Synthesis and Decomposition of Tri- and Tetraoxide Derivatives of Dialkyl Trisulfides

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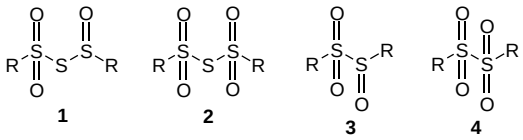
The first isolation and characterization of sulfinyl sulfonyl thioanhydride **1** and its tetrasulfide analog are presented here, along with those of disulfonyl thio- and dithioanhydrides **2**. The oxidation of various substrates at different temperatures has shown that, contrary to current belief, oxidation takes place regiospecifically at the external sulfinyl sulfur rather than at the internal sulfenyl sulfur. The decomposition of these compounds has also been investigated and was found to be consistent with the mechanism proposed for the decomposition of trisulfide monoxides.

The chemistry of trisulfide polyoxide derivatives[1] such as sulfinyl sulfonyl thioanhydride **1** and disulfonyl thioanhydride **2** has received very little attention.[2] To our

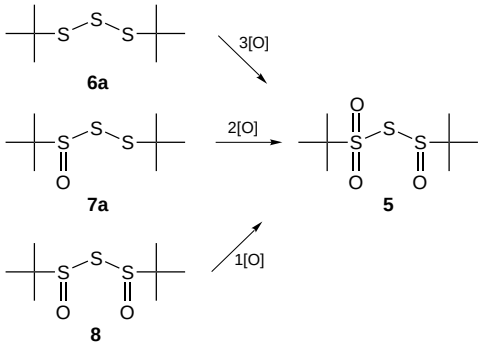


knowledge, no sulfinyl sulfonyl thionahydride derivatives have ever been reported. In contrast, the preparation, characterization, and properties of their disulfide analogs **3** and **4** have been investigated, but the study was somewhat limited by the low stability of this class of compounds.[3]

The synthesis of symmetric disulfonyl thioanhydrides **2** (ethyl, propyl, isopropyl, and *n*-butyl) has been reported using excess hydrogen peroxide.[2a]

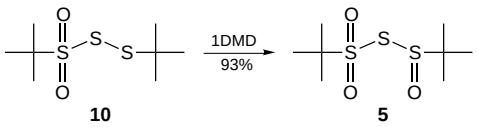
***tert*-Butylsulfinyl *tert*-Butylsulfonyl Thioanhydride (5).** The preparation of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) was achieved by electrophilic oxidation of the corresponding trisulfide **6b**, sulfenyl sulfinyl thioanhydride **7b**, and disulfinyl thioanhydride **8** using 3, 2, and 1 equiv of oxidant, respectively. Although compound **5** could not be separated by column chromatography, pure **5** could be obtained in high yield by recrystallization when the exact number of equivalents of oxidizing agent was employed (*m*-CPBA, dimethyldioxirane, and peracetic acid) (Scheme 1).

Scheme 1



The characterization of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) was carried out by the use of NMR spectroscopy and mass spectrometry. Recrystallization of **5** from *n*-pentane afforded colorless prisms that were suitable for X-ray analysis. Figure 1 represents the ORTEP drawing of **5** and Table 1 its atomic coordinates and temperature factors. The S(O)−S bond is 0.04 Å longer than the $S(O)_2$−S bond, and the lengths of the S−O bonds (1.39−1.43 Å) of the sulfonyl moiety are shorter than expected.

To our knowledge, the isolation of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) is the first example of this class of compounds. The structure of the molecule



(1)

and the NMR data reported for this trioxide **5** are consistent with the ones of the other di-*tert*-butyl polysulfide polyoxides.[4] However, the mechanism of formation of **5** remains unclear as we do not know whether the oxidation occurs at the external sulfinyl sulfur affording **5** directly or at the central sulfenyl sulfur eventually giving **5** by rearrangement of intermediate **9**. In a separate experiment, a high yield of **5** was obtained by the 1 equiv electrophilic oxidation of the *tert*-butylsulfenyl *tert*-butylsulfonyl thioanhydride **10** (eq 1).

By analogy with other oxidations of polysulfides,[5,6] the electrophilic oxidation of **8** is regiospecific and only

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(1) 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 trithiolane 2-oxide derivative (ref 12). We have used the thioanhydride approach, even though there are less correct, but clearer names available.

(2) (a) Feher, F.; Shaefer, K. H.; Becher, W. Z. *Naturforsch., B: Anorg. Chem.. Org. Chem.* **1962**, *17B*, 847. (b) Steudel, R.; Latte, J. *Chem. Ber.* **1977**, *110*, 423. (c) Steudel, R. *Phosphorus Sulfur* **1985**, *23*, 3.

(3) (a) Smiles, S.; Gibson, D. T. *J. Chem. Soc.* **1924**, *125*, 176. (b) Cymerman, J.; Willis, J. B. *J. Chem. Soc.* **1951**, 1331. (c) Bredereck, H.; Wagner, A.; Beck, H.; Klein, R. G. *Ber. Dtsch. Chem. Ges.* **1951**, *93*, 2736. (d) Allen, P., Jr.; Brook, J. W. *J. Org. Chem.* **1962**, *27*, 1019. (e) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898. (f) Kice, J. L.;Guaraldi, G. *J. Am. Chem. Soc.* **1966**, *88*, 5236. (g) Denzer, G. C., Jr.; Allen, P., Jr.; Conway, P.; Van Der Veen, J. M. *J. Org. Chem.* **1966**, *31*, 3418. (h) Kice, J. L.; Ikura, K. *J. Am. Chem. Soc.* **1968**, *90*, 7378. (i) Kice, J. L.; Venier, C. G.; Large, G. B.; Heasley, L. *J. Am. Chem. Soc.* **1969**, *91*, 2028; (j) Kice, J. L.; Favstritsky, N. *J. Org. Chem.* **1970**, *35*, 114. (k) Farng, L.-P. O.; Kice, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1137.

(4) Derbesy, G. Ph.D. Thesis, McGill University, Montreal, 1994.

(5) (a) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 1044. (b) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 4468. (c) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1996**, *61*, 991.

(6) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1995**, *19*, 1.

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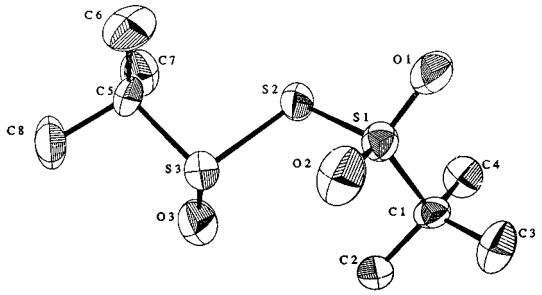


Figure 1. Selected parameters for **5**: S−(S=O), 2.136 Å; S−SO_2, 2.095 Å; S=O of SO_2, 1.427 and 1.393 Å; S=O, 1.490 Å; S−S−S angle, 100.23°; dihedral S−S−S−C angles, 142.6 and −92.8°.

Table 1. Atomic Coordinates (*x*,*y*,*z*) for Non-Hydrogen and Hydrogen Atoms and Temperature Factors (B_{eq}, All Non-Hydrogen Atoms; B_{iso}, All Hydrogen Atoms) of Compound 5

Calculated Non-Hydodrgen Atomic Coordinates and Temperature Factors

	x	*y*	*z*	B_{eq}[a]
S 1	0.7032(4)[b]	0.23381	0.46768(23)	3.90(11)
S 2	0.5309(4)	0.2429(3)	0.25631(22)	4.18(11)
S 3	0.7823(4)	0.1728(3)	0.1313(3)	4.62(12)
O 1	0.5213(11)	0.2279(9)	0.5587(6)	5.8(4)
O 2	0.8654(14)	0.1490(9)	0.4696(8)	6.8(4)
O 3	0.8809(12)	0.2650(9)	0.0485(7)	7.3(4)
C 1	0.8492(15)	0.3680(9)	0.5031(10)	3.2(4)
C 2	1.0129(19)	0.3866(11)	0.3911(12)	5.5(5)
C 3	0.6675(16)	0.4584(10)	0.4988(11)	4.6(5)
C 4	0.9746(20)	0.3559(11)	0.6562(11)	5.8(6)
C 5	0.5824(17)	0.0951(11)	−0.0024(10)	4.3(5)
C 6	0.4195(16)	0.1739(12)	−0.0849(10)	5.2(5)
C 7	0.7478(19)	0.0409(12)	−0.1022(12)	6.2(6)
C 8	0.4630(21)	0.0074(10)	0.0815(12)	6.1(6)

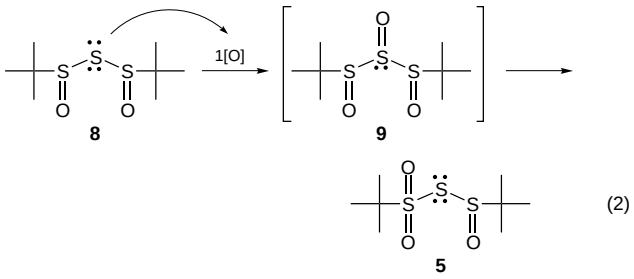
Calculated Hydrogen Atomic Coordinates[c] and Temperature Factors

	x	*y*	*z*	B_{iso}[d]
H 2A	0.938	0.384	0.278	6.6
H 2B	1.053	0.473	0.388	6.6
H 2C	1.130	0.316	0.396	6.6
H 3A	0.788	0.526	0.508	5.4
H 3B	0.554	0.477	0.402	5.4
H 3C	0.551	0.447	0.582	5.4
H 4A	1.072	0.279	0.665	6.5
H 4B	0.848	0.327	0.723	6.5
H 4C	1.047	0.437	0.682	6.5
H 6A	0.321	0.141	−0.181	6.1
H 6B	0.501	0.246	−0.130	6.1
H 6C	0.280	0.191	−0.022	6.1
H 7A	0.870	0.093	−0.157	7.1
H 7B	0.867	−0.011	−0.043	7.1
H 7C	0.661	0.029	−0.213	7.1
H 8A	0.342	0.031	0.156	7.1
H 8B	0.590	−0.041	0.144	7.1
H 8C	0.353	−0.055	0.023	7.1

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid. [b] ESD's are in parentheses. [c] Hydrogen positions calculated assuming C−H distances of 1.08 Å. [d] B_{iso} (H) comes from $U_{iso}(H) = U_{eq}(C) + 0.01$.

delivers **5** in high yield. According to current thinking, the peracid oxidation of **8** should take place at the sulfenyl central sulfur which is believed to be more electron rich than the sulfinyl external sulfur[7] (eq 2).

To confirm this hypothesis, the 1 equiv *m*-CPBA oxidation of di-*tert*-butylsulfinyl thioanhydride (**8**) was followed by ^{1}H and ^{13}C NMR at low temperature. The

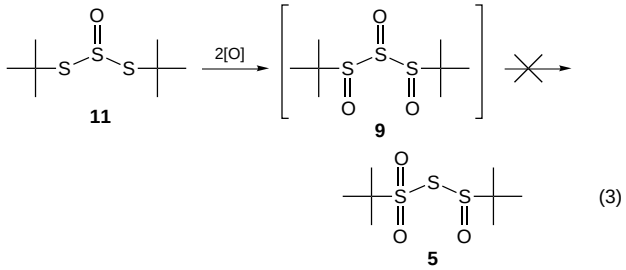


(2)

reaction was carried out at −40 °C, and the 50% conversion NMR spectrum was recorded at the same temperature according to the low-temperature technique previously reported[4,5] (Figure 2). The analysis of these three spectra clearly shows that pure **8** is slowly converted to the trioxide **5** (spectrum −40 °C) and that the complete reaction mainly affords **5** (Table 2).

In contrast with previously reported low-temperature experiments,[4,5] the reaction mixture obtained at −40 °C is very clean and no intermediates can be detected. Therefore, if the reaction was taking place at the central sulfur, the very reactive di-*tert*-butyl *vic*-trisulfoxide (**9**) should be formed and would then rearrange to the corresponding trioxide **5**. By analogy with our previous work,[5] the spectra recorded at −40 °C should at least show the presence of some intermediate if **9** was not stable enough at this temperature. In addition, all the reactions that involve a rearrangement of this type[4,5,8] give complex mixtures of final products in contrast with the results observed here.

To confirm this rearrangement hypothesis, the low-temperature detection of the *vic*-trisulfoxide **9** has been attempted by the 2 equiv *m*-CPBA oxidation of di-*tert*-butyl dithiosulfite (**11**). According to our results,[5c] it was



(3)

[O] = *m*-CPBA ($CDCl_3$, –60 °C, 6 h)
[O] = DMD (acetone, <–80 °C, 5 h)

clear that **9** would be very difficult to detect. The formation of intermediate **9** is more favored in this case than it is in the oxidation of **8**. The external sulfur atoms have been shown in a variety of substrates[5,6,8] to be much more reactive toward electrophilic oxidizing agents than the corresponding internal sulfur atom. Therefore, if any *vic*-trisulfoxide **9** would exist, it has a greater chance to be formed by the oxidation of **11** than by the oxidation of **8**. However, no trace of trioxide **5** has ever been detected in the oxidation of **11** (eq 3). In addition, if the oxidation of **8** proceeded through the formation of intermediate **9**, compound **9** should rearrange cleanly and rapidly to the corresponding **5** as shown by the low-temperature NMR study.

(7) Freeman, F.; Ma, X.-B.; Lin, R. I.-S. *Sulfur Lett.* **1993**, *15*, 253.

(8) Highlights of the most interesting results can be found in the following: (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.

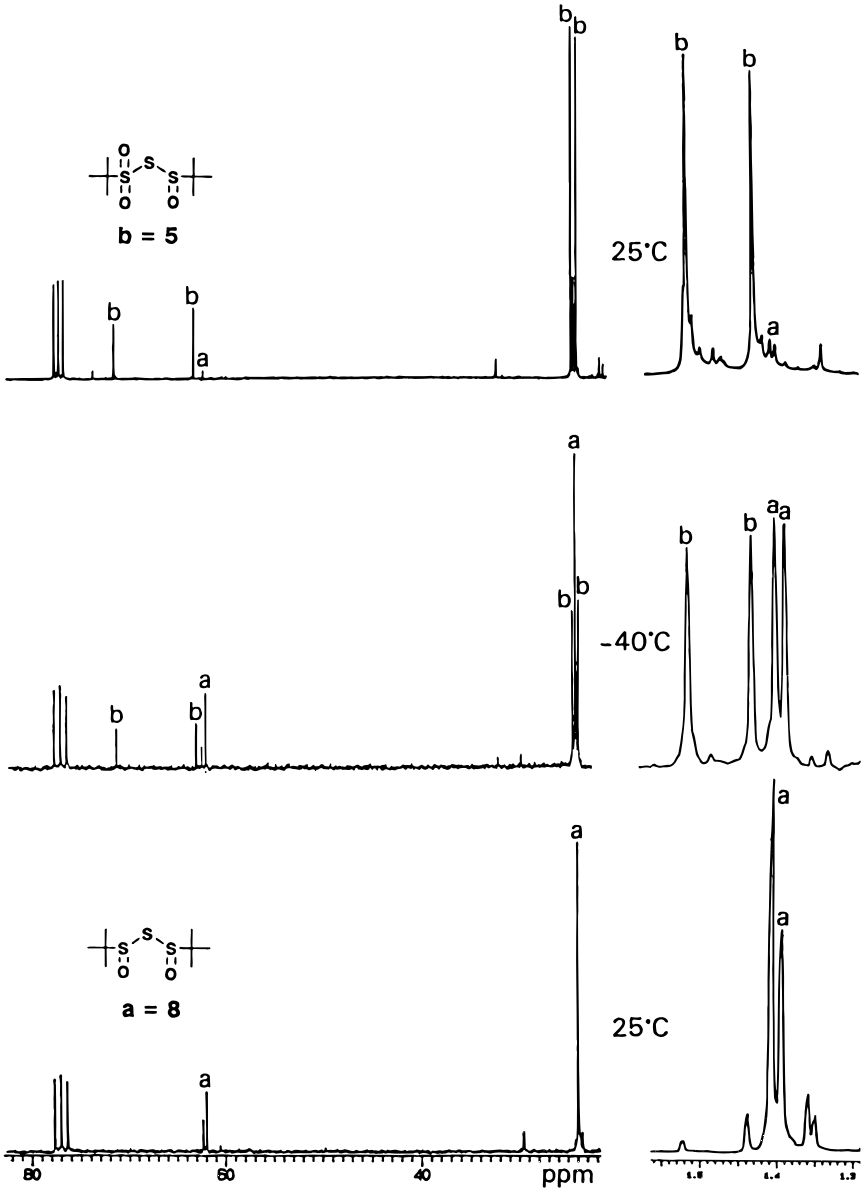
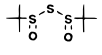
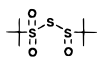


Figure 2. ^{13}C and ^{1}H NMR spectra of the conversion of **8** to **5** at various temperatures.

Table 2. ^{1}H and ^{13}C NMR Chemical Shifts (δ ppm) of 8 and 5[a,b]

Entry	Compound	Spectra	C	CH_3	H	C'	CH'$_3$	H'
8a		a	62.39	24.17	1.410			
8b			62.02	24.18	1.422			
5		b	71.38	23.99	1.551	63.08	24.51	1.463

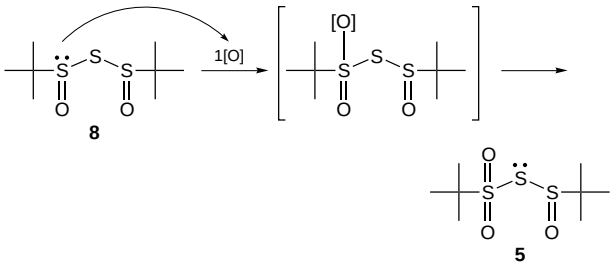
[a] Recorded using deuterated chloroform ($CDCl_3$) as NMR solvent. [b] Relaxation time (t_1) used: t_1= 2 s. [c] **8a** and **8b** represent the two diastereoisomers of **8**.

The low-temperature oxidation of di-*tert*-butyl dithiosulfite **(11)** has been carried out under the exact same conditions as for the one reported for the detection of *tert*-butylsulfenyl *tert*-butyl *vic*-disulfoxide (α-disulfoxide)[5c] (**12**) (−60 °C, $CDCl_3$, 6 h). Considering the results reported for the detection of **12**, it would be surprising to find any *vic*-trisulfoxide **9** as the corresponding disulfoxide **12** even less reactive toward the oxidizing agent than **11** and to find the trisulfoxide **9** formed less stable than **12** at this temperature. As expected, no clear NMR signals of **9** could be detected under these specific conditions. Several other oxidation experiments at various temperatures, using different oxidizing agents, for various reaction times concluded similarly. The extreme conditions were the 2.5 equiv DMD oxidation of di-*tert*-butyl dithiosulfite (**11**) at −78 °C for more than 5 h. Even under these conditions, no trace of **5** could be detected in the final reaction mixture (eq 3).

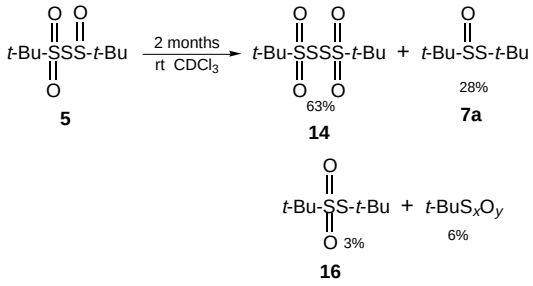
A careful analysis of these results suggests that di-*tert*-butyl dithiosulfite **(11)** was completely oxidized to its *vic*-disulfoxide analog **12** as no more **11** could be detected. At this temperature, we have found **12** to be barely stable.[5c] The fact that no trace of **12** could be observed suggests that it might have reacted with the excess *m*-CPBA to give the corresponding *vic*-trisulfoxide **9** that readily decomposed at this temperature. Although the final decomposition mixture was very complex, no trace of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) was detected.

The detection and rearrangement of intermediate **9** is far from being solved, and considering the results obtained for the *vic*-disulfoxide analog **12**, it will be difficult

Scheme 2



Scheme 3

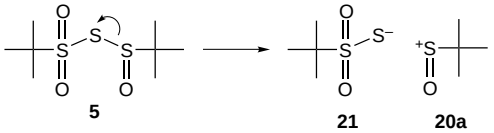


to resolve this problem. However, the main objective was to show that the formation of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) proceeds through the electrophilic oxidation of the external sulfinyl sulfur rather than the internal sulfenyl sulfur. Clear evidence of such a mechanism has been obtained in the present study (Scheme 2).

As mentioned earlier, *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**) is not very stable at room temperature (less than 2 weeks). However, it is much more stable than its disulfide analog **13**.[5,8] The presence of an extra sulfur probably reduces the steric hindrance of the molecule, and **5** is, therefore, more stable than **13**. Silica gel chromatography and a careful analysis of the NMR spectrum of the reaction mixture of the decomposed **5** revealed the presence of several final products. The decomposition of **5** was found to be cleaner than that of most of the other derivatives.[4,5,8] The major product is di-*tert*-butylsulfonyl dithioanhydride (**14**). Moderate quantities of di-*tert*-butyl thiosulfinate (**7a**) were detected, as well as small amounts of di-*tert*-butylsulfonyl thioanhydride (**15**), di-*tert*-butyl thiosulfonate (**16**), *tert*-butyl sulfinic acid (**17**), and *tert*-butyl sulfonic acid (**18**), plus traces of another undefined di-*tert*-butyl derivative believed to be *tert*-butyl sulfonic anhydride **(19)** (*vide infra*) (Scheme 3).

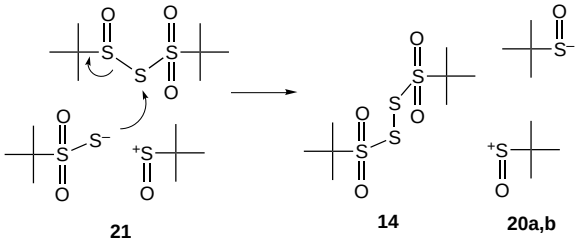
The mechanism proposed for the decomposition of sulfenyl sulfinyl thioanhydrides[5] can be applied to the decomposition of **5**, and most of the products can be rationalized.

By analogy with the previous decomposition studies,[4,5,8] the ionic cleavage of a molecule of **5** should afford the *tert*-butyl sulfinyl cation (**20a**) and the *tert*-butyl thiosulfonate anion **(21)** as the S(O)−S is the longest bond of the S−S linkages[4] (eq 4a).



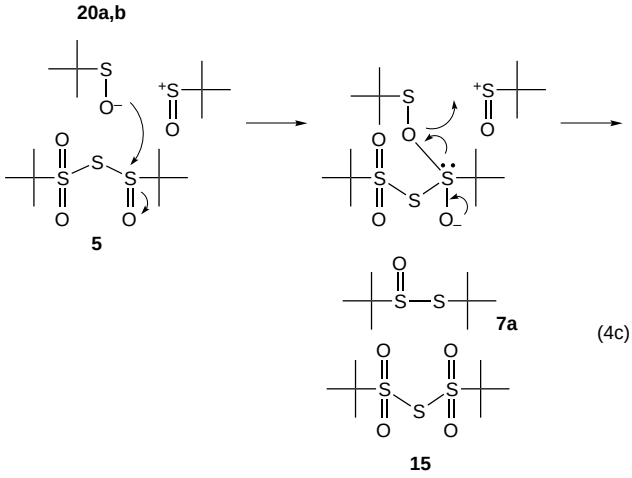
(4a)

The *tert*-butyl thiosulfonate anion (**21**) can react with another molecule of **5** to eventually give the tetraoxide **14** and the *tert*-butyl sulfinyl anion (**20b**) (eq 4b).



(4b)

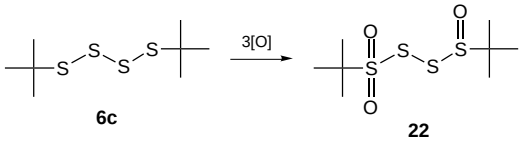
At that point, the ambident *tert*-butyl sulfinyl ions **20a,b** can react with each other and give di-*tert*-butyl thiosulfonate (**16**) or they can react with another molecule of trioxide **5** according to the oxygen transfer mechanism reported earlier and then afford **15** and **7a**. As discussed previously,[5] the oxygen transfer reaction is favored over the formation of thiosulfonate **16** because of steric effects. However, in this case compound **5** is also somewhat hindered, and there is competition between the two paths as small quantities of **16** are observed (eq 4c).



(4c)

The di-*tert*-butylsulfonyl thioanhydride (**15**) formed is not stable under these conditions and gives the tetrasulfide analog **14** and the presumed sulfonic anhydride **19** (*vide infra*). The formation of sulfinic acid **17** and sulfonic acid **18** is explained by the reaction of the ambident ions **20a,b** with the remaining *m*-CBA.[4,8]

The synthesis of *tert*-butylsulfinyl *tert*-butylsulfonyl dithioanhydride **(22)** has also been achieved. Di-*t*-butyl tetrasulfide (**6c**) was oxidized using 3 equivalents of *m*-CPBA and gave a fair yield (88%) of **22** (eq 5). The



(5)

analysis of the crude mixture showed that the reaction was very clean. By analogy to the trisulfide analog **5**, the formation of **22** is expected to proceed by oxidation at a sulfinyl sulfur. If the internal sulfenyl sulfur was oxidized, compound **22** would be obtained by the rearrangement of a very reactive *vic*-disulfoxide. In all cases studied here[4,5] and reported in the literature,[8] such rearrangements are not clean and always deliver at least traces of sulfinic and sulfonic acids **17** and **18** that could not be detected in the preparation of **22**.

The synthesis of di-*tert*-butylsulfonyl thioanhydride (**15**) has been achieved by direct oxidation of various

Scheme 4

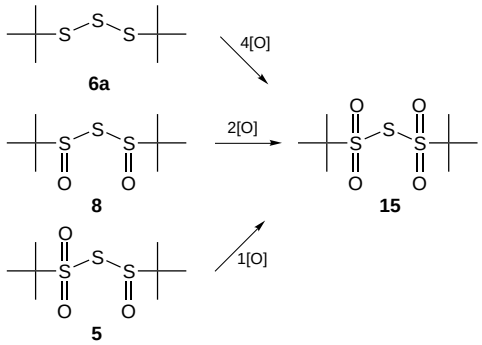


Table 3. Atomic Coordinates (*x,y,z*) for Non-Hydrogen and Hydrogen Atoms and Temperature Factors (B_{eq}, All Non-Hydrogen Atoms; B_{iso}, All Hydrogen Atoms) of Compound 15

	x	*y*	*z*	B_{eq}[a]
S 1	3/4	0.35712(12)	1/4	3.98(6)
S 2	0.93492(10)[b]	0.24154(9)	0.24868(6)	3.67(5)
O 1	0.9051(3)	0.12219(23)	0.20639(19)	4.83(12)
O 2	1.0361(3)	0.3229(3)	0.19891(20)	5.51(14)
C 1	0.9903(4)	0.2257(3)	0.3792(3)	3.76(16)
C 2	0.8759(6)	0.1496(6)	0.4336(3)	5.50(24)
C 3	1.0106(7)	0.3559(5)	0.4239(4)	6.1(3)
C 4	1.1306(5)	0.1517(6)	0.3742(4)	5.53(24)
H 2A	0.906(5)	0.137(4)	0.498(5)	8.0(13)
H 2B	0.783(6)	0.214(5)	0.429(5)	9.2(15)
H 2C	0.859(5)	0.062(5)	0.406(4)	7.4(13)
H 3A	1.034(6)	0.347(5)	0.498(5)	10.1(15)
H 3B	0.922(5)	0.411(5)	0.419(3)	7.6(13)
H 3C	1.088(5)	0.399(4)	0.375(3)	7.2(13)
H 4A	1.159(6)	0.125(4)	0.439(4)	8.4(14)
H 4B	1.209(5)	0.216(4)	0.343(4)	7.6(13)
H 4C	1.122(4)	0.083(4)	0.336(3)	5.4(11)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For hydrogens, $B_{eq} = B_{iso}$. [b] ESD's are in parentheses.

substrates using the appropriate number of equivalents of oxidizing agent (*m*-CPBA, dimethyldioxirane, and peracetic acid) (Scheme 4).

The characterization of bis(*tert*-butylsulfonyl) thioanhydride (**15**) was accomplished using NMR spectroscopy and mass spectrometry. Recrystallization of **15** from *n*-pentane afforded colorless crystals suitable for X-ray analysis. Figure 3 represents the ORTEP drawing of **15** and Table 3 its atomic coordinates and temperature factors. The valency angle of the internal sulfur is 109° presumably because of the repulsion induced by the presence of the four oxygen atoms.

By analogy with the preparation of the disulfide analogs[5,8] **23**, and considering the mechanism of formation of trioxide **5** previously reported, the conversion of **5** to the corresponding tetraoxide **15** is believed to proceed through the oxidation of the external sulfinyl sulfur rather than that of the internal sulfenyl sulfur (Scheme 5).

Further oxidation of **15** was shown to be impossible under these conditions. This result emphasizes the nonreactivity of the central sulfenyl sulfur toward electrophilic oxidizing agents.[9]

The decomposition of di-*tert*-butylsulfonyl thioanhydride (**15**) at room and elevated temperatures has also been investigated. In both cases, the main products were an equimolar mixture of the di-*tert*-butylsulfonyl dithio-

(9) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.

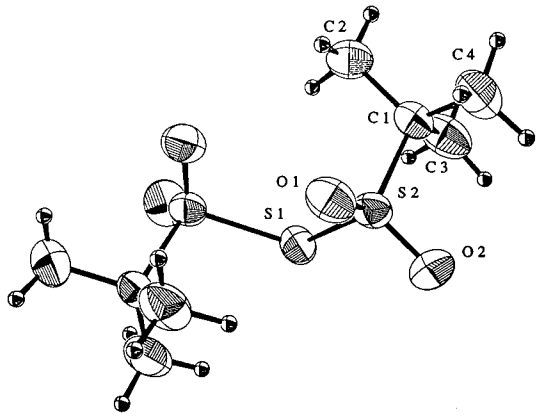
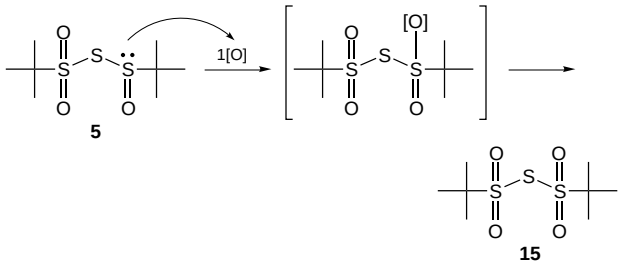
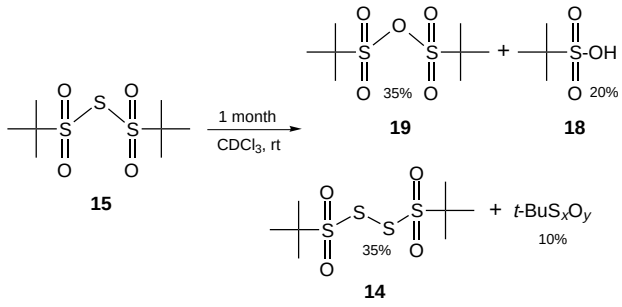


Figure 3. ORTEP drawing of **15**. Selected parameters for **15**: S−SO_2, 2.118 Å; S=O of SO_2, 1.410 and 1.440 Å; dihedral S−S−S−C angles, 95.5 and 95.5°; S−S−S angle,109.52°.

Scheme 5

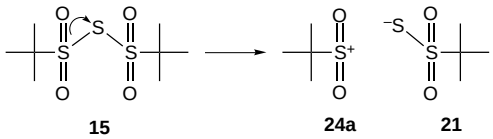


Scheme 6



anhydride (**14**) and *tert*-butyl sulfonic anhydride (**19**) (*vide infra*) as well as significant amounts of *tert*-butyl sulfonic acid (**18**). Very small quantities of sulfinic acid **17,** di-*tert*-butyl thiosulfonate (**16**), and other derivatives were also detected (Scheme 6).

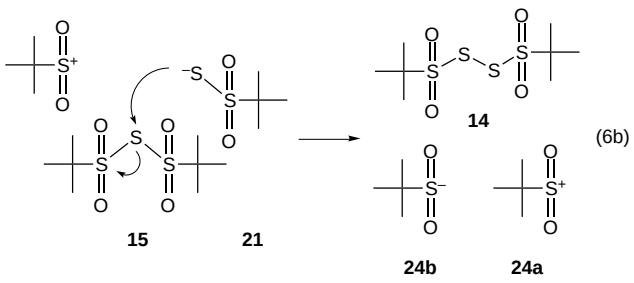
Once again, the formation of these decomposition products can be rationalized by the general mechanisms we have advanced.[5] By analogy with the previous studies,[4,5] the first step should be the ionic cleavage of **15** affording the *tert*-butyl sulfonyl cation **24a** and the *tert*-butyl thiosulfonate anion (**21**) (eq 6a).



(6a)

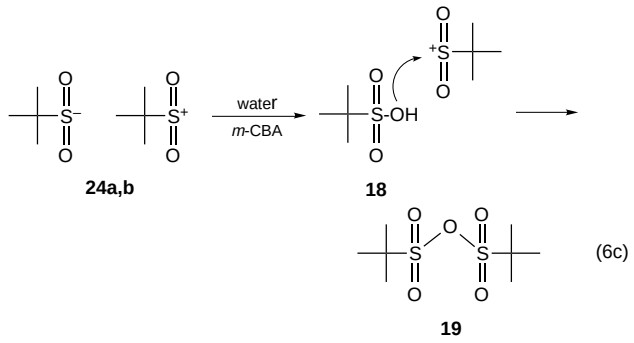
The *tert*-butyl thiosulfonate anion (**21**) formed could eventually react with another molecule of **15** to give the tetrasulfide analog **14** and generate the *tert*-butyl sulfonyl anion **24b** (eq 6b).

The two ambident *tert*-butyl sulfonyl ions **24a,b** should not react together to form the expected di-*tert*-butyl *vic*-



(6b)

disulfone **25** because of steric hindrance.[10] Considering that the ambident sulfinyl ions **20a,b** do not easily recombine for the same reasons, it is not surprising that the corresponding sulfonyl ions **24a,b** do not react with each other. In this case, the oxygen transfer is impossible and the reaction with **15** or **14** would lead to already existing products. As a consequence, the *tert*-butyl sulfonyl ions **24a,b** are converted to sulfonic acid **18** probably because of residual *m*-CBA or traces of water. The *tert*-butyl sulfonic acid (**18**) formed can then react with the remaining *tert*-butyl sulfonyl cation (**24a**) to give the proposed *tert*-butyl sulfonic anhydride (**19**) (eq 6c).



(6c)

The *tert*-butyl sulfonyl anhydride (**19**) could not be identified with certainty as it could not be separated by chromatography. The parallel synthesis of **19** was attempted by dehydration of *tert*-butyl sulfonic acid **18** but was unsuccessful in our hands.[11] However, the chemical shifts recorded are consistent with *tert*-butyl sulfonyl anhydride (**19**). Compound **19** was only detected in decomposition experiments where sulfonyl ions **24a,b** are supposed to be formed and is, therefore, probably derived from the reaction of such ions. The small amounts of the other decomposition products reflect the difficult recombination of these ambident ions.

The isolation of di-*tert*-butylsulfonyl dithioanhydride **(14)** has also been achieved. Compound **14** was fully characterized, and its recrystallization from hexanes afforded suitable crystals for X-ray analysis. Figure 4 represents the ORTEP drawing of **14** and Table 4 its atomic coordinates and temperature factors. Compound **14** shows a big difference (0.12 Å) between the external and the internal S−S bond lengths.

The characterization of **14** was very similar to that of its trisulfide analog **15**, but **14** was found to be very stable at room temperature (unchanged after 6 months). A possible explanation would be that **14** is less hindered than its trisulfide analog **15** or because the cleavage of a molecule of **14** would not lead to the formation of any stable compound.

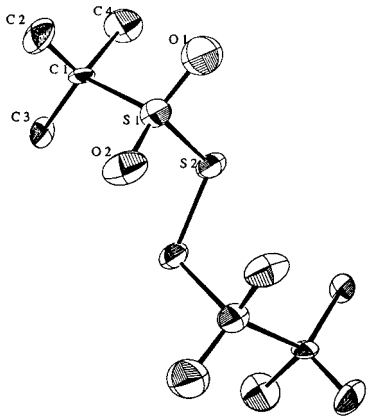


Figure 4. ORTEP drawing of **14**. Selected parameters for **14**: S−SO_2, 2.129 Å; S−S, 2.004 Å; S=O of SO_2, 1.438 and 1.428 Å; dihedral S−S−S−S angles, 90.9°.

Table 4. Atomic Coordinates (*x,y,z*) for Non-Hydrogen and Hydrogen Atoms and Temperature Factors (B_{eq}, All Non-Hydrogen Atoms; B_{iso}, All Hydrogen Atoms) of Compound 14

	x	*y*	*z*	B_{eq}[a]
S 1	0.45861(9)	0.74783(24)	0.20340(5)	3.50(5)
S 2	0.53994(8)	0.99905(21)	0.15023(5)	2.95(4)
O 1	0.4563(3)	1.0691(7)	0.09720(16)	5.40(18)
O 2	0.5892(3)	1.1684(6)	0.19679(15)	4.47(15)
C 1	0.6443(3)	0.8418(8)	0.11297(19)	3.04(17)
C 2	0.5900(6)	0.6592(11)	0.0660(3)	5.0(3)
C 3	0.7013(5)	1.0274(13)	0.0761(3)	4.8(3)
C 4	0.7207(5)	0.7305(13)	0.1696(3)	4.7(3)
H 2A	0.535(5)	0.549(10)	0.084(3)	7.2(16)
H 2B	0.560(4)	0.727(10)	0.030(3)	5.1(15)
H 2C	0.652(4)	0.578(10)	0.047(3)	5.8(14)
H 3A	0.648(4)	1.086(8)	0.0382(24)	4.4(12)
H 3B	0.728(5)	1.139(11)	0.104(3)	8.1(21)
H 3C	0.761(4)	0.965(8)	0.0589(21)	4.1(11)
H 4A	0.753(3)	0.829(8)	0.2041(21)	3.3(11)
H 4B	0.777(5)	0.671(11)	0.155(3)	7.4(17)
H 4C	0.673(5)	0.621(11)	0.192(3)	7.8(17)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For hydrogens, $B_{eq} = B_{iso}$. [b] ESD's are in parentheses.

Summary. The synthesis and characterization of *tert*-butylsulfinyl *tert*-butylsulfonyl thioanhydride (**5**), di-*tert*-butylsulfonyl thioanhydride (**15**), and their tetrasulfide analogs have been achieved by electrophilic oxidation. The analysis of the reaction mixtures and the oxidation of various substrates, as well as low temperature experiments, have shown that, contrary to current belief,[7] *the oxidation takes place regiospecifically at the external sulfinyl sulfur rather than at the internal sulfenyl sulfur*. In all the cases studied here, the central sulfur was found to be surprisingly nonreactive as was also concluded by Ghosh and Bartlett.[12]

Experimental Section

Chemical reagents were obtained from commercial sources and used directly unless otherwise stated. Di-*t*-butyl trisulfide (99%) was provided by Elf Atochem North America, Inc., King of Prussia, PA and used as such. Thionyl chloride ($SOCl_2$) and sulfuryl chloride (SO_2Cl_2) were freshly distilled before using. The *m*-CPBA used was purified by washing the commercial

(10) (a) Haraldson, L.; Olander, C. J.; Sunner, S.; Varde, E. *Acta Chem. Scand.* **1960**, *14*, 1509. (b) Parsons, T. F.; Buckman, J. D.; Pearson, D. E.; Field, L. *J. Org. Chem.* **1965**, *30*, 1923.

(11) (a) Karger, M. H.; Mazur, Y. *J. Org. Chem.* **1971**, *36*, 528. (b) Zefirov, N. F.; Zyk, N. V.; Beloglazkina, E. K.; Kutateladze, A. G. *Sulfur Rep.* **1993**, *14*, 223. (c) Farng, L.-P. O.; Kice, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1137. (d) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1982**, *47*, 4194.

(12) Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499.

Table 5. Crystal Data for the Structure Determination of 5, 14, and 15

	compd **5**	compd **15**	compd **14**
chemical formula	$C_8H_{18}O_3S_3$	$C_8H_{18}O_4S_3$	$C_8H_{18}O_4S_4$
fw	258.41	274.41	306.46
X-ray cryst dimens (mm)[a]	0.30 × 0.30 × 0.07	0.50 × 0.25 × 0.20	0.50 × 0.50 × 0.10
cryst system	monoclinic	orthorhombic	monoclinic
space group	$P2_1$	*Pbnb*	*C*2/*c*
lattice constants			
a (Å)	5.9004(17)[a]	9.3517(10)[b]	12.4036(21)[c]
b (Å)	11.9502(15)	10.5713(12)	5.7613(13)
c (Å)	9.1617(14)	13.3309(12)	20.007(4)
β (deg)	95.927(24)		97.745(15)
V (Å^3)	642.55(22)	1317.89(24)	1416.7(5)
Z	2	4	4
F(000)	276.74	589.24	649.96
density (calcd) (g cm^{-3})	1.336	1.383	1.437
μ (mm^{-1})	0.54	5.05	0.64
radiation	Mo	Cu	Mo
absorption cor		ψ scans	
transmission range		0.189−0.355	
2θ max (deg)	46.9	110.0	55.0
h, *k*, *l* ranges	−6 6, 0 13, 0 10	0 9, 0 11, 0 14	−16 16, 0 7, 0 26
no. of reflctns measd	1189	943	1708
no. of unique (R_{int})	1006 (0.012)	820 (0.054)	1637 (0.009)
No. of reflctns with $I_{net} > 2.5\sigma(I_{net})$	871	726	1315
no. of variables	128	106	110
for significant reflctns	RF = 0.055[d]	RF = 0.043[d]	RF = 0.057[d]
	R_w = 0.053[e]	R_w = 0.054[e]	R_w = 0.068[e]
	G_oF = 2.42[f]	G_oF = 3.39[f]	G_oF = 3.58[f]
maximum shift/σ ratio	0.001	0.071	0.014
deepest hole in D-map (e/Å^3)	−0.360	−0.330	−0.430
highest peak in D-map (e/Å^3)	0.390	0.390	0.400
drop of standard intensities	3.5%	2%	0.17%

[a] Cell dimensions were obtained from 25 reflections with 2θ angle in the range 25.00−30.00°. [b] Cell dimensions were obtained from 25 reflections with 2θ angle in the range 80.00−100.00°. [c] Cell dimensions were obtained from 25 reflections with 2θ angle in the range 27.00−35.00°. [d] $RF = \sum(F_o - F_c)/\sum(F_o)$. [e] $R_w = (\sum[w(F_o - F_c)^2/\sum(wF_o^2)])^{1/2}$. [f] $G_oF = (\sum[w(F_o - F_c)^2/(\text{no. of reflections} - \text{no. of parameters})])^{1/2}$.

80−85% or 50−60% material with a phosphate buffer, followed by drying, filtering, and evaporating at reduced pressure. The solid was then recrystallized from methylene chloride to afford 99% *m*-CPBA.[13] Dimethyldioxirane was prepared according to the literature procedure.[14] It was stored in the freezer over 3 Å molecular sieves and used within a week. The purity was checked by GC analysis prior to use. The dropwise additions of dimethyldioxirane were always carried out using a pressure-equalized dropping funnel equipped with a dry ice cooling jacket. Melting points (mp) were obtained in open capillaries on a Gallenkamp melting point apparatus and are uncorrected. Thin layer chromatography was performed on 0.25 mm Merck silica gel plates (60F-254) with polyester backing and was visualized by UV light and a 10% aqueous sulfuric acid solution of ammonium molybdate−cerium sulfate developing dip. Silica gel chromatography was carried out on Merck Kieselgel 60 (230−400 mesh), and alumina chromatography was carried out on Fisher Scientific neutral alumina (80−200 mesh) that had previously been dried. In both cases flash column procedures[15] were used. X-ray crystallography was performed by Dr. Rosemary C. Hynes at the Department of Chemistry, McGill University, Montreal, Quebec, Canada.

X-ray Crystallographic Data for 5, 14, and 17. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer using graphite-monochromated Cu Kα (λ = 1.540 56 Å) (compound **15**) or Mo Kα (λ = 0.709 30 Å) (compounds **5** and **14**) radiations using the $\theta/2\theta$ scan mode. Structures were solved by direct methods.[16] Solution and refinement were performed using NRCVAX system programs.[17] Hydrogens were calculated for compound **5**. Crystal data and collection and refinement parameters are given in Table 5.[18] Tables of bond lengths and angles, torsion angles, and structure and temperature factors have been deposited as Supporting Information.

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

Oxidized Derivatives of Trisulfides. The preparation and characterization of the oxide and dioxide derivatives of trisulfides mentioned here were previously reported.[5]

Trisulfide Dioxides. The preparation and characterization of the trisulfide dioxides mentioned here were previously reported.[5,6]

Synthesis of *tert*-Butylsulfinyl *tert*-Butylsulfonyl Thioanhydride (5). *m*-CPBA Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (1.05 g, 5.00 mmol) was carried out using *m*-CPBA (−40 °C,12 h, 3.5 equiv) according to procedure 1.[5] The solvent was removed *in vacuo* at room temperature, and **5** (1.02 g, 3.95 mmol, 79%) was crystallized from *n*-pentane in the freezer as colorless needles. Mp: 80−100 °C (**5** probably decomposed before reaching its melting point). ^{1}H NMR ($CDCl_3$) δ: 1.551 (s, 9H), 1.463 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$) δ: 71.38, 63.08, 24.51, 23.99 ppm. MS (CI (NH_3), 70 eV, 100 °C): *m*/*z* (rel intensity) 276 ($M(NH_4)^+$, 4.6), 260 ($M(NH_4)^+ - O$, 3.6), 228 ($M(NH_4)^+ - S{=}O$, 8.3), 172 (*t*-$BuS(O)_2SNH_4^+$, 7.0), 140 (*t*-$BuS(O)_2NH_4^+$, 47.6), 123 (*t*-$BuS(O)_2H_2^+$, 45.0), 57 (*t*-Bu^+, 100).

Peracetic Acid Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (0.93 g, 4.43 mmol) was carried out using CH_3CO_3H (−20 °C, 12 h, 3.5 equiv) according to

(13) Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.
(14) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Singh, M.; Murray, R. W. *J. Org. Chem.* **1992**, *57*, 4263.
(15) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(16) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, M., Doddard, R., Eds.; Oxford University Press: Oxford, U.K., **1985**, pp 175−189.
(17) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(18) The authors have deposited atomic coordinates for **5**, **14**, and **15** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. The X-ray structure of this molecule was reported after submission of this manuscript, see: Freeman, F.; Ma, X.-B.; Ziller, J. W. *Acta Crystallogr.* **1995**, *C51*, 661.

procedure 2.[5] The solvent was removed *in vacuo* at room temperature; compound **5** (0.51 g, 1.99 mmol, 45%) was crystallized from *n*-pentane in the freezer as colorless needles. The analytical data are consistent with previously reported values.

DMD Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (0.56 g, 2.66 mmol) was carried out using DMD (0.08 M) (−78 °C, 6 h, 3.2 equiv) according to procedure 3.[5] The solvent was removed *in vacuo* at room temperature, and compound **5** (0.617 g, 2.39 mmol, 90%) was crystallized from *n*-pentane in the freezer as colorless needles. The analytical data are consistent with previously reported values.

DMD Oxidation of *tert*-Butylsulfenyl *tert*-Butylsulfonyl Thioanhydride (10). The oxidation of **10** (0.50 g, 2.06 mmol) was carried out using DMD (0.08 M) (−78 °C, 2 h, 1 equiv) according to procedure 3. Roto-evaporation of the solvent afforded **5** (0.49 g, 1.92 mmol, 93%) as a colorless solid. Analytical data are consistent with previously reported values.

Decomposition of *tert*-Butylsulfinyl *tert*-Butylsulfonyl Thioanhydride (5). The decomposition of **5** (31 mg, 0.12 mmol) in $CDCl_3$ was followed by ^1H and ^{13}C NMR at room temperature. After 2 weeks under these conditions, no traces of **5** could be detected. The decomposition products were identified by ^1H and ^{13}C NMR as a mixture of **14** (63%), **7a** (28%), and **16** (3%) as well as a mixture of **15**, **17**, **18**, and **19** (6%).

Synthesis of Di-*tert*-butylsulfonyl Thioanhydride (15). *m*-CPBA Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (0.92 g, 4.38 mmol) was carried out using *m*-CPBA (−40 °C, 12 h, 4.5 equiv) according to procedure 1.[5] The solvent was removed *in vacuo* at room temperature, and **15** (0.63 g, 2.32 mmol, 53%) was crystallized from *n*-pentane in the freezer as colorless needles. Mp: 85−105 °C (**15** probably decomposed before reaching its melting point). ^1H NMR ($CDCl_3$) δ: 1.545 (s, 18H) ppm. ^{13}C NMR ($CDCl_3$) δ: 73.45, 24.15 ppm. MS (CI (NH_3), 70 eV, 100 °C) *m*/*z* (rel intensity) 292 ($M(NH_4)^+$, 0.6), 260 ($M(NH_4)^+ - S$, 3.6), 228 ($M(NH_4)^+ - S(O)_2$, 6.3), 172 (*t*-$BuS(O)_2SNH_4^+$, 9.3), 140 (*t*-$BuS(O)_2NH_4^+$, 100.0), 123 (*t*-$BuS(O)_2H_2^+$, 82.5).

Peracetic Acid Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (0.42 g, 2.00 mmol) was carried out using CH_3CO_3H (−20 °C, 12 h, 4.5 equiv) according to procedure 2.[5] The solvent was removed *in vacuo* at room temperature, and **15** (0.14 g, 0.50 mmol, 25%) was crystallized from *n*-pentane in the freezer as colorless needles. Analytical data are consistent with previously reported values.

DMD Oxidation of Di-*tert*-butyl Trisulfide (6b). The oxidation of **6b** (0.39 g, 1.86 mmol) was carried out using DMD (0.07 M) (−78 °C, 6 h, 4.2 equiv) according to procedure 3.[5] The solvent was removed *in vacuo* at room temperature, and **15** (0.32 g, 1.19 mmol, 64%) was crystallized from *n*-pentane in the freezer as colorless needles. Analytical data are consistent with previously reported values.

DMD Oxidation of *tert*-Butylsulfinyl *tert*-Butylsulfonyl Thioanhydride (5). The oxidation of **5** (0.617 g, 2.39 mmol) was carried out using DMD (0.07) (−78 °C, 6 h, 1 equiv) according to procedure 3.[5] Roto-evaporation of the solvent afforded **15** (0.52 g, 1.86 mmol, 78%) as a colorless solid. Analytical data are consistent with previously reported values.

Decomposition of Di-*tert*-butylsulfonyl Thioanhydride (15). The decomposition **15** (37 mg, 0.13 mmol) in $CDCl_3$ was followed by ^1H and ^{13}C NMR at room temperature. After 1 month under these conditions, no traces of **15** could be detected. The decomposition products were identified by ^1H and ^{13}C NMR to be **14** (35%), **19** (35%), and **18** (20%) as well as a mixture of **17**, **16**, **7a,** and other *tert*-butyl derivatives (10%).

Preparation of *tert*-Butylsulfinyl *tert*-Butylsulfonyl Dithioanhydride (22). The oxidation of di-*tert*-butyl tetrasulfide **(6c)** (0.47 g, 1.94 mmol) was carried out using *m*-CPBA (−40 °C, 6 h, 3.5 equiv) according to procedure 1.[5] The solvent was removed at low temperature (−20 °C) under high vacuum (2.5 mmHg) to give **22** (0.49 g, 1.71 mmol, 88%) as a pale yellow solid that was recrystallized in the freezer from a 20% CH_2Cl_2/*n*-pentane solution. Mp: 85−100 °C (**22** probably decomposed before reaching its melting point). ^1H NMR ($CDCl_3$) δ: 1.523 (s, 9H), 1.456 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$) δ: 71.16, 62.33, 23.84, 23.72 ppm. The MS of **22** does not show any parent peak or typical fragmentation. However, compound **22** showed a single spot on TLC, and its NMR data are consistent with those of other polysulfide polyoxide derivatives.

Isolation of Di-*tert*-butylsulfonyl Dithioanhydride (14). Compound **14** was isolated from the decomposition of **8**, **5**, and **15** by silica gel column chromatography using a 25% solution of ethyl acetate/hexanes. It was recrystallized in hexanes. Mp: 80−130 °C (**14** probably decomposed before reaching its melting point). ^1H NMR ($CDCl_3$) δ: 1.53 (s, 18H) ppm. ^{13}C NMR ($CDCl_3$) δ: 72.10, 24.18 ppm.

Attempted Low-Temperature Detection of Di-*tert*-butyl *vic*-Trisulfoxide (9). The oxidation of di-*tert*-butyl dithiosulfite **(11)** (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%) (516 mg, 3.0 mmol, 4 equiv) partially dissolved in 4 mL of $CDCl_3$. After 4 days at −60 °C, the reaction mixture was treated as described in the literature.[4,5]

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Supporting Information Available: NMR spectra of compound **5**, **14**, **15,** and **22** as well as X-ray data of compound **5**, **14**, and **15** (3 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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