Cycloaddition and Oxidation Reactions of a Stable Thioaldehyde, (2,4,6-Tri-*t*-butyl)thiobenzaldehyde

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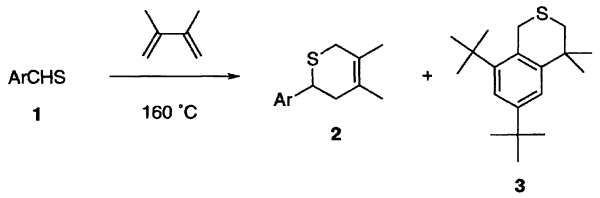
The title thioaldehyde **1** undergoes [4+2] cycloaddition with 2,3-dimethyl-1,3-butadiene at 160 °C and [3+2] cycloadditions with diphenylnitrilimine and mesitonitrile oxide at room temperature. The intermediary cycloadduct with mesitonitrile oxide undergoes cycloreversion to give 2,4,6-tri-*t*-butylbenzaldehyde and mesityl isothiocyanate as the final products. Oxidation of **1** with *m*-chloroperbenzoic acid (mCPBA) and dimethyldioxirane (**9**) gives a mixture of (*E*)- and (*Z*)-isomers of the corresponding *S*-oxides (sulfines), the former and the latter being kinetically and thermodynamically controlled products, respectively. Although both (*E*)- and (*Z*)-sulfines are not further oxidized by mCPBA, the (*Z*)-sulfine is oxidized with **9** to give 7-oxa-8-thia-2,4,6-tri-*t*-butylbicyclo[4.3.0]nona-2,4,9-triene 8,8-dioxide and 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran 2,2-dioxide, both of which are intramolecular cyclization products of an intermediary thioaldehyde dioxide (sulfene).

In a previous paper,[1] we reported the synthesis of a stable aromatic thioaldehyde, (2,4,6-tri-*t*-butyl)thiobenzaldehyde (**1**) (ArCHS; Ar = 2,4,6-tri-*t*-butylphenyl throughout this paper) and its some reactivities such as thermolysis, photolysis, and reactions with radicals and nucleophiles (Grignard and organolithium reagents, amines, and a hydride reagent). In continuation of our work on stable thioaldehydes,[2] we became interested in cycloaddition and oxidation reactions of **1**, because cycloaddition with 1,3-dienes is the most typical reaction of transient thioaldehydes[3] and oxidation of **1** bearing an extremely bulky substituent might afford an interesting reactive species such as a sulfene. We present here a detailed account of these reactions of **1**.

Results and Discussion

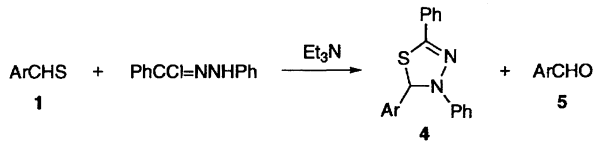
Cycloaddition Reactions. Transient thioaldehydes are known to undergo Diels–Alder reactions with 1,3-dienes,[3] while Vedejs et al. reported that 2,2-dimethylpropanethial, a moderately stable aliphatic thioaldehyde, reacts with some 1,3-dipolar reagents such as diazomethane and nitrone.[4]

When thioaldehyde **1** was allowed to react with 2,3-dimethyl-1,3-butadiene as solvent at 160 °C in a sealed tube, a cycloadduct **2** was obtained in 26% yield in addition to dihydrobenzothiopyran **3** (35%). Since we have already found that **1** undergoes thermal isomerization into **3** at high temperatures,[1] it is considered that **3** was formed competitively with **2** even in the presence of a large excess of the diene, because the reactivity of the thioformyl group of **1** is highly reduced by a very bulky group, 2,4,6-tri-*t*-butylphenyl; thiobenzophenone and thioacetophenone reportedly react with 2,3-dimethyl-1,3-butadiene at room temperature.[5]



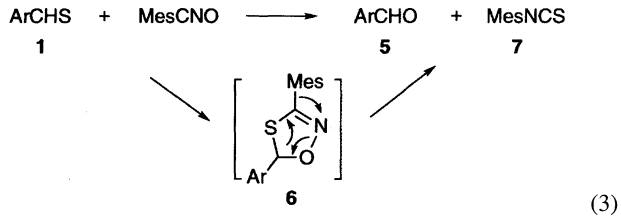
(1)

The thioaldehyde **1** was able to react also with 1,3-dipolar reagents. Diphenylnitrilimine, generated by the reaction of *N*-phenylbenzenecarbohydrazonoyl chloride with triethylamine,[6] reacted with **1** at room temperature in benzene to afford a cycloadduct **4** in 34% yield besides 2,4,6-tri-*t*-butylbenzaldehyde **5** (10%), which was most likely formed by oxidation of **1** during work-up procedure.



(2)

The compound **1** also reacted with mesitonitrile oxide at room temperature in THF. The products, however, are not a cycloadduct **6**, but mesityl isothiocyanate **7** (76%) and the aldehyde **5** (79%). We think that the initial cycloadduct **6** was actually formed, but it underwent rapid cycloreversion accompanied with the migration of a mesityl group to give **5** and **7**. A similar thermal cycloreversion is known for an oxathiazole obtained from a substituted thiobenzophenone and *p*-nitrobenzonitrile oxide.[7] The thermal instability of **6** most probably results from its labile N–O bond and steric repulsion between two bulky aryl substituents, as judged from its molecular model. Attempts at the spectroscopic detection of **6** by ^{1}H NMR met with failure.



(3)

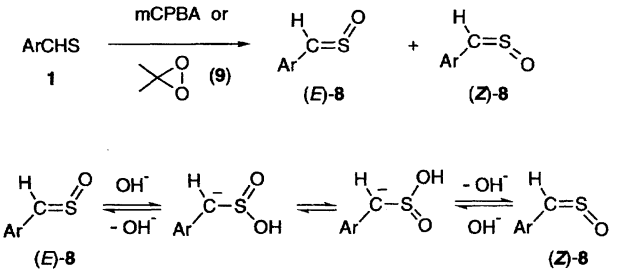
Oxidation Reactions. As previously reported,[1] **1** reacts with molecular oxygen in solution to give the aldehyde **5**, although it is stable toward oxygen for a long time (several years) in the solid state.

(a) Oxidation with an Equimolar Amount of Oxidizing Agents. When **1** was allowed to react in dichloromethane with one molar amount of *m*-chloroperbenzoic acid (mCPBA) at 0 °C, a mixture of (*E*)- and (*Z*)-thioaldehyde oxides (sulfines) ((*E*)-**8** and (*Z*)-**8**) was obtained, with the *E*/*Z* ratio being 16 : 1 (Scheme 1 and Table 1). The stereochemistry was determined by ^{1}H NMR using a shift reagent Eu(fod)$_3$ [tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium]. When the reaction was carried out at reflux under otherwise identical conditions, the *E*/*Z* ratio became 11 : 1.

In order to avoid any influence of an acid on the reaction course, we also attempted the oxidation of **1** with a neutral and strong oxidizing agent, dimethyldioxirane (**9**) in acetone.[8] The reaction with an equimolar amount of **9** at −78 °C afforded (*E*)-**8** exclusively, whereas that at room temperature gave a 20 : 1 mixture of (*E*)- and (*Z*)-**8**.

The formation of (*E*)-**8** as a major product in each reaction is most reasonably explained by an attack of mCPBA or **9** onto the sulfur lone pair from the less hindered site; thus (*E*)-**8** can be considered to be a kinetically controlled product. This is consistent with the temperature dependence of the *E*/*Z* ratio in the reactions using both oxidants.

The sulfine (*E*)-**8** was stable with regard to thermal isomerization; (*E*)-**8** did not change into (*Z*)-**8** even after refluxing for 2 d in methanol or toluene. In the presence of a



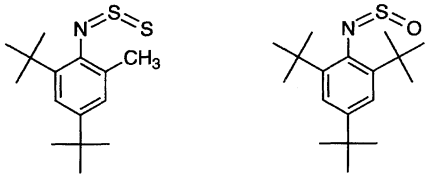
Scheme 1.

Table 1. Oxidation of **1** to **8** with an Equimolar Amount of mCPBA or **9**

Oxidant	Solvent	Reaction temp	Yield/%	*E* : *Z*
mCPBA	Dichloromethane	0 °C	91	16 : 1
mCPBA	Dichloromethane	Reflux	81	11 : 1
9	Acetone	−78 °C	100	*E* only
9	Acetone	20 °C	100	20 : 1

base, however, it underwent a facile isomerization into (*Z*)-**8**. Thus, when (*E*)-**8** was dissolved in a 0.02 M sodium hydroxide solution (1 M=1 mol dm^{-3}) of THF and kept at room temperature for 15 h, the *E*/*Z* ratio of **8** was changed to 1 : 20, as judged by ^{1}H NMR. The *E*/*Z* isomerization probably proceeds as shown in Scheme 1. The above base-induced isomerization indicates that (*Z*)-**8** is thermodynamically more stable than (*E*)-**8**. It is interesting that the (*Z*)-isomer is thermodynamically more stable than the (*E*)-isomer, in spite of probable steric interaction between the oxygen atom and the very bulky tri-*t*-butylphenyl group.

It has been previously reported that both *N*-sulfinothioylaniline **10**[9] and *N*-sulfinylaniline **11**[10] have (*Z*)-configuration, as revealed by X-ray crystallographic analysis, and that a stabilization factor common to both **10** and **11** is most probably the electronic attractive interaction between the aryl ring and the terminal heteroatom.[11] We think that the *Z*-preference in **8** is similarly explicable.



(4)

Block et al. have shown that there is a similar preference of the (*Z*)-isomer over the (*E*)-isomer also for aliphatic sulfines (alkanethial oxides) formally derived from thioaldehydes[12] and this can be explained by preference in terms of σ-stabilization.[13] It is of interest that the *Z*-preference is a general phenomenon common to both aromatic and aliphatic thioaldehyde oxides.

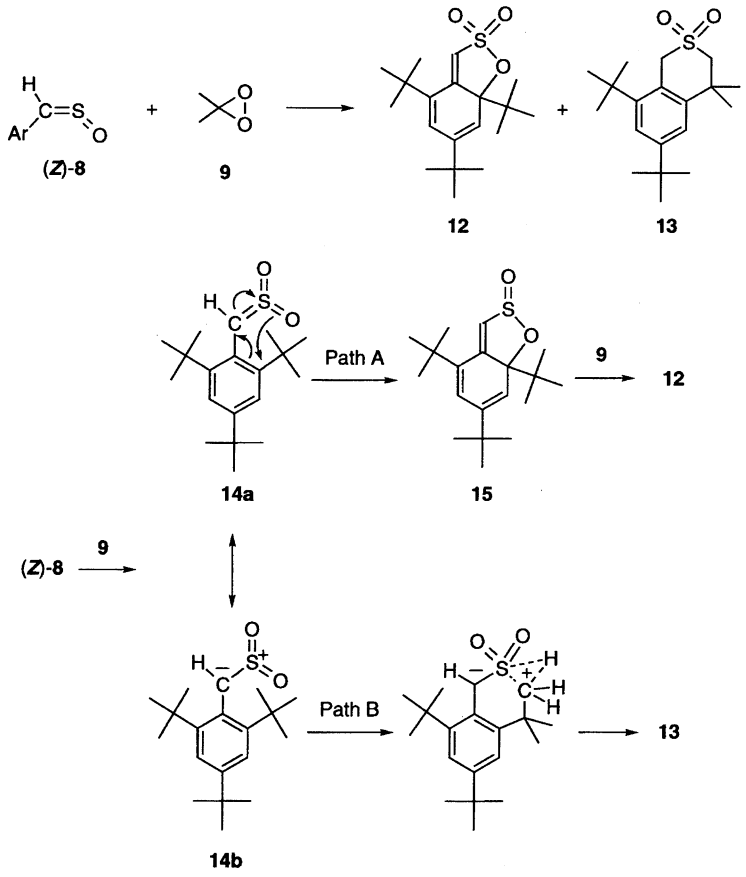
(b) Oxidation of the Sulfine 8. In contrast to the high chemical stability of sulfines (thioketone or thioaldehyde oxides), sulfenes (thioketone or thioaldehyde dioxides) have been known to be elusive, no stable examples having been reported.[2a,14,15] Since a principal decomposition pathway of sulfenes is oligomerization,[2a] it is reasonably expected that a sulfene ArCH=SO$_2$ having the very bulky 2,4,6-tri-*t*-butylphenyl group might exist as a stable monomer. To this end we oxidized the sulfine **8** with mCPBA and the dioxirane **9**.

Oxidation of (*E*)- and (*Z*)-**8** with mCPBA did not proceed in refluxing dichloromethane although only a trace amount of the aldehyde **5** was formed in the reaction of (*Z*)-**8**.

Although the reaction of (*E*)-**8** with the dioxirane **9** in acetone at room temperature did not proceed at all, probably because of steric hindrance, that of (*Z*)-**8** gave interesting oxidation products **12** (20%) and **13** (63%) (Scheme 2).

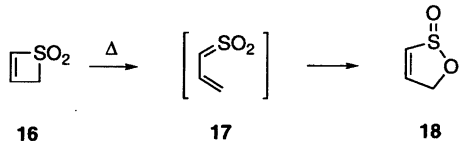
The formation of **12** and **13** can be explained in terms of intermediacy of the expected sulfene **14** (Scheme 2), which is so reactive that it undergoes either a 6-electron pericyclic reaction leading to **15** followed by further oxidation to give **12** (Path A) or a C–H bond insertion of the electrophilic sulfene sulfur center (Path B).

A cyclization similar to the Path A involving a vinyl sulfene **17** has been described by King et al. in the ther-



Scheme 2.

molysis of sulfone **16** giving sulfinate **18**. It is noteworthy, however, that in the present reaction the cyclization takes place at the expense of aromaticity.



16 **17** **18** (5)

Path A is considered to be mechanistically similar also to intramolecular cyclizations of thiocumulenes onto the 2- (or 6-) position of a 2,4,6-tri-*t*-butylphenyl[16] or 2,4-di-*t*-butyl-6-cyanophenyl group[17] (Scheme 3) which we reported previously. It is of great interest that these thiocumulenes including **14** can undergo facile electrocyclic reactions involving an aromatic π-bond.

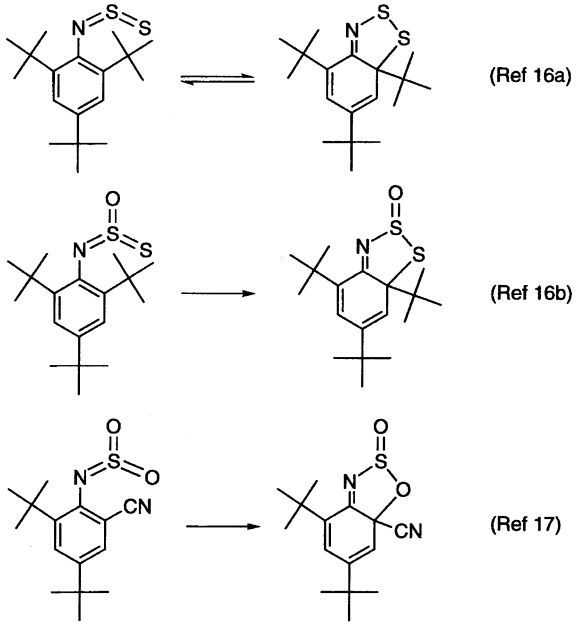
The intramolecular C–H insertion at the *o*-*t*-butyl group involving an electrophilic center (Path B) also has some precedents (Scheme 4).[18]

In order to trap the intermediary sulfene **14**, the oxidation of (*Z*)-**8** with **9** was carried out in the presence of methanol, but no trapping product (i.e., $ArCH_2SO_3Me$) was obtained. This is probably because the trapping reaction cannot compete with the intramolecular cyclization on account of steric congestion around the C=S bond.

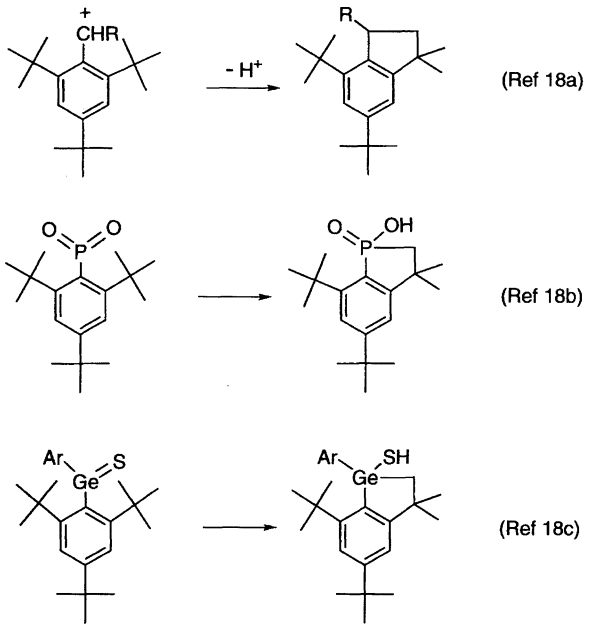
Conclusion

Although the thioaldehyde **1** has a very bulky group on the thioformyl carbon, it can undergo a [4+2] cycloaddition with 2,3-dimethyl-1,3-butadiene and [3+2] cycloadditions with diphenylnitrilimine and mesitonitrile oxide, suggesting the high reactivity of **1** toward cycloadditions.

The thioaldehyde **1** is oxidized by mCPBA and the dioxirane **9** to give (*E*)- and (*Z*)-sulfines **8**, which are kineti-



Scheme 3.



Scheme 4.

cally and thermodynamically controlled products, respectively. The (*Z*)-isomer undergoes further oxidation by **9** to give products **12** and **13** resulting from intramolecular cyclization of the intermediary sulfene **14**. The formation of **12** and **13** in spite of relatively mild reaction conditions, i.e., room temperature, suggests the extremely high reactivity of a sulfene not only in oligomerization, addition of active hydrogen compounds across the C=S bond, and fragmentation reaction, which are already known, but also in electrocyclic reaction involving an aromatic π-bond and in an insertion reaction into a C–H bond in a *t*-butyl group which is usually believed to be chemically quite stable. Therefore, further exploration of appropriate bulky substituents is necessary for the isolation of a stable sulfene.

Experimental

All melting points were uncorrected. All solvents used in reactions were purified by the reported methods. THF was purified by distillation from sodium diphenylketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or an LC-908-C60 instrument with JAIGEL 1H+2H columns and JAIGEL 1H−40+2H−40 columns (Japan Analytical Industry) and chloroform as solvent. Dry column chromatography (DCC), preparative thin-layer chromatography (PTLC), and wet column chromatography (WCC) were performed with ICN silica DCC 60A, Merck Kieselgel 60 PF254 (Art No. 7747), and Wakogel C-200, respectively. The ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker AM-500, a JEOL EX-270 or a FX-90Q spectrometer using TMS as internal standard. Infrared spectra were recorded on a Horiba FT-200 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reaction of (2,4,6-Tri-*t*-butyl)thiobenzaldehyde (1) with 2,3-Dimethyl-1,3-butadiene. The thioaldehyde[1] (99.3 mg, 0.34 mmol) was dissolved in 2,3-dimethyl-1,3-butadiene (0.4 ml, 3.5 mmol) and the solution was degassed and sealed in a glass tube. After the solution was heated at 160 °C for 2 d, the diene was removed by evaporation under reduced pressure. The residue was purified by GPLC and PTLC (SiO_2, hexane) to give 6-(2,4,6-tri-*t*-butylphenyl)-3,4-dimethylthia-3-cyclohexene (**2**) (32.8 mg, 26%) and 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran (**3**) (36.2 mg, 35%), the latter of which was identified by comparison of its ^{1}H NMR spectrum with that of the authentic sample.[1]

2: Colorless crystals; mp 117.5—119.2 °C (decomp); ^{1}H NMR δ=1.30 (s, 9H), 1.50 (br s, 9H), 1.59 (br s, 9H), 1.62 (s, 3H), 1.78 (s, 3H), 1.92 (d, J=18 Hz, 1H), 2.83 (dd, J=17 Hz, J=4.4 Hz, 1H), 2.98 (dd, J=17 Hz, J=12 Hz, 1H), 3.50 (d, J=18 Hz, 1H), 4.94 (dd, J=12 Hz, J=4.4 Hz, 1H), 7.40 (br s, 1H), and 7.50 (br s, 1H); ^{13}C NMR δ=19.81 (q), 20.16 (q), 31.35 (q), 33.16 (q), 34.78 (t), 34.84 (s), 35.21 (q), 37.82 (s), 38.67 (s), 39.80 (t), 41.81 (d), 119.44 (s), 122.35 (d), 124.33 (s), 124.83 (d), 128.12 (s), 137.10 (s), 147.56 (s), and 149.91 (s); HRMS: Found: *m/z* 372.2841. Calcd for $C_{25}H_{40}{}^{32}S$: M, 372.2850. Found: C, 80.30; H, 10.75; S, 8.78%. Calcd for $C_{25}H_{40}S$: C, 80.58; H, 10.82; S, 8.60%.

Reaction of 1 with Mesitonitrile Oxide. To a THF (5 ml) solution of **1** (133.8 mg, 0.46 mmol) was added a THF solution (5 ml) of mesitonitrile oxide[19] (80.5 mg, 0.5 mmol) at room temperature and the solution was stirred for 5.5 h. Since TLC monitoring indicated the presence of **1**, a THF solution (2 ml) of mesitonitrile oxide (87.3 mg, 0.54 mmol) was added again and the solution was stirred for 1.5 d. After removal of the solvent under reduced pressure, the crude products were purified by GPLC to give the aldehyde **5**[1] (99.3 mg, 79%) and mesityl isothiocyanate (61.5 mg, 76%) along with a recovery of mesitonitrile oxide (84.8 mg). Mesityl isothiocyanate was identified by comparison of its spectral data with those of the literature.[19]

Reaction of 1 with Diphenylnitrilimine.[6] To a benzene solution (5 ml) of **1** (149 mg, 0.51 mmol) and *N*-phenylbenzenecarbohydrazonoyl chloride (118 mg, 0.51 mmol) was added triethylamine (0.22 ml, 1.6 mmol) at room temperature; the solution was stirred for 6 h, during which time the solution became yellow. The solution was filtered through Celite and the solvent was evaporated from the filtrate. The residue was repeatedly purified by GPLC and DCC (SiO_2, hexane–dichloromethane 1 : 1) to afford 2-(2,4,6-tri-*t*-butylphenyl)-2,3-dihydro-3,5-diphenyl-1,3,4-thiadiazole (**4**) (85.1 mg, 34%) and 2,4,6-tri-*t*-butylbenzaldehyde (**5**) (14.4 mg, 10%).

4: Yellow crystals; mp 159.8—161.0 °C (decomp); ^{1}H NMR δ=1.34 (s, 9H), 1.48 (s, 18H), 6.62 (d, J=8.1 Hz, 2H), 6.79 (t, J=7.3 Hz, 1H), 6.99 (dd, J=8.1 Hz, J=7.3 Hz, 2H), 7.38—7.43 (m, 3H), 7.47 (s, 1H), 7.54 (br s, 2H), and 7.76 (d, J=6.8 Hz, 2H); ^{13}C NMR (330 K) δ=31.14 (q), 34.05 (q), 34.80 (s), 38.93 (s), 75.25 (d), 117.12 (d), 121.23 (d), 125.01 (d), 126.56 (d), 128.21 (d), 128.38 (d), 129.20 (d), 131.87 (s), 131.89 (s), 142.92 (s), 146.42 (s), 150.00 (s), and 151.76 (s); IR (KBr) 2960, 2939, 1597, 1493, 964, 762, 752, and 690 cm^{-1}; HRMS: Found: *m/z* 484.2914. Calcd for $C_{32}H_{40}H_2{}^{32}S$: M, 484.2912. Found: C, 79.26; H, 8.41; N, 5.96; S, 7.01%. Calcd for $C_{32}H_{40}N_2S$: C, 79.29; H, 8.32; N, 5.78; S, 6.61%.

Reaction of 1 with *m*-Chloroperbenzoic Acid (mCPBA). (a) To a dichloromethane solution (10 ml) of **1** (580 mg, 2.0 mmol) was added a dichloromethane solution (8 ml) of mCPBA (485 mg, 2.20 mmol) at 0 °C over 10 min. After being stirred for 30 min at 0 °C, the solution was washed with 5% aq sodium carbonate and water. Removal of the solvent gave a mixture of almost pure (*E*)-(2,4,6-tri-*t*-butyl)thiobenzaldehyde oxide [(*E*)-**8**] and its (*Z*)-isomer (567 mg, 93%), the *E*/*Z* ratio being 16 : 1 as measured by ^{1}H NMR. Separation of the mixture by DCC (SiO_2, hexane–CH_2Cl_2 1 : 2) gave pure (*E*)-**8** (474 mg, 79.6%) and (*Z*)-**8** (54 mg, 8.8%).

The stereochemical assignment was carried out with a shift reagent Eu(fod)$_3$ [tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium] by observing the change in chemical shifts of **H**–C(=SO) proton upon changing the concentration of the shift reagent. The results were as follows (in the order of the molar ratio of Eu(fod)$_3$/**8** and the chemical shift): for (*E*)-**8**; 0.00, 9.93; 0.190, 12.38; 0.422, 14.03 and for (*Z*)-**8**; 0.00, 9.37; 0.210, 9.73; 0.379, 9.90.

(*E*)-8: Colorless crystals; mp 181.0—182.0 °C; ^{1}H NMR (CCl_4) δ=1.33 (s, 9H), 1.47 (s, 18H), 7.33 (s, 2H), and 9.86 (s, 1H). Found: C, 74.32; H, 9.95; S, 10.44%. Calcd for $C_{19}H_{32}SO$: C, 74.46; H, 9.87; S, 10.46%.

(*Z*)-8: Colorless crystals; mp 175.0—176.5 °C; ^{1}H NMR (CCl_4) δ=1.31 (s, 9H), 1.45 (s, 18H), 7.34 (s, 2H), and 9.37 (s, 1H). Found: C, 74.53; H, 9.77; S, 10.46%. Calcd for $C_{19}H_{32}SO$: C, 74.46; H, 9.87; S, 10.46%.

(b) To a refluxing dichloromethane solution (10 ml) of **1** (593 mg, 2.03 mmol) and 2,6-di-*t*-butyl-4-methylphenol (3 mg)[21] was added a dichloromethane solution (8 ml) of mCPBA (486 mg, 2.82 mmol) over 10 min. The solution was cooled to room temperature and stirred for 1 h. The ^{1}H NMR of the solution indicated the ratio of (*E*)-**8**/(*Z*)-**8** was 11 : 1. After work-up similar to that in (a), a mixture of (*E*)- and (*Z*)-**8** was obtained in 81% yield (506 mg).

Attempted Thermal Isomerization of (*E*)-8. A toluene (3 ml) solution of (*E*)-**8** (71 mg, 0.23 mmol) was refluxed for 2 d. Monitoring by ^{1}H NMR indicated (*E*)-**8** did not change under these conditions. The solution was sealed in a glass tube and heated at 200 °C for 5 h. After work-up, no identifiable products were found. A similar experiment in refluxing methanol was carried out, but no isomerization was observed by ^{1}H NMR.

Base Induced Isomerization of (*E*)-8. To a THF solution (3 ml) of (*E*)-**8** (59 mg, 0.193 mmol) was added a THF solution (10 ml) of sodium hydroxide (12 mg, 0.30 mmol) at room temperature and the solution was stirred for 15 h. After removal of the solvent, the residue was extracted by dichloromethane. The extract was washed with water, dried with anhydrous $MgSO_4$, and the solvent was evaporated to give 49 mg of white crystals, which were found to be a 1 : 20 mixture of (*E*)- and (*Z*)-**8** by ^{1}H NMR. Two times recrystallization of the crystals from methanol gave pure (*Z*)-**8** (22 mg).

Reaction of 1 with Dimethyldioxirane (9). (a) When an acetone solution of **9**[22] (0.044 M, 0.64 ml, 0.028 mmol) was added to **1** in acetone, the solution became colorless immediately. Removal of the solvent left **8** in a quantitative yield, the ratio of (*E*)-**8**/(*Z*)-**8** being 20 : 1 (^{1}H NMR). Reaction at −78 °C under otherwise similar conditions afforded only (*E*)-**8**.

Reaction of (*E*)-8 with Dimethyldioxirane (9). To an acetone solution (10 ml) of (*E*)-**8** (154 mg, 0.50 mmol) was added an acetone solution (0.084 M, 6.0 ml, 0.50 mmol) of **9** at −78 °C. The solution was warmed up to room temperature and stirred overnight. Removal of the solvent and DCC purification (SiO_2, hexane–CH_2Cl_2 1 : 1) gave (*E*)-**8** (113 mg, 74%), no identifiable product being detected.

Reaction of (*Z*)-8 with Dimethyldioxirane (9). To an acetone solution (15 ml) of (*Z*)-**8** (289 mg, 0.94 mmol) was added an acetone solution (0.084 M, 12.3 ml, 1.03 mmol) of **9** at −78 °C. The solution was warmed up to room temperature and stirred overnight. Since the monitoring by TLC indicated the presence of a considerable amount of (*Z*)-**8**, **9** (0.084 M, 22 ml, 1.68 mmol) was again added to the solution, which was stirred for a day. After removal of the solvent, the residue was purified by DCC (SiO_2, hexane–dichloromethane 1 : 1) and GPLC to give 7-oxa-8-thia-2,4,6-tri-*t*-butylbicyclo[4.3.0]nona-2,4,9-triene 8,8-dioxide (**12**) (27 mg, 9% (20% based on the recovered (*Z*)-**8**)) and 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran 2,2-dioxide (**13**) (89 mg, 29% (63% based on the recovered (*Z*)-**8**)) along with recovered (*Z*)-**8** (155 mg, 54%). **12**: Colorless crystals; mp 136.5—138.0 °C (decomp); ^{1}H NMR δ=1.06 (s, 9H), 1.09 (s, 9H), 1.28 (s, 9H), 5.87 (d, *J*=1.2 Hz, 1H), 6.05 (d, *J*=1.2 Hz, 1H), and 6.53 (s, 1H); ^{13}C NMR δ=25.50 (q), 28.44 (q), 30.43 (q), 34.60 (s), 35.24 (s), 42.70 (s), 103.05 (s), 117.53 (d), 121.76 (d), 125.32 (d), 142.16 (s), 147.15 (s), and 155.11 (s); IR (KBr) 2962, 2906, 2873, 1703, 1601, 1475, 1363, 1246, 1221, and 1198 cm^{-1}. HRMS: Found: *m/z* 338.1910. Calcd for $C_{19}H_{30}O_3{}^{32}S$: 338.1916. Found: C, 67.41; H, 8.92; S, 9.61%. Calcd for $C_{19}H_{30}O_3S$: C, 67.42; H, 8.93; S, 9.47%.

The structure of **13** was established by comparison of its spectral data (^{1}H NMR, IR) with those of the authentic sample prepared in the following way by oxidation of 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiopyran.

The benzothiopyran[1] (109 mg, 0.374 mmol) was dissolved in dichloromethane (2 ml) and to this solution was added a dichloromethane solution (7 ml) of mCPBA (206 mg, 0.956 mmol) at room temperature over 10 min. After being stirred for 2 h, the solution was washed with 5% aq Na_2CO_3 (10 ml×3) and dried with anhydrous $MgSO_4$. TLC (SiO_2, dichloromethane) purification of the residue obtained by removal of the solvent from the reaction solution gave **13** (93 mg, 77%).

13: Colorless crystals; mp 202.0—203.0 °C; ^{1}H NMR δ=1.35 (s, 9H), 1.46 (s, 9H), 1.57 (s, 6H), 3.16 (s, 2H), 4.61 (s, 2H), 7.25 (d, *J*=1.3 Hz, 1H), and 7.35 (d, *J*=1.3 Hz, 1H); IR (KBr) 1318, 1128, and 1113 cm^{-1}; MS *m/z* 322 (M$^+$; 10), 306 (9), and 57 (100). Found: C, 70.63; H, 9.26; S, 10.28%. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38; S, 9.94%.

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