio which has been found after the desilylation, or after the isomerization reached the equilibrium, depends on the type of solvent and not from the isomer distribution of the thioacylsilanes (see Results and Discussion section). Relevant spectroscopic data of *E*-**3d** were: ^1H NMR ($CDCl_3$) δ 10.2 (9.7 in C_6D_6) (s, 1 H of C*H*SO); ^{13}C NMR ($CDCl_3$) δ 182.0 (CHSO).

Stability of Thioacylsilanes *E*- and *Z*-3d in the Presence of TBAF. A 5:95 mixture of *E*/*Z*-**3d** was generated from desilylation of 0.4 g (1.59 mmol) of an *E*/*Z* = 66:33 mixture of **2d**, in THF (10 mL) at −50 °C. The solution was thermostatted for one week at 30 °C in a pressure tight tube under argon atmosphere. Workup of the reaction mixture and chromatography (silica, benzene–petroleum ether, 1:3) yielded in order: **(*E*)-2,2′,4,4′,6,6′-hexamethylstilbene** (0.3 g, 1.14 mmol, 71.4%): oil; ^1H NMR ($CDCl_3$) δ 1.95 (s, 12 H, 4 *o*-Me), 2.2 (s, 6 H, 2 *p*-Me), 6.67 (s, 2 H), 6.8 (s, 4 *m*-H's); mass spectrum, *m*/*e* 264 (M^+), 249; IR (CCl_4) 3050, 2980, 2860. Anal. Calcd for $C_{20}H_{24}$: C, 90.88; H, 9.15. Found: C, 91.35; H, 9.01; **(*Z*)-2,2′,4,4′,6,6′-hexamethylstilbene** (0.07 g, 0.26 mmol, 16%): mp 113–117 °C (from benzene–*n*-pentane); ^1H NMR ($CDCl_3$) δ 2.3 (s, 6 H, 2 *p*-Me), 2.4 (s, 12 H, 4 *o*-Me), 6.55 (s, 2 H), 6.95 (s, 4 *m*-H's); mass spectrum, *m*/*e* 264 (M^+), 249; IR (CCl_4) 3050, 2980, 2860.

(*E*)- and (*Z*)-2,2-Dimethylpropanethial *S*-Oxides (3e). In one experiment 0.05 g (0.42 mmol, 69.0%) of *E*/*Z*-**3e** = 23:77 was obtained from *E*-**2e** (0.12 g, 0.61 mmol). In another experiment an *E*/*Z* = 60:40 mixture of **2e** (0.11 g, 1.0 mmol) gave 0.053 g (0.45 mmol, 44%) of *E*/*Z* = 30:70. Spectroscopic data for compounds *E*- and *Z*-**3e** were fully consistent with that reported in literature.

TFA and BF_3·Et_2O-Induced *Z* to *E* Isomerization of Thioaldehyde *S*-Oxides 3b, 3d, 3e. General Procedure. The solutions of sulfines **3b**, **3d**, and **3e** (0.1–0.5 mmol) were dissolved in $CDCl_3$ in a pressure-tight NMR tube. The solutions were saturated with argon and cooled at 0 °C. TFA or BF_3·Et_2O was added under argon atmosphere, and the tube was closed. The *Z*/*E* equilibration and the subsequent decomposition of the two sulfines into sulfur and the corresponding aldehyde were followed at intervals by ^1H NMR spectroscopy at 25 °C. Selected examples are given below:

(a) Reaction of *Z*-3d and TFA. Sulfine *Z*-**3d** (0.02 g, 0.11 mmol) was reacted with TFA (0.06 mL, 0.78 mmol, TFA/*Z*-**3d** = 7.0). Selected absorbances were at δ 9.00 (C*H*SO of *Z*), 10.7 (C*H*SO of *E*), and 10.5 ppm (CHO). After 150 min isomer *E* reached its maximum (*E*/*Z* = 0.78). The ^{13}C NMR ($CDCl_3$) spectrum showed resonances at δ 173.7 (*C*HSO of *Z*), 188.6 (*C*HSO of *E*), 197.2 (*C*HO). The decomposition of the two sulfines after they reached the equilibrium was followed with the time at room temperature. The two isomers disappeared with the same rate in ca. 15 days, mesitylaldehyde being the major product.

(b) Reaction of 3b with TFA. Compound **3b** (0.026 g, 0.17 mmol, *E*/*Z* = 1:99) was reacted with TFA (0.10 mL, 1.34 mmol, TFA/**3b** = 7.7) in $CDCl_3$ (0.5 mL). Selected ^1H NMR absorptions were observed at δ 8.53 (*Z*-C*H*SO), 10.13 (*E*-C*H*SO), 9.9 (C*H*O). After 25 min the ^1H NMR spectrum gave a *E*-**3d**/*Z*-**3d** ratio of 7:93. Decomposition of the two sulfines occurred in ca. 1 day, *p*-tolylaldehyde being the major product.

Stability of the Sulfine *E*-3d. Sulfine *Z*-**3d** (0.02 g, 0.1 mmol) was isomerized with an equimolar amount of BF_3·Et_2O in $CDCl_3$ (0.6 mL). After 4 min the isomer ratio reached the equilibrium (*E*/*Z* = 1.67). The acid was extracted with few milliliters of 5% aqueous solution of $NaHCO_3$. The organic layer was quickly dried by repeated filtration through a pipette containing cotton and Na_2SO_4. The first spectrum was scanned after 10 min quenching. Isomer *E* disappeared totally in 5 h. ^1H NMR spectroscopy of the crude product revealed traces of mesitylaldehyde, *trans*- and *cis*-stilbenes, and unreacted *Z*-**3d**.

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