Synthesis and Decomposition of Some Dialkyl Oxide Derivatives of Organotrisulfides

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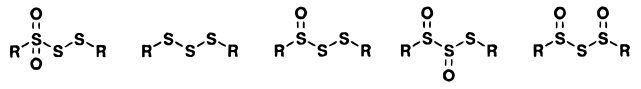
The isolation or detection of sulfenic sulfonic thioanhydrides **1** (*e.g.*, **6**), sulfenyl *vic*-disulfoxides **4** (*e.g.*, **9**, **14**), and sulfinic thioanhydrides **5** (*e.g.*, **20**) has been carried out by oxidative procedures at various temperatures. The decomposition of these compounds has been investigated and is shown to be consistent with the mechanism proposed for the decomposition of trisulfide monoxides.[8]

The preparation, characterization, and applications of thiosulfonates[1] and *vic*-disulfoxides (α-disulfoxides)[2] has been extensively reviewed.[3] In contrast, only a few dioxide derivatives of alkyl trisulfides (RS_3O_2R') have been isolated and characterized.[4−6] A variety of sulfenic sulfonic thioanhydrides **1** have been reported and were prepared by nonoxidative, synthetic procedures.[7] Sulfenic sulfonic thioanhydrides **1** are relatively stable and are isolated as decomposition products of various polysulfide−polyoxides.[3,8]

The electrophilic oxidation of trisulfide **2** or sulfenic sulfinic thioanhydride **3** has been postulated to take place at the central sulfur giving the corresponding sulfenyl *vic*-disulfoxide **4** that would rapidly rearrange to the sulfenic sulfonic thioanhydride **1** derivatives.[4c] However, no clear evidence of this mechanism has been reported. To our knowledge, dioxides **4** have never been detected.

The more electron-rich sulfur atom of **3** is believed to be the external sulfenyl sulfur which should preferentially react with the oxidizing agent to give the disulfinic thioanhydride **5** analog.[9] Such compounds were first postulated by Steudel,[4a,b] and clear evidence of diastereomeric **5** has been found.[3,9]

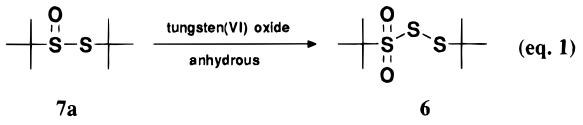


1 **2** **3** **4** **5**

Although various dioxides **1** have been reported,[3−5,7,8] little is known about their chemical properties or their preparation by direct oxidation. In addition, little has been reported on the trisulfide dioxide derivatives **4** and **5**.[4a,c,9] Therefore, it was decided to further investigate this class of compounds, focusing on the di-*tert*-butyl derivatives.

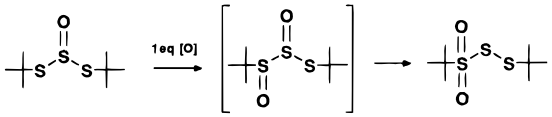
tert-Butylsulfenic *tert*-Butylsulfonic Thioanhydride (6)

tert-Butylsulfenic *tert*-butylsulfonic thioanhydride **(6)** has been isolated from the decomposition of various oxidized derivatives of di-*tert*-butyl trisulfide[8] probably because **6** is one of the most stable of this class of compounds. Bass and Evans[10] reported that the peracid oxidation of di-*tert*-butyl thiosulfinate **7a** in the presence of anhydrous tungsten(VI) oxide affords **6** in high yield (eq 1).



7a **6** (eq. 1)

By analogy with the oxidation of disulfides,[1a,11] the nucleophilic oxidation of *tert*-butylsulfenic *tert*-butylsulfinic thioanhydride **(7b)** (*t*-BuS(O)SSBu-*t*) should have given **6**. In our hands, these nucleophilic oxidation experiments were unsuccessful. However, the oxidation of di-*tert*-butyl dithiosulfite **(8)** gives a high yield of dioxide **6** using dimethyldioxirane (DMD), and moderate yields were observed using *m*-CPBA (eq 2).



8 **9** **6** (eq. 2)

[O] = *m*-CPBA 48%
[O] = DMD 85%

Such a conversion provides further demonstration of the formation of the *vic*-disulfoxide **9** which rapidly rearranges to the *tert*-butylsulfenic *tert*-butylsulfonic thioanhydride **(6)**. Compound **6** was fully characterized by NMR and mass spectrometry. Recrystallization from

⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) (a) Zefirov, N. F.; Zyk, N. V.; Beloglazkina, E. K.; Kutateladze, A. G. *Sulfur Rep.* **1993**, *14*, 223. (b) Farng, L.-P. O.; Kice, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1137. (c) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1982**, *47*, 4194.

(2) Highlights of the most interesting results can be found in: (a) Freeman, F. *Chem. Rev.* **1984**, *84*, 117. (b) Folkins, P. L.; Harpp, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 8998. (c) Folkins, P. L.; Harpp, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 3066 and references cited therein.

(3) (a) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 1044. (b) For NMR and structural information on these and related compounds see: Derbesy, G.; Harpp, D. N. *Sulfur Rep.* **1995**, *16*, 363. (c) Derbesy, G. Ph.D. Thesis, McGill University, 1994.

(4) (a) Steudel, R.; Latte, J. *Chem. Ber.* **1977**, *110*, 423. (b) Steudel, R. *Phosphorus Sulfur* **1985**, *23*, 33. (c) Freeman, F.; Ma, X.-B.; Lin, R. I.-S. *Sulfur Lett.* **1993**, *15*, 253.

(5) Freeman, F.; Lee, C. *Magn. Reson. Chem.* **1988**, *26*, 813.

(6) The naming of these polysulfide−polyoxide derivatives has caused concern in that the IUPAC names do not permit the reader to visualize the molecule. As a consequence, a variety of simpler names have survived. For example, one literature reference for compound 3,4,5-trithia-4-oxotricyclo[5.2.1.0]decane names it as a trithiolane 2-oxide derivative (ref 20a). We have used the thioanhydride approach, even though the names are less correct, but clearer names are available. Compound **1** might be termed sulfenyl thiosulfonate.

(7) Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1979**, *44*, 4135.

(8) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 4468.

(9) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1995**, *18*, *167.*

(10) Bass, F. W.; Evans, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 710.

(11) Kim, Y. H.; Takata, T.; Oae, S. *Tetrahedron Lett.* **1978**, 2305.

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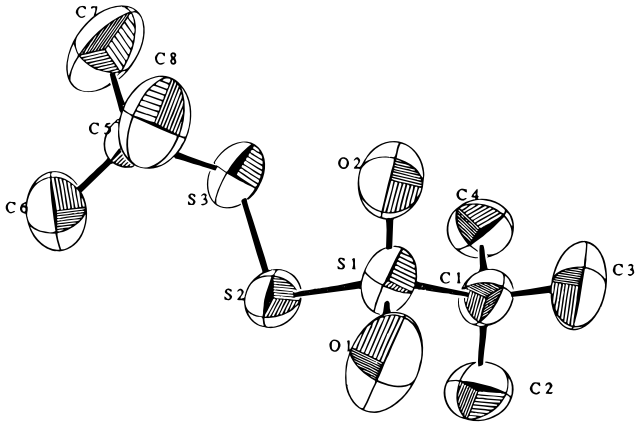
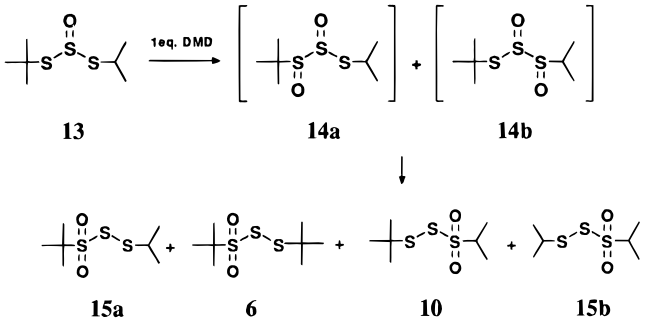


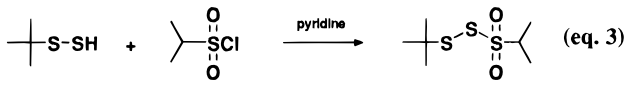
Figure 1. ORTEP drawing of **6**.

Scheme 1



hexane gave colorless crystals that were suitable for X-ray analysis. The ORTEP drawing is represented by Figure 1. It is interesting to note that the presence of the two oxygen atoms has a great effect on the S−S bonds and there is a difference of 0.11 Å between the length of the $S(O)_2$−S bond and the S−S bond. Full details on this and related molecules are available in ref 3b.

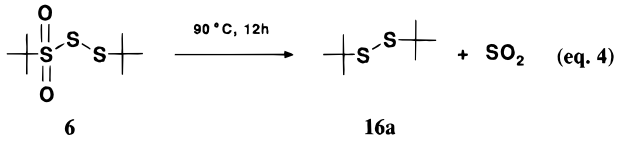
An unsymmetrical sulfenic sulfonic thioanhydride **10** has also been prepared by the reaction of *tert*-butyl hydrodisulfide[12] **(11)** with 2-propanesulfonyl chloride[13] **(12)** in the presence of pyridine. Pure *tert*-butylsulfenic isopropylsulfonic thioanhydride **(10)** was isolated in low yield by chromatography; it was found to be relatively stable at room temperature (>2 months) (eq 3).



The direct oxidation of *tert*-butyl isopropyl dithiosulfite **(13)** using 1 equiv of DMD was not regioselective. A careful analysis of the reaction mixture (*vide infra*) suggests the formation of the two possible *vic*-disulfoxides **(14a,b)** which rearrange to give a mixture of the two symmetric compounds **6** and **15b** and the two unsymmetric sulfenic sulfonic thioanhydrides **10** and **15a** (Scheme 1).

As we found,[3,8] the rearrangement of *vic*-disulfoxide derivatives is solvent and concentration dependent. The cleanest results were observed using DMD as oxidizing agent.

A decomposition study of **6** at varying temperatures reveals that it is very stable at 25 °C. However, it readily decomposes to di-*tert*-butyl disulfide **(16a)** after 12 h at 90 °C (eq 4). Strong evidence of the evolution of sulfur dioxide was given by the change of color (yellow to red) of the pH paper that was placed over the reaction mixture.



tert-Butylsulfenyl *tert*-Butyl *vic*-Disulfoxide (9)

The formation of *tert*-butylsulfenic *tert*-butylsulfonic thioanhydride **(6)** by oxidation of the corresponding dithiosulfite **8** implies the formation of *tert*-butylsulfenyl *tert*-butyl *vic*-disulfoxide **(9)** as an intermediate. By analogy with the low temperature detection of *vic*-disulfoxides,[2,3,8] we felt it might be possible to detect this trisulfide analog **9**.

The low temperature oxidation of di-*tert*-butyl dithiosulfite **(8)** was carried out according to our established procedure[3,8] (−60 °C for 12 h). The reaction mixture was filtered and transferred to the NMR spectrometer at the same temperature. The ^{13}C and ^{1}H NMR were recorded at various temperatures from −60 °C to room temperature (Figure 2). Although the spectra obtained are not completely clean, significant amounts of **9** can be detected at −60 °C. Compound **9** is barely stable at this temperature and rapidly decomposes at −50 °C; only traces can be observed at −40°C. As expected, compound **9** is far less stable than its disulfide analog **17**, which was very stable at −40 °C.[3,8] However, clear evidence for such an intermediate could be obtained by comparing its NMR signals and its behavior with the ones of **17**. The ^{13}C NMR signals of **9** could be clearly identified as they are consistent with those of the various di-*tert*-butyl trisulfide−polyoxides[3,8,9] as well as with the ones of **17**.

The presence of the two diastereoisomers of *tert*-butylsulfenyl *tert*-butyl *vic*-disulfoxides **9a,b** could not be defined with certainty due to the small quantities of **9** formed and the complexity of the reaction mixture. The analysis of the spectrum obtained at −60 °C revealed that some starting material **8** (∼30%) was not oxidized under these conditions. Large quantities (∼45%) of unknown compounds could also be detected. The study of the decomposition of **9** from −60 to −40 °C clearly shows that these unknown compounds correspond to the decomposition products of **9**.

Table 1 clearly shows that the signals of the di-*tert*-butyl *vic*-disulfoxide **17** and the trisulfide analog **9** are very similar. In both cases, the *tert*-butyl group attached to the sulfinyl sulfur has its chemical shifts at slightly higher field than the ones in the corresponding oxides **7a** and **7b**. Finally, the chemical shifts observed for the *tert*-butyl group bonded to the sulfenyl sulfur of **9** are slightly lower field than the ones of the corresponding monoxide **8**. These results are consistent with other NMR studies.[3,14] The ^{1}H NMR were very difficult to interpret owing to problems with overlapping signals.

In order to further understand these spectra and to optimize the reaction conditions, this low temperature

(12) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1992**, *14*, 199.
(13) Douglass, I. B.; Norton, R. V. *J. Org. Chem.* **1968**, *33*, 2104.
(14) (a) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1982**, *47*, 4194. (b) Mieloszynski, J. L.; Weber, J. V.; Schneider, M.; Paquer, D.; Boen, M.; Pare, G. *Sulfur Lett.* **1988**, *8*, 27. (c) Freeman, F.; Lee, C. *Magn. Reson. Chem.* **1988**, *26*, 813.

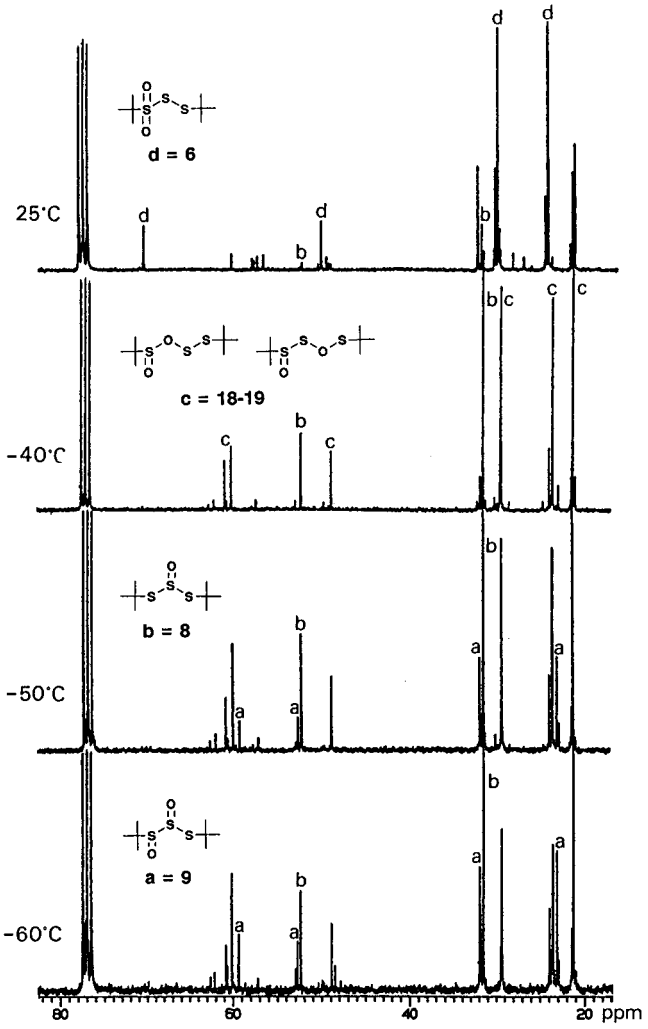


Figure 2. ^{13}C NMR spectra at several temperatures of the product mixture of the *m*-CPBA oxidation of **8**.

Table 1. ^{13}C and ^{1}H NMR Chemical Shifts of 9 and Its Related Derivatives[a,b]

Entry	Compound	Spectra	C	CH_3	H	C'	CH'_3	H'
7a			59.35	24.18	1.530	48.65	32.21	1.351
17[c]			57.08	22.95	1.294			
7b			60.67	23.79	1.385	48.73	29.80	1.390
9[c]		a	59.34	23.06	1.393	52.77	31.91	1.293
8		b	52.10	31.80	1.545			

[a] Recorded using deuterated chloroform ($CDCl_3$) as NMR solvent. [b] Relaxation time (t_1) used: t_1 = 2s. [c] The spectra were obtained at low temperature and do not represent a specific diastereoisomer.

experiment was repeated several times using excess *m*-CPBA (2 equiv), at different temperatures, in a different solvent (CD_2Cl_2), and for various reaction times (4 h to 4 days).

The analysis of these results reveals that the oxidation of monoxide **8** was not even complete using 2 equiv of *m*-CPBA at −60 °C for 4 days. This result points out the lack of reactivity of the substrate at this temperature. At higher temperatures (>−60 °C), no *vic*-disulfoxide **9** can be observed, which emphasizes the low stability of **9**. As mentioned previously, **9** is barely stable at −60 °C, and several decomposition products could be observed. To avoid this stability problem and increase the reactivity of the substrate, the low temperature experiment was attempted using methylene chloride-d_2 which has a lower freezing point (−93 °C) and is more polar than chloroform-*d*. The reaction was carried out at −80 °C but did not afford good results because of low conversion (<30%), variation of the chemical shifts, and overlapping of the solvent and the reaction product peaks. From these results, it was concluded that the temperatures either were too low to allow a suitable conversion of the starting material **8** or too high for **9** to be stable enough to detect.

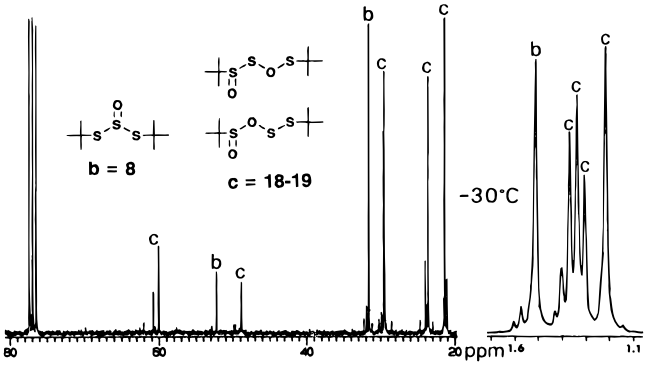


Figure 3. ^{1}H and ^{13}C NMR spectra of intermediates **18** and **19**.

The study of the decomposition of *tert*-butylsulfenyl *tert*-butyl *vic*-disulfoxide **9** is complicated by the remaining starting material and the impossibility of detecting undecomposed **9**. However, the main, final decomposition product (spectrum at room temperature) is **6**, which is consistent with the preparation of **6** (*vide supra*). Analysis of the spectra from −60 °C to room temperature revealed the presence of eight carbon and four proton signals corresponding to four different *tert*-butyl groups. The chemical shifts observed are consistent with an unsymmetrical di-*tert*-butyl diastereomeric derivative or two very closely related unsymmetrical di-*tert*-butyl analogs **18** and **19**. These signals were observable in various ratios up to room temperature (Figure 3).

An NMR comparison of the different classes of di-*tert*-butyl polysulfide−polyoxides[3,8,9] clearly reveals that the chemical shifts of a given *tert*-butyl group can be unambiguously interpreted depending on which sulfur it is bonded to (sulfenyl, sulfinyl, sulfonyl, or sulfinate). This carbon NMR study was used to assign the unknown signals observed in the decomposition of **9**. These unknown chemical shifts and the ranges of the different types of di-*tert*-butyl derivatives are presented in Table 2.

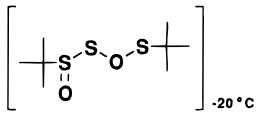
This comparison clearly shows that intermediates **18** and **19** present two different *tert*-butyl groups bonded to a sulfenyl sulfur (~49 and ~29.5 ppm), another one bonded to a sulfinate sulfur (~60 and 21.5 ppm), and finally corresponding to a moiety in between a *tert*-butylsulfinyl and a *tert*-butyl sulfinate (~60 and ~23.5 ppm). Considering that **6** is the main decomposition product and that no diastereoisomer should be observed, the unknown intermediates are believed to be two closely related unsymmetrical di-*tert*-butyl analogs **18** and **19**.

Table 2. ^{1}H and ^{13}C NMR of 18 and 19 and Chemical Shifts Ranges (δ ppm) of the *tert*-Butyl Groups Bonded to Differently Oxidized Sulfur[a]

Compound	C	CH_3	H	C'	CH'_3	H'
18, 19[b]	60.81 60.10	21.36 23.63	1.368 1.337	48.91 48.86	29.56 29.48	1.305 1.217
	60 - 61	21 - 22	1.1 - 1.2			
	59 - 64	24 - 26	1.3 - 1.6			
	68 - 74	23 - 26	1.4 - 1.6			
				48 - 53	29 - 33	1.3 - 1.5

[a] All the spectra were recorded in $CDCl_3$. [b] The spectra were obtained at −60 °C.

Scheme 2



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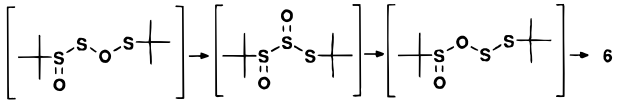
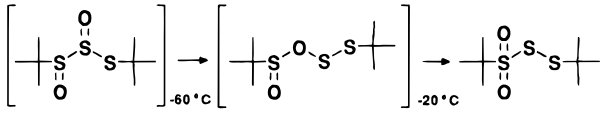
Scheme 3



19 **9** **18a**

Although the structure of these intermediates cannot be determined with certainty, it is clear that **9** is formed under these low temperature conditions and that the final decomposition product is mainly **6**. The structure of **9** is completely consistent with related ^{13}C NMR signals[3b] as well as a logical series of likely intermediates as shown in Scheme 2 and displayed in Figure 2. Therefore, considering the mechanism proposed[3,8] for the decomposition of the di-*tert*-butyl *vic*-disulfoxide **(17)** and according to the previous NMR study, a consistent intermediate would be *tert*-butylsulfinic *tert*-butylthiosulfenic anhydride **(18a)**, which is the expected intermediate of the rearrangement of **9** to **6** (Scheme 2).

The only unsymmetrical *tert*-butyl derivative closely related to intermediate **18a** that would match the required chemical shifts would be the *tert*-butylsulfenic *tert*-butyl thiosulfinic anhydride **(19)**.

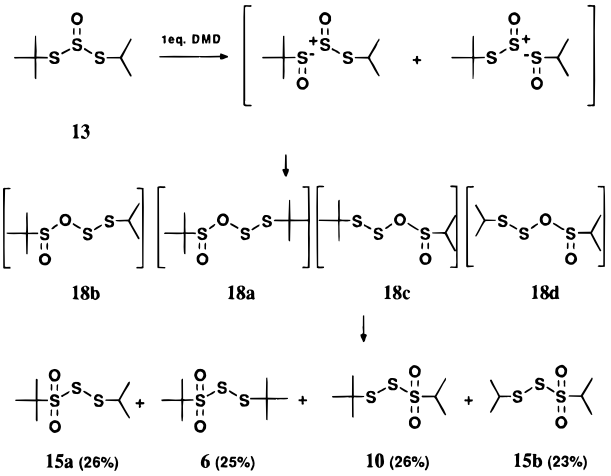


9 **18a** **6**

It is conceivable that intermediate **19** rearranges to give back the *vic*-disulfoxide **9**. At this temperature, **9** would immediately redecompose to a mixture of **18a** and **19**. Considering that intermediate **18a** gives the dioxide **6**, the final decomposition mixture should be mainly composed of **6** (Scheme 3).

The 1-equiv DMD oxidation of *tert*-butyl isopropyl dithiosulfite **(13)** reported above (Scheme 1), afforded an almost equimolar mixture of the two symmetrical and two unsymmetrical possible dioxides **(6, 15b, 10, 15a)**.

Scheme 4



13

18b **18a** **18c** **18d**

15a (26%) **6 (25%)** **10 (26%)** **15b (23%)**

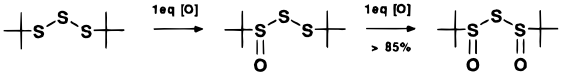
These results can be rationalized by proposing that, under these reaction conditions, both sulfenyl *vic*-disulfoxides **14a** and **14b** are formed. The formation of large quantities of both symmetrical dioxides **6** and **15b** is consistent with the previously proposed cleavage of the S(O)−S(O) bonds,[3,8] and random recombination of ions (less steric hindrance here because of the extra sulfur) should eventually give the four possible sulfinic thiosulfenic anhydrides **18a**−**d** which should rearrange to the four possible **6**, **15b**, **10**, and **15a** (Scheme 4).

It is surprising that small quantities of di-*tert*-butyl *vic*-disulfoxide **(17)** and *tert*-butylsulfinic thioanhydride **(20)** were detected because the di-*tert*-butyl dithiosulfite **(8)** used did not contain any traces of the corresponding polysulfides or polysulfide−monoxides **7a** or **b**. However, the remaining **8** was not stable under these conditions and probably participates in the decomposition of **9**. Considering the complexity of the mechanism reported, it is not unusual that many different di-*tert*-butyl derivatives are observed.

To our knowledge, this is the first detection of a sulfenyl *vic*-disulfoxide. However, the rearrangement of **9** to **6** could not be fully understood because under these conditions the detection of **9** is temperature controlled. Therefore, it considerably limits the decomposition study as other derivatives are always present in the reaction mixture. Low temperature experiments using stronger oxidizing agents such as DMD should afford better results. Unfortunately, we were unable to develop a suitable technique for the low temperature DMD oxidation.

tert-Butylsulfinic Thioanhydride (20)

As we have found,[9] the 1-equiv electrophilic oxidation of *tert*-butylsulfenic *tert*-butylsulfinic thioanhydride **(7b)** and the 2-equiv electrophilic oxidation of di-*tert*-butyl trisulfide **(16b)** afforded a high yield of the diastereomeric di-*tert*-butylsulfinic thioanhydrides **(20)** (eq 5).

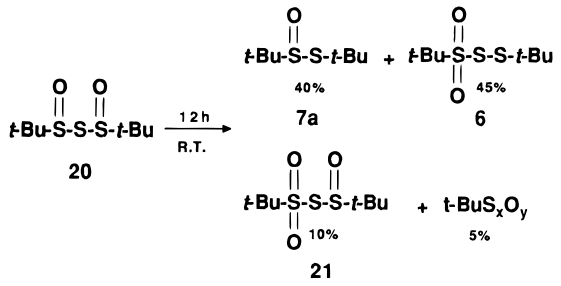


(eq. 5)

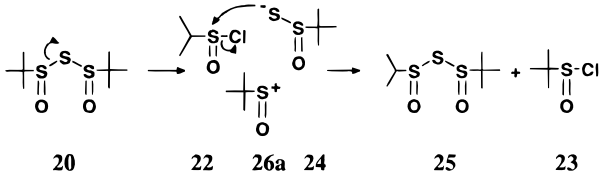
16b **7c** **20**

tert-Butylsulfinic thioanhydride **(20)** is barely stable at room temperature and cannot be kept in the freezer for more than 1 week. The decomposition of **20** was also investigated and afforded a complex mixture. Various

Scheme 5



Scheme 6



attempts under slightly different conditions have shown that the two main decomposition products were the corresponding thiosulfinate **7a** and sulfenic sulfonic thioanhydride **6**. Significant quantities of *tert*-butylsulfinic *tert*-butylsulfonic thioanhydride **(21)** were detected in most cases as well as other di-*tert*-butyl polysulfide−polyoxides (Scheme 5).

In a separate experiment, the decomposition of **20** was carried out in the presence of 1 equiv of isopropylsulfinyl chloride **(22)** as trapping agent. Although the final decomposition mixture was even more complex, *ca.* 40% of *tert*-butylsulfinyl chloride **(23)** could be clearly identified by ^{13}C and ^{1}H NMR. The detection of *tert*-butylsulfinyl chloride **(23)** confirms our current hypothesis[3,8] of ionic cleavage of **20** at the S−S(O) bond. Under these conditions, the *tert*-butyl thiosulfinate anion **(24)** formed can react with isopropylsulfinyl chloride **(22)** to give the unsymmetrical *tert*-butylsulfinic isopropylsulfinic thioanhydride **(25)** and the *tert*-butyl sulfinyl cation **(26a)** can then react with the remaining chloride ion to afford the observed *tert*-butylsulfinyl chloride **(23)** (Scheme 6).

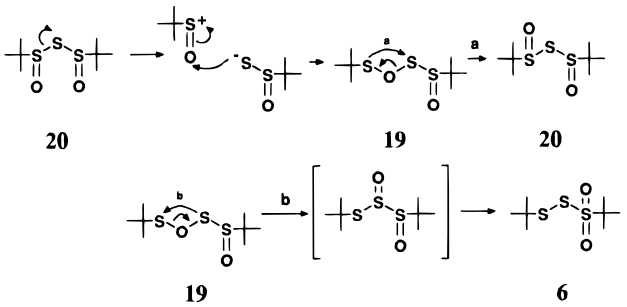
Although compound **25** could not be detected, significant amounts of its decomposition products, isopropylsulfenic *tert*-butylsulfonic thioanhydride **(15b)** and isopropyl *tert*-butylthiosulfonate **(27a)**,[3,13] were identified as well as other derivatives issued from the normal and mixed decompositions.

The results observed in this decomposition study of **20** are even more complex than other systems we have studied.[3,8] Therefore, it is very difficult to give a detailed decomposition mechanism. However, using the mechanistic principles developed in the previous cases,[3,8] these results can be reasonably rationalized.

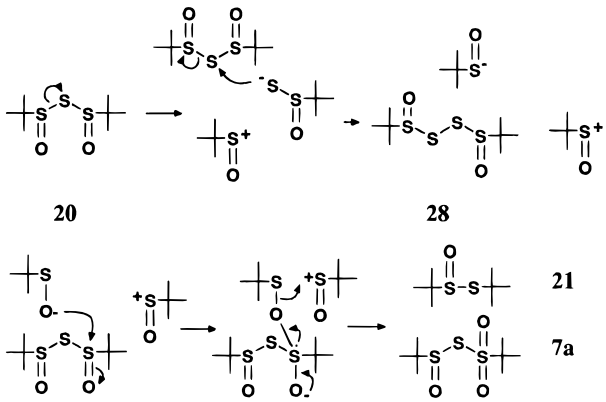
First, good evidence of the cleavage of the S−S(O) bond is given by the formation of *tert*-butylsulfinyl chloride **(23)** (Scheme 6). The presence of **6** (Scheme 7) can be explained by the recombination of these ions to form intermediate **19**. Rearrangement of such an intermediate could give back the starting material **20** or eventually afford the corresponding sulfenyl *vic*-disulfoxide **9** that would immediately be converted to **6**. This theory is suggested because chemical shifts in the region of this type of intermediate such as **19** were detected by NMR (Scheme 7).

Finally, the formation of *tert*-butylsulfinic *tert*-butylsulfonic thioanhydride **(23)** suggests that an oxygen transfer reaction[3,8] also takes place in this case. This

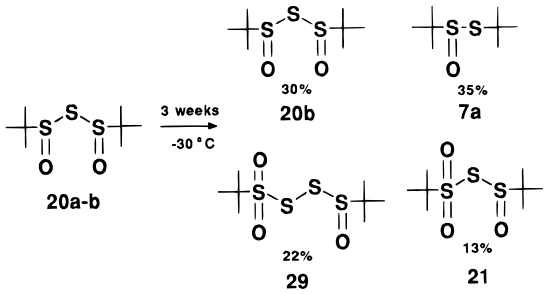
Scheme 7



Scheme 8



Scheme 9

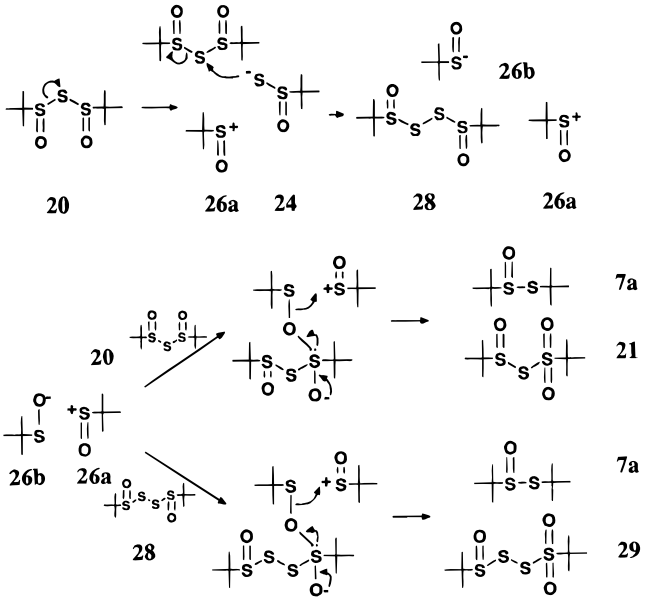


would also account for the formation of thiosulfinate **7a**. The formation of *tert*-butylsulfinic dithioanhydride **(28)** is also possible (low intensity NMR signals in the region of **28** could be detected) (Scheme 8).

As mentioned earlier, *tert*-butylsulfinic thioanhydride **(20)** is not stable at −30 °C when stored in the freezer. The determination of the decomposition products of **20** at this temperature confirmed the previous results. After 3 weeks in the freezer, the decomposition mixture presented 30% of the thermodynamic diastereoisomer **20b**, 35% of **7a**, 22% of *tert*-butylsulfinic *tert*-butylsulfonic dithioanhydride **(29)**,[3b] and 13% of the trisulfide analog **21** (Scheme 9).

This low temperature study allowed the detection of the decomposition intermediates; the ratios and products observed are completely consistent with the mechanism previously proposed. It is clear that the decomposition of **20a,b** proceeds through the ionic cleavage of the S(O)−S bond. The reaction of the anion **24** formed with another molecule of **20** affords **28** and the *tert*-butylsulfinyl anion **(26b)**. The ambident sulfinyl ions **26a,b** formed in the two previous steps react with **28** or **20** by an oxygen transfer reaction[8] affording the corresponding trioxides **29** or **21**, respectively. The difference in reactivity of **28** (22%) and **20** (13%) can be explained by steric

Scheme 10



and electronic effects as the tetrasulfide derivative is less hindered and has an extra sulfur atom (Scheme 10).

A number of different mechanisms can take place, and it is probably a combination of all of them that delivers this rather complex mixture. In addition, products such as **20** and **28** can participate in the decomposition and even further complicate the study. As a consequence, the more stable compounds, dioxide **6** and thiosulfinate **7a**, are the major products observed at room temperature because they are thermodynamically favored.[15]

Experimental Section[8]

X-ray Crystallographic Data for 6. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer using graphite-monochromated Cu Kα (λ = 1.54056 Å) radiation using the $\theta/2\theta$ scan mode.[16]

Oxidized Derivatives of Disulfides. The preparation and characterization of the oxidized derivatives of disulfides mentioned here were previously reported.[3,5,8]

Oxidized Derivatives of Trisulfides. The preparation and characterization of the sulfenic sulfinic thioanhydrides, dithiosulfites, and sulfinic sulfonic thio- and dithioanhydrides mentioned here were previously reported.[3,8]

Synthesis of *tert*-Butylsulfenic *tert*-Butylsulfonic Thioanhydride (6). *m*-CPBA Oxidation of 7b. The oxidation of **7b** (1.09 g, 4.82 mmol) was carried out using *m*-CPBA (−40 °C, 5 h, 1.4 equiv) according to the procedure in ref 8. Compound **6** was formed in 48% yield, mp 58−65 °C (lit.[20] 56.5−62.5 °C).

Attempted Nucleophilic Oxidation of *tert*-Butylsulfenic *tert*-Butylsulfinic Thioanhydride (7b). The oxidation of **7b** (0.4−0.6 g, 1.77−2.65 mmol) was attempted using H_2O_2/1 N NaOH,[17] *t*-BuOOH/1 N NaOH,[17] KO_2,[17] $KMnO_4$,[18] and $NaIO_4$[11] according to literature procedures. In all cases, the final products were a mixture of di-*tert*-butyl di-, tri-, and tetrasulfides that were characterized by NMR spectrometry and GC analysis.

***m*-CPBA Oxidation of Di-*tert*-butyl Dithiosulfite (8)**. A solution of *m*-CPBA (990 mg, 5.75 mmol, 1.4 equiv) in methylene chloride (25 mL) was added dropwise to a cooled solution (−40 °C) of **8** (0.93 g, 4.11 mmol) in CH_2Cl_2 (15 mL) during 0.5 h under nitrogen. After a stirring period of 5 h at −40 °C, the mixture was concentrated to 10 mL by rotoevaporation. The solution was cooled to −78 °C, and the *m*-CBA that crystallized was collected. The solvent was removed *in vacuo* to give an oily residue. Silica gel column chromatography using a 10% ethyl acetate/hexanes solution afforded the desired **6** (0.48 g, 1.97 mmol, 48%) as a colorless solid: mp 58−65 °C (lit.[19] 56.5−62.5 °C) (it is likely that **6** decomposes near the melting point); ^{1}H NMR ($CDCl_3$) δ 1.465 (s, 9H), 1.395 (s, 9H), ppm; ^{13}C NMR ($CDCl_3$) δ 70.06, 49.95, 29.86, 24.18 ppm;[20] MS (EI, 70 eV, 30 °C) *m/z* (rel int) 242 ($M^{\bullet+}$, 0.4), 178 ($M^{\bullet+} - S(O)_2$, 6.6), 122 (*t*-Bu$S(O)_2^{\bullet+}$, 14), 90 ($C_4H_{10}S^{\bullet+}$, 16), 64 ($S(O)_2$, 20), 57 (*t*-Bu^+, 100), 41 ($C_3H_5^{\bullet+}$, 46).

Peracetic Acid Oxidation of Di-*tert*-butyl Dithiosulfite (8). The oxidation of **8** (1.09 g, 4.82 mmol) was carried out using CH_3CO_3H (40%) (−20 °C, 5 h, 1.4 equiv) according to the procedure described above. The solvent was removed *in vacuo*, and silica gel column chromatography using a 10% ethyl acetate/hexanes solution gave **6** (0.41 g, 1.69 mmol, 35%) as a colorless solid. Analytical data were consistent with previously reported values.

DMD Oxidation of Di-*tert*-butyl Dithiosulfite (8). A 0.05 M solution of DMD in acetone (104 mL, 5.20 mmol, 1.2 equiv) was added dropwise to a cooled solution (−78 °C) of **8** (0.98 g, 4.33 mmol) in acetone (10 mL) during 30 min under nitrogen. After a stirring period of 2 h at −78°C, the solvent was removed *in vacuo* to give **6** (0.89 g, 3.68 mmol, 85%) as a colorless solid. Analytical data were consistent with previously reported values.

Decomposition of *tert*-Butylsulfenic *tert*-Butylsulfonic Thioanhydride (6). The decomposition of **6** (87 mg, 0.36 mmol) in $CDCl_3$ was followed by ^{1}H and ^{13}C NMR at room temperature. After 6 months under these conditions no decomposition occurred. The decomposition of **6** (198 mg, 0.82 mmol) at 80 °C in CCl_4 gave di-*tert*-butyl disulfide **(16a)** as the sole product after 15 h (identified by NMR and GC). The condenser employed was equipped with a trap of wet pH paper. Clear evidence of sulfur dioxide evolution was given by the strongly acidic coloration of the pH paper by the end of the decomposition.

Synthesis of *tert*-Butylsulfinic Thioanhydride[9] (20). *m*-CPBA Oxidation of Di-*tert*-butyl Trisulfide (16b). Compound **16b** (0.53 g, 2.52 mmol) was oxidized using *m*-CPBA (12 h, −40 °C, 2.5 equiv) according to the procedure previously described. The solvent was removed at −10 °C *in vacuo* (2.5 mmHg) using a dry ice condenser rotoevaporator to give an oily residue. Compound **20** (0.58 g, 2.42 mmol, 96%) crystallized from *n*-pentane in the freezer: mp 60−85 °C (it is likely that **20** decomposes near the melting point). ^{1}H and ^{13}C NMR chemical shifts are reported in the literature.[9] Compound **20** was not stable enough to give consistent results on MS.

Synthesis of *tert*-Butylsulfonic *tert*-Butylsulfinic Thioanhydride (21). Compound **21** was prepared according to the general oxidizing conditions summarized in ref 8 using *m*-CPBA. The solid was crystallized from pentane as colorless needles, mp 80−100 °C (probably decomposed before its

(15) We thank a reviewer for a thoughtful suggestion concerning a mechanism to explain the complex product formation of **8** and **13**; it involved a bimolecular process. A "Steven's"-type of reaction was portrayed involving a series of 1,2 shifts and a cross thioalkylation using RSO_2S^-. We cannot easily carry out kinetics on these systems; however, for a related molecule (the 1-oxide), the kinetics suggest a unimoleulcar process (ref 8) and the formation of two oppositely charged, ambident anions. That such anions are involved is not without literature precedent; see ref 3a as well as: Schreiner, P. R.; Schleyer, P. v. R; Hill, R. K. *J. Org. Chem.* **1993** *58*, 282. Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1994**, *59*, 1849.

(16) The authors have deposited atomic coordinates for **6** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(17) Adams, W.; Hass, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.

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(19) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3929.

(20) For comparative NMR values of related structures see refs 3b, 8, and 10.

melting point). MS (CI (NH_3), 70 eV, 100 °C) *m/z* (rel int) 276 ($M(NH_4)^+$, 4.6; X-ray crystallographic analysis confirmed the structure.[21]

DMD Oxidation of Di-*tert*-butyl Trisulfide (16b). Compound **16b** (0.53 g, 2.52 mmol) was oxidized using DMD (0.05 M) (1.5h, −78 °C, 2.1 equiv) according to the procedure described above. The solvent was removed at 0 °C *in vacuo* (2.5 mmHg) to give di-*tert*-butyl trisulfide 1,3-dioxide **(20)** as a solid (0.60 g, 2.47 mmol, 98%): mp 60−85 °C (**20** probably decomposed before it reached its melting point). Analytical data were consistent with previously reported values.

Decomposition of *tert*-Butylsulfinic Thioanhydride (20). The decomposition of **20** (87 mg, 0.36 mmol) in $CDCl_3$ was followed by ^1H and ^{13}C NMR at room temperature. After 12 h no traces of **20** could be detected. The decomposition products were identified by ^1H and ^{13}C NMR as a mixture of **6** (45%), **7a** (40%), **21** (10%),[3b] and other undefined *tert*-butyl derivatives (3%).

Preparation of *tert*-Butylsulfenic *tert*-Butylsulfinic Dithioanhydride (7c). The oxidation of di-*tert*-butyl tetrasulfide **(16c)** (1.05 g, 4.34 mmol) was carried out using *m*-CPBA (0 °C, 2 h, 1.2 equiv) according to the procedure described above. The solvent was removed *in vacuo* to give an oily residue that was chromatographed on alumina using a 13% ethyl acetate/hexanes solution to give **7c** (0.82 g, 3.17 mmol, 73%) as a solid: mp 65−68 °C (lit.[4] 68−78 °C); ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H) 1.32 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 60.60, 49.91, 29.76, 23.82 ppm.

DMD Oxidation of *tert*-Butyl Isopropyl Dithiosulfite[8] (13). The DMD (0.05 M, −78 °C, 1.2 equiv) oxidation of **13** (1.053 g, 4.97 mmol) was carried out according to procedure 3.[8] After evaporation of the solvent, the crude mixture was analyzed by ^1H and ^{13}C NMR and presented a close to equimolar mixture of the four possible symmetrical and unsymmetrical sulfenyl sulfonyl thioanhydrides, **15a** (26%), **6** (25%), **10** (26%), and **15b** (23%). These percentages were estimated from the crude NMR spectrum according to the calibration experiments reported earlier. Silica gel chromatography using 10% ethyl acetate/hexanes as eluent gave a mixture of **15a** (85%) and **6** (15%) as a first fraction and **10** (83%) and **15b** (17%) as second fraction. The similarity of the ^{13}C NMR signals between the symmetrical and unsymmetrical trisulfide−dioxides and the previous characterization of one of the two derivatives in each fraction allowed a clear NMR characterization of the unknown trisulfide−dioxides. **15a**: ^1H NMR ($CDCl_3$) δ 3.38 (h, 1H), 1.48 (s, 9H), 1.39 (d, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ: 70.28, 43.32, 24.02, 21.92 ppm. **15b**: ^1H NMR ($CDCl_3$) δ 3.36 (h, 1H), 3.58 (s, 1H), 1.41 (d, 6H), 1.36 (d, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 60.30, 42.88, 21.92, 16.36 ppm. Compound **15a** was also isolated from the decomposition of **20** in the presence of isopropylsulfinyl chloride **(22)**.[8]

Preparation of *tert*-Butylsulfinic Dithioanhydride (28). The oxidation of di-*tert*-butyl tetrasulfide **(16c)** (0.50 g, 2.06 mmol) was carried out using *m*-CPBA (−40 °C, 6 h, 2.2 equiv) according to the procedure described above. The solvent was removed at low temperature (−20 °C) under high vacuum (2.5 mmHg) to give a diastereomeric mixture of **28** (0.53 g, 1.96 mmol, 95%) as a pale yellow solid that was recrystallized in the freezer from a 5% CH_2Cl_2/*n*-pentane solution: mp 70−80 °C (**28** probably decomposed before reaching its melting point) (lit.[4] mp 68−78 °C); ^1H NMR ($CDCl_3$) δ 1.41 (s, 9H) 1.37 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 61.51, 61.20, 23.77, 23.50 ppm.

Preparation of *tert*-Butylsulfenic Isopropylsulfonic Thioanhydride (10). Isopropyl sulfonyl chloride **(12)** was most conveniently prepared according to the Douglass procedure[13] using 4 equiv of acetic anhydride. A solution of isopropylsulfonyl chloride **(12)** (0.257 g, 1.81 mmol) in 15 mL of ether was added dropwise over a 1 h period under nitrogen to an ice-cooled solution of *tert*-butyl hydrodisulfide **(11)**[12] (0.221 g, 1.81 mmol) and pyridine (0.160 g, 2 mmol) in 25 mL of ether. After a stirring period of an additional 5 h at room temperature, the reaction mixture was washed with 2 × 25 mL portions of water, 3 × 25 mL portions of 1 N NaOH solution, and 25 mL portions of water until neutral to pH paper. The organic phase was separated, dried with $MgSO_4$, filtered, and evaporated. The solvent was removed *in vacuo* to give an oily residue that was chromatographed on silica gel using a 13% ethyl acetate/hexanes solution to give **10** (0.090 g, 0.39 mmol, 22%) as a liquid. The first fraction was *tert*-butyl tetrasulfide **(16c)** (65%). **10**: ^1H NMR ($CDCl_3$) δ 3.52 (h, 1H), 1.42 (d, 6H), 1.38 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 61.85, 50.17, 30.34, 17.02 ppm; MS (CI, 70 eV, 100 °C) *m/z* (rel int) 246 $(M + NH_4)^+$, 100.0), all the other peaks have an intensity less than 3%.

Decomposition of *tert*-Butylsulfinic Thioanhydride (20) in the Presence of 1 Equiv of Isopropyl Sulfinyl Chloride (22). The decomposition of a solution **20** (300 mg, 1.24 mmol) and isopropylsulfinyl chloride **(22)** (156 mg, 1.24 mmol, 1 equiv) in 10 mL of $CHCl_3$ was carried out at room temperature for 12 h. The ^1H and ^{13}C NMR of the crude mixtures clearly revealed the formation of *tert*-butylsulfinyl chloride **(23)**[13] (∼40%). The partial separation of the reaction mixtures by silica gel chromatography and the careful analysis of the crude NMR spectra allowed the detection of the decomposition products of **20** and the mixed decomposition.

Low Temperature Detection of *tert*-Butylsulfenyl *tert*-Butyl *vic*-Disulfoxide (9). The oxidation of di-*tert*-butyl dithiosulfite **(8)** (170 mg, 0.75 mmol) dissolved in 0.5 mL of dry $CDCl_3$ was achieved by the slow addition of pure anhydrous *m*-CPBA (>99%) (194 mg, 1.12 mmol, 1.5 equiv) partially dissolved in 2.5 mL of $CDCl_3$. After 4 days at −60 °C the reaction mixture was treated as described in the literature.[8] The NMR spectra are given in Table 2.

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Supporting Information Available: NMR spectra of compound **10** as well as X-ray data of compound **6** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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