Synthesis, Structure, and Reactions of the First Rotational Isomers of Stable Thiobenzaldehydes, 2,4,6-Tris[bis(trimethylsilyl)methyl]thiobenzaldehydes

Nobuhiro Takeda, Norihiro Tokitoh, and Renji Okazaki*

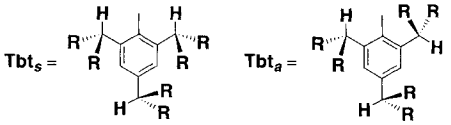
Abstract: The first rotational isomers of thiobenzaldehydes, TbtCH=S (**2a** and **2b**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), were synthesized and isolated as stable crystalline compounds by the desulfurization of the corresponding overcrowded cyclic polysulfides $TbtCHS_n$ (n = 5 or 8) with phosphine reagents. The molecular structures of **2a** and **2b** in the solid state, determined by X-ray crystallographic analysis, differed in their conformations, which were essentially identical with those in solution as revealed by $^1H\{^1H\}$ nuclear Overhauser effect (NOE) experiments. The isomeric thiobenzaldehydes **2a** and **2b** were found to undergo thermal interconversion. A kinetic study of this process gave reasonable kinetic and thermodynamic parameters for conformational isomerizations of this type. Interesting differences in reactivity among the two isomers **2a**,**b** and 2,4,6-tri-*tert*-butylthiobenzaldehyde (**1**) were shown in the reactions with hydrazine and *m*-chloroperoxybenzoic acid.

Keywords
competition experiments · conformation determination · isomerizations · rotamers · thioaldehydes

Introduction

Thiocarbonyl compounds are reactive sulfur analogues of carbonyl compounds and play a very important role in organic chemistry. The chemistry of thiocarbonyl compounds has been well established only in relatively recent years, because of the instability associated with the low π-bond energy.[1] Thioaldehydes are highly reactive and unstable species, because the hydrogen atom at the sp^2 carbon is neither electronically stabilizing nor sterically bulky, and they usually undergo rapid oligomerization or polymerization.[2] For example, thiobenzaldehyde is reported to be stable at 77 K, but decomposes giving polymers at 110 K.[3] Even thiopivaldehyde, bearing a bulky *tert*-butyl group, cannot be isolated because of its high tendency to polymerize, although it is relatively stable in solution.[4] Transient thioaldehydes have been studied extensively,[5] and various thioaldehydes have been isolated, stabilized by mesomeric effects due to heteroatoms such as nitrogen, oxygen, and sulfur[6] or by coordination to transition metals.[7] Since our first successful isolation of kinetically stabilized thioaldehyde, 2,4,6-tri-*tert*-butylthiobenzaldehyde (**1**),[8] the syntheses[9] and reactions[10] of some electronically unperturbed stable thioaldehydes have been reported. However, in contrast to the chemistry of thioketones, which has been studied by taking advantage of kinetic stabilization, the intrinsic nature of the unique thioaldehyde functional group has not been fully disclosed because of the limited examples of stable thioaldehydes.

We have recently succeeded in synthesizing novel metalanethiones containing Group 14 metals, such as Tbt(Tip)M=S (M = Si, Ge, Sn; Tip = 2,4,6-triisopropylphenyl, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),[11] through a desulfurization of the cyclic tetrasulfides, $Tbt(Tip)MS_4$,[12] taking advantage of the efficient steric protecting group Tbt.[13] We became interested in the synthesis of thiobenzaldehydes incorporating the Tbt group, and recently reported, in a preliminary form, the first isolation of rotational isomers of stable thiobenzaldehydes TbtCHS, **2a** and **2b**.[14] As shown in Scheme 1, the two *o*-



Scheme 1. R = $SiMe_3$.

bis(trimethylsilyl)methyl (disyl) groups of thiobenzaldehyde **2a** are symmetric with regard to the thioformyl group (denoted as Tbt_s in this paper), whereas those of its rotamer **2b** are asymmetric (denoted as Tbt_a in this paper).

The early studies on rotational isomerism in substituted benzenes due to hindered rotation about a bond between sp^2 (benzene) and sp^3 (substituent) carbon atoms were mainly conducted on methoxyphenyl(*tert*-butyl)methanol (Ar(*t*Bu)RCOH) by dynamic NMR spectroscopy.[15] Lomas et al. reported the isolation of two rotamers of *o*-tolyldi(*tert*-butyl)methanol and relat-

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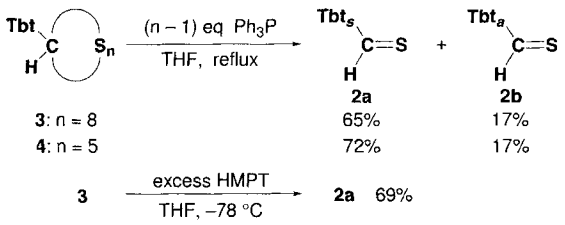
ed compounds with very high rotational barriers.[16] Crystallographic studies[17] and calculations[16b] show that the hydroxyl group of the $CR^1R^2(OH)$ group lies close to the plane of the benzene ring. The stereochemistry of systems bearing vicinal isopropyl or dichloromethyl groups (CHR_2; R = CH_3, Cl) attached to a benzene ring, such as hexaisopropylbenzene, has been studied by NMR spectroscopy, crystallographic analysis, and calculations.[18] The vicinal CHR_2 groups tend to assume a gear-meshed conformation, in which a methine hydrogen tooth is tucked into the notch created by the R groups of a neighboring CHR_2 group. A variety of studies on the reactivities of rotamers have revealed that there are substantial differences in the reactivities of some rotational isomers.[19]

In this paper we give a detailed account of the synthesis and structure of the thiobenzaldehydes **2a** and **2b** and of the differences in reactivities observed for these two rotational isomers and for another stable thiobenzaldehyde, 2,4,6-tri-*tert*-butylthiobenzaldehyde (**1**).

Results and Discussion

Recently, we reported the synthesis of Tbt-substituted cyclic polysulfides, $TbtCHS_8$ (**3**) and $TbtCHS_5$ (**4**).[20] As in the case of the synthesis of metalanethiones, Tbt(Tip)M=S (M = Si, Ge, Sn),[11] we chose the desulfurization of cyclic polysulfides as a synthetic approach to thiobenzaldehydes.

Synthesis of Thiobenzaldehydes 2a and 2b: When Tbt-substituted octathionane **3** was treated with 7 equiv of triphenylphosphine in refluxing THF (Scheme 2), the reaction solution turned



Scheme 2. Synthesis of stable thioaldehydes **2a** and **2b**.

blue. The mixture was separated by flash column chromatography on silica gel at −20 °C under a nitrogen atmosphere to give two isomeric thiobenzaldehydes, Tbt_sCHS (**2a**) (purple crystals) and Tbt_aCHS (**2b**) (green crystals), in 65 and 17% yields, respectively, resulting from the very high rotational barriers of the *o*-disyl groups. Both isomers were found to be quite stable in the solid state, even when exposed to air. Thiobenzaldehyde **2b** is stable at −10 °C for several days in an ether solution left open to air and is thus more stable than **2a**. The desulfurization of cyclic polysulfides by phosphorus reagents described above is a novel synthetic approach to thiocarbonyl compounds.

Pentathiane **4** was also desulfurized with 4 equiv of triphenylphosphine under similar reaction and separation conditions to afford **2a** and **2b** in almost the same yields as obtained from **3** (Scheme 2). Treatment of **3** with an excess of hexamethyl phosphorous triamide (ca. 15 equiv) in THF at −78 °C afforded only **2a** (69%) as a desulfurized product. According to its X-ray structural analysis, **3** contains Tbt_s,[20] and the formation of **2b** in the reactions with triphenylphosphine can therefore be interpreted in terms of the thermal isomerization of **2a** under the reaction conditions (i.e., in refluxing THF).

Crystal Structures of Thiobenzaldehydes 2a and 2b: Both **2a** and **2b** showed satisfactory spectral and analytical data characteristic of thiobenzaldehydes (Table 1), and X-ray crystallographic analyses gave definitive confirmation of their molecular geometries in the solid state (Figures 1 and 2). In **2a** the methine

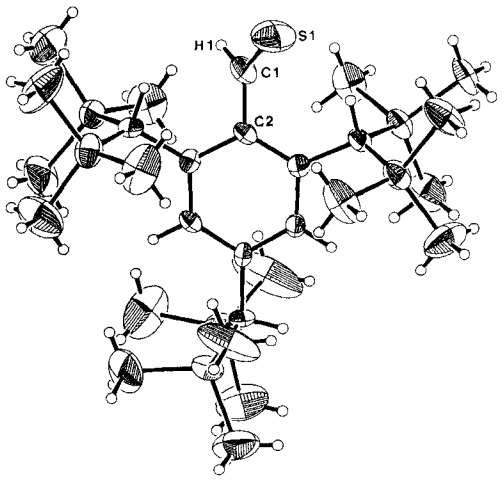


Fig. 1. ORTEP drawing of Tbt_sCHS (**2a**) (thermal ellipsoids at the 30% probability level for non-hydrogen atoms). Selected bond lengths (Å) and angles (°): C1–S1 1.588(11), C1–C2 1.469(13), C1–H1 0.946(11), S1-C1-C2 131.5(9), C2-C1-H1 114(1), S1-C1-H1 114(1).

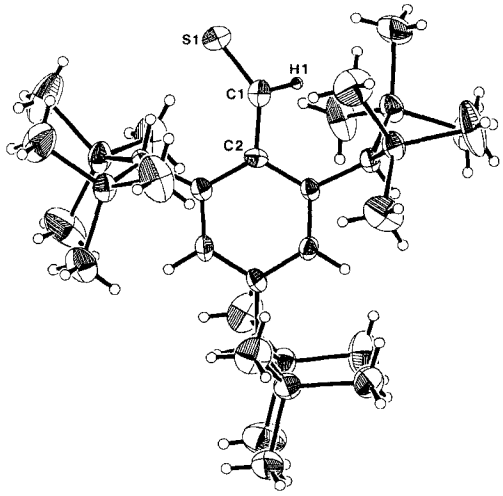


Fig. 2. ORTEP drawing of Tbt_aCHS **2b** with thermal ellipsoid plot (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (°): C1–S1 1.602(7), C1–C2 1.433(8), C1–H1 0.89(5), S1-C1-C2 137.6(6), C2-C1-H1 110(4), S1-C1-H1 112(4).

hydrogens of *o*-disyl groups both point towards the thioformyl group, and the dihedral angle between the CH=S π plane and benzene ring is 48.7°. In contrast, the *o*-disyl groups of **2b** are unsymmetrically oriented relative to the thioformyl group, and the CH=S π plane is almost coplanar with the benzene ring (dihedral angle is 10.6°); this suggests that some conjugation is

occurring between the two π systems. The X-ray crystallographic analysis of **1** has shown that the dihedral angle between the CH=S π plane and the benzene ring is 89.8°, which indicates essentially no conjugation between the two π systems.[10g] The differences in the C1–C2 bond lengths [1.469(13) Å for **2a**, 1.433(8) Å for **2b**, and 1.499(4) Å for **1**[10g]] can be interpreted in terms of conjugation between the π systems, which gives some double bond character to the C1–C2 bond. As shown in Figure 2, the thioformyl hydrogen of **2b** lies between the two trimethylsilyl groups of the *o*-disyl group that is rotated relative to that in Tbt_s, and the sulfur atom of the thioformyl group is directed toward the methine hydrogen of the other *o*-disyl group, probably to avoid steric repulsion with the two trimethylsilyl groups of the former *o*-disyl group. The thioformyl groups of **2a** and **2b** were found to have completely trigonal planar geometries and short C–S bond lengths [1.588(11) Å for **2a** and 1.602(7) Å for **2b**], which are in good agreement with the calculated C–S bond length for $H_2C{=}S$ (1.599 Å)[21] and the C–S bond length for **1** (1.602(5) Å).[10g]

Structure of Thiobenzaldehydes 2a and 2b in Solution: The ^1H and ^{13}C NMR spectra of **2a** and **2b** show signals at low field corresponding to the thioformyl group, and the UV/Vis spectra of **2a** and **2b** exhibit absorption maxima at longer wavelength, identified as n–π* transitions (Table 1). Comparing the spectral

Table 1. Spectral data and dihedral angles (ω) of thiobenzaldehydes **2a**, **2b**, and **1**.

	^1H NMR/δ		^{13}C NMR/δ	UV/Vis/nm	$^1J_{CH}$/Hz	ω/° [a]	
	o-methine	*H*–C=S	H–*C*=S	n–π*	*H*–*C*=S		
2a	2.97	3.25	12.05	234.1	587	162.4	48.7
2b	1.72	5.54	11.77	229.8	604	156.9	10.6
1			13.02	250.4	564	171.8	89.4

[a] Dihedral angle between the CH=S π plane and the benzene ring observed by X-ray crystallographic analysis.

data of thiobenzaldehydes **1**, **2a**, and **2b**, we see that the thioformyl signals in the ^1H and ^{13}C NMR spectra shift to higher fields, in the order **1** → **2a** → **2b**; the coupling constants between the thioformyl ^1H and ^{13}C atoms, ^1J(CH), become smaller, and λ_{max} for the n–π* transition in the UV/Vis spectra are red-shifted. These comparisons suggest that the conjugation between the thioformyl group and the benzene ring increases in the order **1** < **2a** < **2b**, in solution as well as in the solid state. It is noteworthy that the methine proton in one *o*-disyl group of **2b** resonates at a much lower field (δ = 5.54) than the other (δ = 1.72). This can be explained in terms of the strong anisotropic effect of the C=S double bond, which is directed toward the low-field methine hydrogen, as was observed in the solid state.

It is known that the C–R^1 bond in a C$R^1R^2R^3$ group attached to a benzene ring, where R^1 is the smallest substituent, tends to lie close to the plane of the ring. MMP2 calculations and dynamic NMR studies show that TbtBr is also most stable in the conformation where the methine hydrogens of all the disyl groups lie close to the plane of the benzene ring.[13b] Therefore, we determined the conformations of **2a** and **2b** by difference $^1H\{^1H\}$ NOE experiments (Figure 3) by assuming the methine hydrogens of the disyl groups in **2a** and **2b** to be in the plane of the benzene ring.

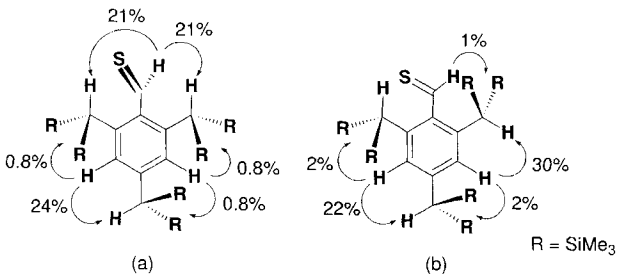


Fig. 3. Schematic representation of the observed NOEs: a) **2a** (270 MHz, C_6D_6, 20.0 °C) and b) **2b** (270 MHz, $CDCl_3$, 20.0 °C) (R = $SiMe_3$).

When the aromatic proton at δ = 6.68 of **2a** was irradiated, the other aromatic proton at δ = 6.56 was also irradiated, probably because the rotation of the *p*-disyl group was faster than the timescale of the NOE experiment; the NOEs were observed at the methyl protons of trimethylsilyl groups (δ = 0.11, 0.14) and the methine proton of the *p*-disyl group (δ = 1.52). Irradiation of the thioformyl proton (δ = 12.41) of **2a** resulted in enhancement at the methine protons of the *o*-disyl groups (δ = 3.10, 3.42). These difference NOEs observed for **2a** strongly suggest that the molecular structure in solution is essentially identical with that in the solid state (i.e., Tbt_s form), although the thioformyl group is considered to rotate freely, like the *p*-disyl group.

Irradiation of the aromatic protons (δ = 6.40) in **2b** (Figure 3) caused NOEs at the methine protons of the *p*-disyl group (δ = 1.46) and of one of the *o*-disyl groups (δ = 1.72), and at the methyl protons of *p*- and *o*-trimethylsilyl groups (δ = − 0.01, 0.07). Irradiation of the thioformyl proton (δ = 11.77) only resulted in enhancement at the methyl protons of *o*-trimethylsilyl groups (δ = 0.05). The observed difference NOEs for **2b** and the absence of enhancement between the thioformyl proton and the methine protons of the *o*-disyl groups in **2b** strongly suggest that, in solution as well as in the solid state, the Tbt group in **2b** is Tbt_a and the sulfur atom of the thioformyl group points toward the methine proton of the *o*-disyl group in the most stable conformation.

In the difference NOE experiments at −60 °C for **2a**, enhancement was observed between the thioformyl proton and the two methine protons of the *o*-disyl groups, and the two aromatic protons could be distinguished by irradiation; this suggests that there is restricted rotation of the *p*-disyl group on the timescale of NOE experiments, although definite NOEs between the aromatic protons and the methine proton of the *p*-disyl group were not observed. These results indicate that there is free rotation of the thioformyl group in **2a** even at −60 °C.

Thermolysis, Photolysis, and Oxidation with Molecular Oxygen of Thiobenzaldehyde 2a: Heating of **2a** at 165 °C for 4 h caused no decomposition although the equilibrium with **2b** was observed by ^1H NMR spectroscopy. Additional heating at 170–180 °C for 42 h resulted in a complex mixture containing benzothiirane **5** (17%) (Scheme 3). Photolysis of **2a** gave **5** in good yield (72%). A similar intramolecular cyclization has been reported in the thermolysis and photolysis of **1**.[10b] The formation of **5** can most likely be explained in terms of a radical mechanism, as in the reactions of **1**.[10b]

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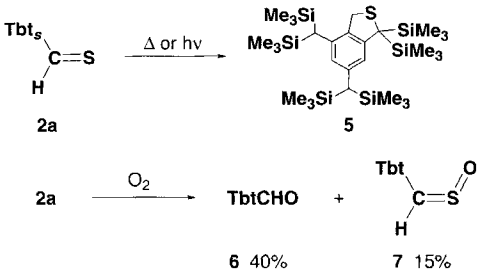
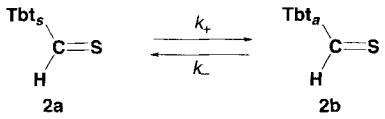


Scheme 3. Thermolysis, photolysis, and oxidation of **2a**.

Thiobenzaldehyde **2a** is fairly stable toward oxygen; no reaction was observed by thin-layer chromatography even after oxygen had been bubbled into an *n*-hexane solution of **2a** at 0 °C for 1 h. Additional bubbling at room temperature for 26 h, however, led to the production of benzaldehyde **6** (40%) and (*Z*)-sulfine **7** (15%).[22] It has been reported that the reaction of thiobenzophenone with oxygen gives the corresponding ketone and sulfine.[24]

Kinetic Studies of Thermal Isomerization: As described above, thermal interconversion between **2a** and **2b** was observed by ^{1}H NMR spectroscopy. Measurements of the rate and equilibrium constants for isomerization (**2a**⇌**2b**, Scheme 4) at several temperatures led to the kinetic and thermodynamic parameters shown in Tables 2 and 3. The value of $\Delta H^{\neq}$ is large enough for



Scheme 4.

Table 2. Rate and equilibrium constants, and kinetic parameters [a] for **2a**⇌**2b**.

T/°C	$k_+ \times 10^5$/s^{-1}	K(**2b**/**2a**)
50.0	2.53±0.03	0.271
60.0	6.7±0.3	0.275
70.0	16.6±0.4	0.276
75.0	31±1	0.274
80.0	47.5±0.5	0.278

[a] $\Delta H^{\neq} = 21.5 \pm 0.4$ kcal mol^{-1}; $\Delta S^{\neq} = -13 \pm 1$ cal mol^{-1} K^{-1}.

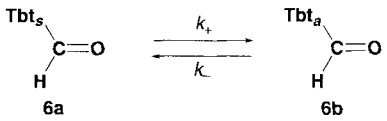
Table 3. Equilibrium constants and thermodynamic parameters [a] for **2a**⇌**2b**.

T/°C	K(**2b**/**2a**)
50.0	0.271
80.0	0.278
110.0	0.286
140.0	0.298

[a] $\Delta H^{\circ} = 0.27 \pm 0.02$ kcal mol^{-1}; $\Delta S^{\circ} = -1.77 \pm 0.07$ cal mol^{-1} K^{-1}.

the two isomers to be isolated as stable and discrete thiobenzaldehydes, and the ΔH° value indicates that **2a** is thermodynamically more stable than **2b**, as a result of the less severe steric congestion around the thioformyl group of **2a**.

When benzaldehyde **6a** bearing Tbt$_s$ group was heated in *n*-hexane at reflux for 3 h, the ^{1}H NMR spectrum showed a signal ($\delta = 10.13$) due to a formyl proton other than that of **6a** ($\delta = 10.38$) in a ratio of 1 ($\delta = 10.13$):5 ($\delta = 10.38$). As in the case of thiobenzaldehyde **2b**, the methine proton of one *o*-disyl group was observed at a lower field ($\delta = 3.95$) than that of the other ($\delta = 1.67$), probably owing to the anisotropic effect of the formyl group. This ^{1}H NMR spectrum suggests the formation of an isomeric benzaldehyde **6b** having Tbt$_a$ group (Scheme 5), although pure **6b** was not isolated, owing to difficulties encountered in separating it from **6a**.



Scheme 5.

Kinetic and thermodynamic parameters for isomerization (**6a** → **6b**) were also obtained as in the case of thiobenzaldehyde **2** (Tables 4 and 5). The kinetic parameters for benzaldehyde **6** were almost the same as those for thiobenzaldehyde **2**; this indicates that both isomerizations follow the same mechanism, namely, the rotation of *o*-disyl groups.

Table 4. Rate and equilibrium constants, and kinetic parameters [a] for **6a**⇌**6b**.

T/°C	$k_+ \times 10^5$/s^{-1}	K(**6b**/**6a**)
45.0	2.18±0.05	0.130
50.0	3.9±0.2	0.140
55.0	6.4±0.1	0.135
60.0	10.5±0.3	0.140

[a] $\Delta H^{\neq} = 21.2 \pm 0.4$ kcal mol^{-1}. $\Delta S^{\neq} = -13 \pm 1$ cal mol^{-1} K^{-1}.

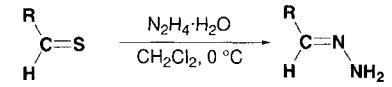
Table 5. Equilibrium constants and thermodynamic parameters [a] for **6a**⇌**6b**.

T/°C	K(**6b**/**6a**)
50.0	0.140
80.0	0.156
110.0	0.177
140.0	0.193

[a] $\Delta H^{\circ} = 0.96 \pm 0.03$ kcal mol^{-1}. $\Delta S^{\circ} = -0.94 \pm 0.08$ cal mol^{-1} K^{-1}.

Competitive Reactions of Thiobenzaldehydes 2a, 2b, and 1: As described above, the structures of thiobenzaldehydes **2a** and **2b** differ mainly in the degree of congestion around the thioformyl group and in the dihedral angle between the CH=S π plane and the benzene ring. Since the dihedral angle should reflect the degree of conjugation between the thioformyl group and the benzene ring, the reactivities of the two rotamers are expected to differ. This was investigated by performing competitive reactions for **2a** and **2b**, and another stable thiobenzaldehyde **1**.

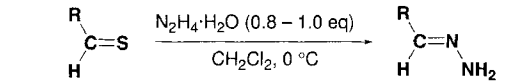
Thiobenzaldehydes **2a**, **2b**, and **1** each reacted with hydrazine monohydrate in dichloromethane at 0 °C to afford the corresponding hydrazones **8a**, **8b**, and **9**, respectively, in almost quantitative yields (Scheme 6).



2a R = Tbt_s	**8a** 96%
2b R = Tbt_a	**8b** 93%
1 R = Mes*	**9** 97%

Scheme 6. Reactions of **2a**, **2b**, and **1** with hydrazine.

Competitive reaction of **2a** and **2b** (1:1 mixture) with ca. 0.8 equiv of hydrazine monohydrate at 0 °C gave only **8a**, resulting from reaction of **2a**, with complete recovery of **2b** (Scheme 7). Competitive reaction of **2b** and **1** (1:1 mixture) with

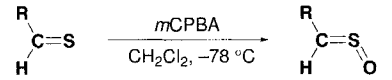


2a + **2b** + **1**			**8a** + **8b** + **1**		
R=Tbt_s	R=Tbt_a	R=Mes*	R=Tbt_s	R=Tbt_a	R=Mes*
1 eq	1 eq	—	100%	0%	—
—	1 eq	1 eq	—	80%	20%

Scheme 7. Competitive reactions of **2a**/**2b** and **2b**/**1** with hydrazine (Mes* = 2,4,6-tri-*tert*-butylphenyl).

the same reagent at 0 °C afforded the corresponding hydrazones **8b** and **9** in a ratio of 4:1. These results show that the reactivity of the thiobenzaldehydes toward hydrazine monohydrate increases in the order **1** < **2b** < **2a**, which probably reflects the degree of congestion around the carbon atom of the thioformyl group.

Treatment of thiobenzaldehydes **2a** and **2b** with *m*-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane at −78 °C resulted in the rapid formation of the corresponding (*E*)-sulfines **10a**[22] and **10b**,[25] respectively, in almost quantitative yields (Scheme 8). Since (*Z*)-sulfines are known to be thermodynami-

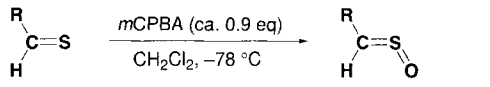


2a R=Tbt_s	**10a** 88%
2b R=Tbt_a	**10b** 89%

Scheme 8. Oxidations of **2a** and **2b** with *m*CPBA.

cally more stable than (*E*)-sulfines,[26] the formation of (*E*)-sulfines **10a** and **10b** can be interpreted in terms of a kinetically controlled process, that is, *m*CPBA attacks at the less hindered side of the sulfur atom of the thioformyl group. It has been reported that the reaction of **1** with *m*CPBA gives the corresponding sulfine **11** almost quantitatively.[10h]

Competitive reaction of **2a** and **2b** (1:1 mixture) with ca. 0.8 equiv of *m*CPBA at −78 °C resulted in the production of the corresponding sulfines **10a** and **10b** in a ratio of 1:4 (Scheme 9). Competitive reaction of **2a** and **1** (1:1 mixture) with the same reagent at −78 °C gave only **10a**, formed from **2a**, with complete recovery of **1**. These results show that the reactivity of these thiobenzaldehydes toward *m*CPBA, which attacks the sulfur atom of the thioformyl group electrophilically, increases in the order **1** < **2a** < **2b**. The lower reactivity of **1** is probably due to the higher steric congestion around the thioformyl group in



2a + **2b** + **1**			**10a** + **10b** + **11**		
R=Tbt_s	R=Tbt_a	R=Mes*	R=Tbt_s	R=Tbt_a	R=Mes*
1 eq	1 eq	—	20%	80%	—
1 eq	—	1 eq	100%	—	0%

Scheme 9. Competitive reactions of **2a**/**2b** and **2a**/**1** with *m*CPBA

1. The higher reactivity of **2b** than **2a** contrasts with its lower reactivity towards hydrazine monohydrate, and is presumably due to the higher electron density at the sulfur atom of **2b**, as a result of the conjugation of the thioformyl group with the benzene ring bearing disyl substituents, which are known as highly electron-donating groups.[27]

Conclusion

We have succeeded in the isolation and structural determinations of two rotational isomers of thiobenzaldehydes, Tbt_sCHS (**2a**) and Tbt_aCHS (**2b**). These rotational isomers undergo interesting interconversions, which were studied kinetically. The analogous rotamers having Tbt_s and Tbt_a groups were also characterized for the corresponding benzaldehyde, hydrazone, and sulfine (i.e., TbtCH=X; X = O, NNH_2, and SO, respectively). Almost all other compounds containing the Tbt group (e.g., TbtBr,[13b, 28] Tbt(Tip)M=Y,[11] and Tbt(Tip)MY_4; M = Si, Ge, Sn; Y = S, Se)[12] exist in the Tbt_s conformation, as deduced from X-ray diffraction analysis or NMR spectroscopy. Compounds with Tbt_a groups had not previously been obtained, except in the case of TbtH, which adopts the Tbt_a conformation at −54 °C (observed by ^{1}H NMR spectroscopy).[13b] These results suggest that the rotamer of Tbt_a conformation can only exist when the Tbt group is attached to a group as small as hydrogen or to an sp^2 carbon bearing a hydrogen atom. The comparison of the reactivities of the thiobenzaldehydes **1**, **2a**, and **2b** revealed that **2a** and **2b** are more reactive than **1** and that the rotational isomers **2a** and **2b** show interesting differences in reactivity. It is noteworthy that Tbt-substituted thioaldehydes still have a high reactivity toward nucleophilic and electrophilic reagents, such as hydrazine monohydrate and *m*CPBA, in spite of the severe steric congestion, which prevents them from dimerizing. The differences in reactivities between the rotamers are probably caused by differences in the degree of congestion around the thioformyl group and of conjugation between the thioformyl group and the benzene ring. Similar rotational isomerism involving Tbt_s and Tbt_a groups has recently been found for selenobenzaldehydes TbtCHSe.[29]

Experimental Procedure

General Procedure: All melting points are uncorrected. All solvents used in reactions were purified by the methods reported below. THF was purified by distillation from sodium diphenyl ketyl before use. All reactions were carried out under an argon atmosphere. Preparative gel-permeation liquid chromatography (GPLC) was performed on an LC-908 (JAI gel 1H+2H columns) or an LC-908-C60 instrument (JAI gel 1H-40+2H-40 columns) (Japan Analytical Industry) with chloroform as eluent. Preparative thin-layer

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chromatography (PTLC), wet column chromatography (WCC), and flash column chromatography (FCC) were performed with Merck Kieselgel 60 PF254 (Art. No. 7747), Wakogel C-200, and Merck Silica Gel 60, respectively. The ^{1}H NMR (500 or 270 MHz) and ^{13}C NMR (125 or 68 MHz) spectra were measured in $CDCl_3$, C_6D_6, or $Cl_2CDCDCl_2$ with a Bruker AM-500, a JEOLα-500, or a JEOL EX-270 spectrometer with $CHCl_3$, C_6H_6, or 1,1,2,2-tetrachloroethane as internal standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. The electronic spectra were recorded on a JASCO Ubset-50 UV/Vis spectrometer. Infrared spectra were obtained on a Horiba FT-200 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

Desulfurization of Octathionane 3 with Ph_3P (7 equiv): To a THF suspension (80 mL) of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyloctathionane (**3**) (320 mg, 0.389 mmol) was added Ph_3P (714 mg, 2.72 mmol) at −78 °C. The reaction mixture was gradually warmed and heated under reflux for 12 h. After removal of the solvent under reduced pressure, *n*-hexane was added to the reaction mixture and evaporated to remove remaining THF. A small amount of *n*-pentane was added to the residue, and insoluble Ph_3P=S (767 mg, 2.61 mmol, 96%) was filtered off. The filtrate was separated by low-temperature FCC (− 30 °C, *n*-pentane) to afford symmetric (sym)-2,4,6-tris[bis(trimethylsilyl)methyl]thiobenzaldehyde (**2a**) (151 mg, 0.253 mmol, 65%) and asymmetric (asym)-2,4,6-tris[bis(trimethylsilyl)methyl]thiobenzaldehyde (**2b**) (38.3 mg, 0.0641 mmol, 16%). All these procedures, except for the concentration of the chromatographed *n*-pentane solution of **2b**, were performed under Ar or N_2 atmosphere. All solvents used in the separation had been distilled under a N_2 atmosphere. Thiobenzaldehydes **2a** and **2b** thus isolated were handled below room temperature in order to protect them from thermal interconversion.

2a: purple crystals; M.p. 172–174 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.01 (s, 36H), 0.08 (s, 18H), 1.45 (s, 1H), 2.97 (s, 1H), 3.25 (s, 1H), 6.37 (s, 1H), 6.49 (s, 1H), 12.05 (s, 1H); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.11 (s, 36H), 0.14 (s, 18H), 1.52 (s, 1H), 3.10 (s, 1H), 3.42 (s, 1H), 6.56 (s, 1H), 6.68 (s, 1H), 12.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.4 (q), 0.8 (q), 24.5 (d), 24.7 (d), 32.2 (d), 122.9 (d), 127.7 (d), 138.5 (s), 146.6 (s), 146.9 (s), 148.4 (s), 234.1 (d); ^{13}C NMR (68 MHz, $CDCl_3$): ^1J(C,H) (CHS) = 162.4 Hz; UV/Vis (*n*-hexane): λ_{max} (ε) = 587 nm (30); HRMS calcd for $C_{28}H_{60}SSi_6$: 596.3032, found: 596.3012. $C_{28}H_{60}SSi_6 \cdot 5/2\,H_2O$: calcd C 52.35, H 10.19, S 4.99; found C 52.48, H 9.94, S 5.80.

2b: green crystals; M.p. 135–145 °C (decomp.); ^{1}H NMR (270 MHz, $CDCl_3$): δ = − 0.01 (s, 18H), 0.05 (s, 18H), 0.07 (s, 18H), 1.46 (s, 1H), 1.72 (s, 1H), 5.54 (s, 1H), 6.40 (s, 1H × 2), 11.77 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 0.5 (q), 1.0 (q), 21.9 (d), 32.4 (d), 33.9 (d), 126.8 (d), 129.8 (d), 135.7 (s), 150.3 (s), 151.2 (s), 153.2 (s), 229.8 (d); ^{13}C NMR (68 MHz, $CDCl_3$): ^1J(C,H) (CHS) = 156.9 Hz; UV/Vis (*n*-hexane): λ_{max} (ε) = 604 nm (30); HRMS calcd for $C_{28}H_{60}SSi_6$: 596.3032, found 596.3027. $C_{28}H_{60}SSi_6 \cdot H_2O$: calcd C 54.65, H 10.15, S 5.21; found C 54.39, H 9.88, S 5.98.

Desulfurization of Pentathiane 4 with Ph_3P (4 equiv): To a THF suspension (42 mL) of 2,4,6-tris[bis(trimethylsilyl)methyl]phenylpentathiane (**4**) (125 mg, 0.173 mmol) was added Ph_3P (182 mg, 0.695 mmol) at −78 °C. The reaction mixture was gradually warmed and heated under reflux for 12 h. After removal of the solvent under reduced pressure, *n*-hexane was added to the reaction mixture and evaporated to remove the remaining THF. A small amount of *n*-pentane was added to the residue, and insoluble Ph_3P=S (197 mg, 0.668 mmol, 96%) was filtered off. The filtrate was separated by low-temperature FCC (− 30 °C, *n*-pentane) to afford thiobenzaldehyde **2a** (73.9 mg, 0.124 mmol, 72%) and its rotamer **2b** (17.1 mg, 0.0286 mmol, 17%). Precautions similar to those in the above experiments for **3** were taken to avoid oxidation and thermal interconversion of **2a** and **2b**.

Desulfurization of Octathionane 3 with Hexamethyl Phosphorous Triamide (excess): To a THF solution (5 mL) of hexamethyl phosphorous triamide (0.37 mL, 1.73 mmol) was added dropwise a THF solution (25 mL) of **3** (95.3 mg, 0.116 mmol) over 45 min at −78 °C, and the reaction mixture was warmed to room temperature. After removal of the solvent under reduced pressure, the residue was separated by low-temperature FCC (− 30 °C, *n*-pentane) to afford **2a** (47.9 mg, 0.0802 mmol, 69%). The fraction eluted by CH_2Cl_2 was chromatographed (GPLC) to give hexamethyl thiophosphoric triamide (87.1 mg, 0.446 mmol, 55% from **3**). All these procedures except for GPLC were performed under Ar or N_2 atmosphere, and the solvent used in FCC was distilled under a N_2 atmosphere. Compound **2a** thus isolated was handled below room temperature in order to protect it from the thermal interconversion to **2b**.

Thermolysis of Thiobenzaldehyde 2a: In a 5 mm NMR tube was placed a [D_8]toluene solution (1 mL) of **2a** (63.2 mg, 0.106 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. When the solution was heated at 145 °C for 3 h and then at 165 °C for 4 h, only **2a** and **2b** were observed by ^{1}H NMR spectroscopy. After additional heating at 170–180 °C for 42 h the solution turned yellow. After removal of the solvent, the residue was separated by GPLC and PTLC (*n*-hexane) to afford 4,6-bis[bis-(trimethylsilyl)methyl]-1,1-bis(trimethylsilyl)-2-benzothiolane (**5**) (10.4 mg, 0.0174 mmol, 17%). **5**: white crystals; M.p. 140–141 °C (decomp.); ^{1}H NMR (500 MHz, $Cl_2CDCDCl_2$, 100 °C): δ = 0.05 (s, 18H), 0.07 (s, 18H), 0.10 (s, 18H), 1.387 (s, 1H), 1.393 (s, 1H), 4.02 (s, 2H), 6.36 (s, 1H), 6.40 (s, 1H); ^{13}C NMR (125 MHz, $Cl_2CDCDCl_2$, 100 °C): δ = 0.6 (q), 2.1 (q), 2.2 (q), 28.4 (d), 31.8 (d), 39.7 (t), 42.9 (s), 121.4 (br d), 126.4 (br d), 135.1 (s), 141.6 (s), 143.4 (s), 148.1 (s); HRMS calcd for $C_{28}H_{60}SSi_6$: 596.3032, found 596.3037. $C_{28}H_{60}SSi_6 \cdot 1/2\,H_2O$: calcd C 55.46, H 10.14, S 5.29; found C 55.58, H 9.94, S 5.05.

Photolysis of Thiobenzaldehyde 2a: In a 5 mm NMR tube was placed a C_6D_6 solution (1 mL) of **2a** (29.1 mg, 0.0487 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The blue solution was irradiated (medium pressure Hg lamp, 100 W) at room temperature for 5 h. The resulting yellow solution was evaporated to dryness and purified by PTLC (*n*-hexane) to afford benzothiolane **5** (20.9 mg, 0.0350 mmol, 72%).

Reaction of Thiobenzaldehyde 2a with Molecular Oxygen: Oxygen gas dried through conc. H_2SO_4 was bubbled into an *n*-hexane solution (5 mL) of **2a** (21.3 mg, 0.0357 mmol) at −20 °C for 1 h. The reaction mixture was warmed to room temperature and stirred for 26 h. After removal of the solvent under reduced pressure, the residue was chromatographed (PTLC, *n*-hexane:CH_2Cl_2 = 2:1) to afford 2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde (**6**) (8.2 mg, 0.014 mmol, 40%) and (*Z*)-2,4,6-tris[bis(trimethylsilyl)methyl]thiobenzaldehyde-*S*-oxide (**7**) (3.2 mg, 0.0052 mmol, 15%). **7**: white crystals; M.p. 175–177 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03 (s, 36H), 0.05 (s, 18H), 1.37 (s, 1H), 1.66 (s, 1H), 1.76 (s, 1H), 6.33 (s, 1H), 6.48 (s, 1H), 8.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.5 (q), 0.7 (q), 28.0 (d × 2), 30.9 (d), 121.8 (d), 124.3 (s), 126.4 (d), 143.5 (s), 144.1 (s), 145.5 (s), 171.2 (d); IR (KBr): $\tilde{\nu}$ = 1101, 1120 cm^{-1} (C=S=O); HRMS calcd for $C_{28}H_{60}OSSi_6$: 612.2981, found 612.2987. $C_{28}H_{60}OSSi_6$: calcd C 54.83, H 9.86, S 5.23; found C 54.26, H 9.55, S 5.78.

Equilibration Studies on Thiobenzaldehydes 2: In a 5 mm NMR tube was placed a [D_8]toluene solution of **2a** (25 mmol L^{-1}). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at each temperature on a thermostat (LAUDA K6), and the temperature was monitored by a digital thermometer CT-500P (Custom Co.) with a calibration error of ±0.1 °C. At each temperature, the data showed that the isomerization was a reversible, first-order reaction. The rate constants, k(**2a** → **2b**) and k(**2b** → **2a**), were calculated by use of Equations (1) and (2), where

$$\ln\{([\mathbf{2a}]_t - [\mathbf{2a}]_\infty)/([\mathbf{2a}]_0 - [\mathbf{2a}]_\infty)\} = -\{k(\mathbf{2a} \rightarrow \mathbf{2b}) + k(\mathbf{2b} \rightarrow \mathbf{2a})\}t \quad (1)$$

$$K = k(\mathbf{2a} \rightarrow \mathbf{2b})/k(\mathbf{2b} \rightarrow \mathbf{2a}) = [\mathbf{2b}]_\infty/[\mathbf{2a}]_\infty \quad (2)$$

$[A]_t$ is the concentration of compound A at time t and K is the equilibrium constant. The concentration [A] was determined by observation of thioformyl signals in the ^{1}H NMR spectra. The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were calculated by using the Eyring equation. The thermodynamic parameters, ΔH° and ΔS°, were obtained from Equations (2) and (3), where

$$\ln K = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \quad (3)$$

where R is the gas constant and T is the absolute temperature. The statistical errors were calculated by a standard method. The activation and thermodynamic parameters for benzaldehyde **6** were obtained by the same method as for thiobenzaldehyde **2**.

Thermolysis of Benzaldehyde 6a: An *n*-hexane solution (10 mL) of (sym)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde (**6a**) (51.9 mg, 0.0893 mmol) was refluxed for 3 h, and the solvent was removed under reduced pressure.

The ^{1}H NMR spectrum of the residue showed that benzaldehyde **6a** and (asym)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde (**6b**) were produced in a ratio of 5:1. Separation of **6a** and **6b** by PTLC (*n*-hexane:CH_2Cl_2 = 5:1) was unsuccessful. **6b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.00 (s, 18H), 0.03 (s, 18H), 0.04 (s, 18H), 1.40 (s, 1H), 1.67 (s, 1H), 3.95 (s, 1H), 6.29 (s, 1H), 6.36 (s, 1H), 10.13 (s, 1H).

Reaction of Thiobenzaldehyde 2a with Hydrazine Monohydrate: To a CH_2Cl_2 solution (4 mL) of **2a** (23.4 mg, 0.0392 mmol) was added an ethanol solution of $N_2H_4\cdot H_2O$ (0.404 M, 0.49 mL, 0.198 mmol) at 0 °C. When the reaction mixture was stirred for 5 min at the same temperature, the solution turned colorless. After being stirred for further 30 min, the solution was washed with water, and the water layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure to give (sym)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde hydrazone (**8a**) (22.4 mg, 0.0376 mmol, 96%). **8a**: white crystals; M.p. 172–176 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.01 (s, 36H), 0.04 (s, 18H), 1.33 (s, 1H), 1.99 (s, 1H), 2.10 (s, 1H), 5.39 (brs, 2H, NH_2), 6.28 (s, 1H), 6.41 (s, 1H), 7.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.5 (q), 0.6 (q), 0.7 (q), 24.5 (d), 30.2 (d), 121.7 (d), 126.4 (d), 127.4 (s), 142.5 (s), 143.08 (s), 143.15 (s), 145.0 (d, TbtH*C*=N); HRMS calcd for $C_{28}H_{62}N_2Si_6$: 594.3529, found 594.3567. $C_{28}H_{62}N_2Si_6$: calcd C 56.49, H 10.50, N 4.71; found C 56.48, H 10.47, N 4.73.

Reaction of Thiobenzaldehyde 2b with Hydrazine Monohydrate: To a CH_2Cl_2 solution (3 mL) of **2b** (14.4 mg, 0.0241 mmol) was added an ethanol solution of $N_2H_4\cdot H_2O$ (0.404 M, 0.30 mL, 0.121 mmol) at 0 °C. After the reaction mixture had been stirred for 2 h at this temperature, the solution turned pale yellow. The reaction mixture was washed with water, and the water layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure to give (asym)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde hydrazone (**8b**) (13.4 mg, 0.0225 mmol, 93%). **8b**: white crystals; M.p. 170–173 °C (decomp.); ^{1}H NMR (270 MHz, $CDCl_3$): δ = −0.02 (s, 18H), 0.02 (s, 18H), 0.03 (s, 18H), 1.29 (s, 1H), 1.57 (s, 1H), 3.50 (s, 1H), 5.21 (s, 2H, NH_2), 6.21 (s, 1H), 6.35 (s, 1H), 7.81 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 0.4 (q), 1.1 (q), 22.9 (d × 2), 29.8 (d), 117.6 (d), 125.1 (s), 128.2 (d), 142.6 (s), 143.7 (s), 144.1 (s), 146.5 (d, TbtH*C*=N); HRMS calcd for $C_{28}H_{62}N_2Si_6$: 594.3529, found 594.3506. $C_{28}H_{62}N_2Si_6\cdot 1/2H_2O$: calcd C 55.65, H 10.51, N 4.64; found C 55.86, H 10.45, N 4.79.

Reaction of Thiobenzaldehyde 1 with Hydrazine Monohydrate: To a CH_2Cl_2 solution (5 mL) of **1** (48.3 mg, 0.166 mmol) was added an ethanol solution of $N_2H_4\cdot H_2O$ (2.06 M, 0.40 mL, 0.824 mmol) at 0 °C, and the reaction mixture was stirred for 3.5 h at this temperature. The solvent and excess of $N_2H_4\cdot H_2O$ were removed under reduced pressure to give 2,4,6-tri-*tert*-butylbenzaldehyde hydrazone (**9**) (46.4 mg, 0.161 mmol, 97%). The spectra of **9** were identical with those previously reported [10g].

Competitive Reaction of Thiobenzaldehydes 2a and 2b with Hydrazine Monohydrate: To a CH_2Cl_2 solution (3 mL) of **2a** (15.8 mg, 0.0264 mmol) and **2b** (15.8 mg, 0.0264 mmol) was added an ethanol solution of $N_2H_4\cdot H_2O$ (0.204 M, 0.10 mL, 0.0204 mmol) at 0 °C. After the solution had been stirred for 2 h at the same temperature, the solvent was evaporated at room temperature under argon. ^{1}H NMR analysis (270 MHz, $CDCl_3$) of the residue showed that only (sym)-hydrazone **8a** was produced without any formation of (asym)-hydrazone **8b**.

Competitive Reaction of Thiobenzaldehydes 2b and 1 with Hydrazine Monohydrate: To a CH_2Cl_2 solution (3.5 mL) of **2b** (23.4 mg, 0.0392 mmol) and **1** (11.4 mg, 0.0392 mmol) was added an ethanol solution of $N_2H_4\cdot H_2O$ (0.404 M, 0.10 mL, 0.0404 mmol) at 0 °C. The reaction mixture was stirred for 2 h, and the solvent was evaporated at room temperature under an Ar atmosphere. ^{1}H NMR analysis (270 MHz, $CDCl_3$) of the residue showed that hydrazones **8b** and **9** were produced in a ratio of 4:1, which was calculated from the intensity of the methine signals of R*H*CNNH$_2$.

Reaction of Thiobenzaldehyde 2a with *m*CPBA: To a CH_2Cl_2 solution (13 mL) of **2a** (142 mg, 0.238 mmol) was added a CH_2Cl_2 solution (8 mL) of *m*CPBA (purity: min. 70%; 59.6 mg, >0.24 mmol) at −78 °C, and then the reaction mixture was warmed to room temperature. After removal of the solvent under reduced pressure, the residue was separated by WCC (*n*-pentane:CH_2Cl_2 = 1:1) and GPLC to give (sym)-(*E*)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde-*S*-oxide (**10a**) (129 mg, 0.210 mmol, 88%) and benzaldehyde **6a** (11.3 mg, 0.0194 mmol, 8%). **10a**: yellow crystals; M.p. 171–173 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.02 (s, 36H), 0.05 (s, 18H), 1.38 (s, 1H), 1.81 (s, 1H), 1.85 (s, 1H), 6.38 (s, 1H), 6.50 (s, 1H), 9.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.4 (q), 0.7 (q), 28.0 (d), 28.3 (d), 31.2 (d), 121.5 (s), 122.1 (d), 126.9 (d), 144.2 (s), 144.5 (s), 146.2 (s), 184.9 (d); UV/Vis (*n*-hexane): λ_{max} (ε) = 365 nm (5200); IR (KBr): $\tilde{\nu}$ = 1103 cm^{-1} (C=S=O); HRMS calcd for $C_{28}H_{60}OSSi_6$: 612.2981, found 612.2977. $C_{28}H_{60}OSSi_6\cdot 1/2H_2O$: calcd C 54.04, H 9.88, S 5.15; found C 54.01, H 9.68, S 5.22.

Reaction of Thiobenzaldehyde 2b with *m*CPBA: To a CH_2Cl_2 solution (3 mL) of **2b** (20.5 mg, 0.0343 mmol) was added a CH_2Cl_2 solution (2.5 mL) of *m*CPBA (purity: 80–85%; 11.4 mg, 0.053–0.056 mmol) at −78 °C. After having been stirred for 30 min, the reaction mixture was warmed to room temperature. The solvent was removed under reduced pressure, and the residue was separated by WCC (*n*-hexane:CH_2Cl_2 = 1:1) to give (asym)-(*E*)-2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde-*S*-oxide (**10b**) (18.7 mg, 0.0305 mmol, 89%). **10b**: yellow crystals; M.p. 168–171 °C (decomp.); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.04 (s, 36H), 0.11 (s, 18H), 1.39 (s, 1H), 1.54 (s, 1H), 1.70 (s, 1H), 6.38 (s, 1H), 6.41 (s, 1H), 10.14 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, 0 °C): δ = 0.3 (q), 0.9 (q), 31.4 (d), 33.0 (d), 33.4 (d), 125.3 (s), 126.7 (d), 127.4 (d), 145.5 (s), 147.2 (s), 147.9 (s), 188.8 (d); IR (KBr): $\tilde{\nu}$ = 1081 cm^{-1} (C=S=O); HRMS calcd for $C_{28}H_{60}OSSi_6$: 612.2981, found 612.3037. $C_{28}H_{60}OSSi_6\cdot H_2O$: calcd C 53.27, H 9.90, S 5.08; found C 53.10, H 9.64, S 4.72.

Competitive Reaction of Thiobenzaldehydes 2a and 2b with *m*CPBA: To a CH_2Cl_2 solution (3 mL) of **2a** (20.5 mg, 0.0343 mmol) and **2b** (20.5 mg, 0.0343 mmol) was added a CH_2Cl_2 solution (1.5 mL) of *m*CPBA (purity: 80–85%; 6.3 mg, 0.029–0.031 mmol) at −78 °C. After having been stirred for 15 min at this temperature, the reaction mixture was warmed to room temperature, and the solvent was evaporated at room temperature under an Ar atmosphere. A small amount of *n*-hexane, which was distilled under a N_2 atmosphere, was added to the mixture, and slightly soluble *m*-chlorobenzoic acid was filtered off under an Ar atmosphere through a glass filter. The solvent of the filtrate was evaporated at room temperature under an Ar atmosphere. ^{1}H NMR analysis (270 MHz, $CDCl_3$) of the residue showed that sulfines **10a** and **10b** were produced in a ratio of 1:4, which was calculated from the intensity of the methine signals of R*H*CSO.

Competitive Reaction of Thiobenzaldehydes 2a and 1 with *m*CPBA: To a CH_2Cl_2 solution (4 mL) of **2a** (29.5 mg, 0.0494 mmol) and **1** (14.4 mg, 0.0496 mmol) was added a CH_2Cl_2 solution (2 mL) of *m*CPBA (purity: 80–85%; 9.0 mg, 0.042–0.044 mmol) at −78 °C. After having been stirred for 15 min at this temperature, the reaction mixture was warmed to room temperature. After workup similar to the above competitive reaction, ^{1}H NMR analysis (270 MHz, $CDCl_3$) showed the formation of only sulfine **10a** without that of sulfine **11**.

Crystallographic Data for 2a and 2b: **2a**: $C_{28}H_{60}SSi_6$, M_r = 597.35, crystal size (mm) 0.2 × 0.1 × 0.7, triclinic, space group $P\bar{1}$; a = 13.230(6), b = 16.658(3), c = 9.488(1) Å; α = 93.30(1), β = 99.50(2), γ = 102.92(2)°; V = 2000(1) Å^3, Z = 2, ρ = 0.992 g cm^{-3}, μ = 2.68 cm^{-1}, R = 0.058 (R_w = 0.055). **2b**: $C_{28}H_{60}SSi_6$, M_r = 597.35, crystal size (mm) 0.2 × 0.1 × 0.8, triclinic, space group $P\bar{1}$, a = 12.596(3), b = 17.866(4), c = 9.453(2) Å; α = 91.25(2), β = 108.14(2), γ = 102.38(2)°; V = 1965.8(9) Å^3, Z = 2, ρ = 1.009 g cm^{-3}, μ = 2.72 cm^{-1}, R = 0.057 (R_w = 0.056). The intensity data for **2a** and **2b** ($6 \le 2\theta \le 50.1°$ for **2a**, $6 \le 2\theta \le 55.1°$ for **2b**) were collected on a RIGAKU AFC5R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71069 Å). In **2a**, the intensities of three representative reflections, which were measured after every 150 reflections, declined by −7.10%. A linear correction factor was applied to the data for **2a** to account for this phenomenon. The structures of **2a** and **2b** were solved by direct methods [30]. All calculations were performed using TEXSAN [31] crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms except for thioformyl hydrogen atom (H1) of **2b** were located by calculation. The thioformyl hydrogen (H1) of **2b** was isotropically refined. The final cycle of full-matrix least-squares refinement was based on 1622 [for **2a**] and 2737 [for **2b**] observed reflections ($I > 3.00\sigma(I)$) for **2a** and **2b**) and 316 [for **2a**] and 320

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[for **2b**] variable parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1220-40. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

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