Detection and Decomposition of Di-*tert*-butyl Disulfide–Polyoxide Derivatives

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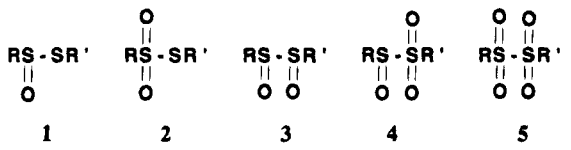
The chemistry of di-*tert*-butyl disulfide polyoxide derivatives has been investigated. Low-temperature experiments permit the clear detection of *vic*-disulfoxides (α-disulfoxides). In addition, a proposal for a decomposition mechanism that accounts for the detection of one of the diastereoisomers and the formation of the final products has been advanced. The formation of di-*tert*-butyl thiosulfonate was also shown to be solvent and concentration dependent. Finally, low-temperature experiments permit the detection of the sulfinyl sulfone and *vic*-disulfone derivatives. A general mechanism has been proposed for the decomposition of these disulfide polyoxide derivatives.

The chemistry of thiosulfinates[1] **1** and thiosulfonates[2] **2** has been extensively studied and reviewed in terms of mechanistic aspects, chemical properties, and practical applications. The detection of *vic*-disulfoxides (α-disulfoxides) **3** as intermediates in the electrophilic oxidation of thiosulfinates **1** to thiosulfonates **2** has been one of the most challenging projects in this area of organosulfur chemistry.[3] In contrast, sulfinyl sulfones **4** and *vic*-disulfones **5** have received little attention.[4]

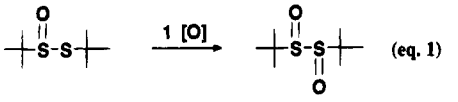


1 **2** **3** **4** **5**

This study focuses on the special case of the di-*tert*-butyl analogs that often present unusual properties (*vide infra*). Earlier work[5–7] in this area has been advanced by Freeman.

Formation and Decomposition of Di-*tert*-butyl *vic*-Disulfoxide (7). Freeman's[5,7b] contributions are notable in terms of the first clear detection of *vic*-disulfoxides and the development of a number of sophisticated low-temperature experiments. There is, however, a need for a further investigation of the oxidation of di-*tert*-butyl disulfide (**6**) (*t*-BuSSBu-*t*). Our initial concerns relate to aspects of this oxidation and can be summarized as follows.

1. Only *one* of the two possible diastereoisomers of di-*tert*-butyl *vic*-disulfoxide (**7**) is reported to be formed when di-*tert*-butyl thiosulfinate (**8**) is oxidized by *m*-CPBA at low temperature[5c] (eq 1), although the two diastereomeric **7** are observed in all other non-*tert*-butyl examples.[3,5e,7b]



8 **7**

2. The mechanisms proposed[5c,7b] for the formation of the rearrangement products of di-*tert*-butyl *vic*-disulfoxide (**7**) appear to be mutually incompatible because the intermediate proposed (*O,S*-sulfenyl sulfinate) could not be detected by low-temperature NMR, and these two suggested mechanisms gives different final products for no apparent reasons.

3. We have noted apparent inconsistencies in the oxidation of thiosulfinates. In contrast with other thiosulfinate oxidations,[3] only traces of thiosulfonate **9** could be detected from the low-temperature oxidation of the corresponding thiosulfinate **8**; however, various amounts of **9** have been isolated under similar oxidation conditions.[5–7]

We have resolved these points and, in addition, wish to clarify some other difficult mechanistic features of this chemistry and to extend several previous conclusions[3a,4f,5c,7b] about the chemistry of this unusual class.

Low-Temperature Experiment. In the first part of this work, it was decided to reinvestigate the low-temperature oxidation of thiosulfinate **8**. The procedure used is unavoidably somewhat different from the one

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

(1) (a) Isenberg, N.; Grdinic, M. *Int. J. Sulfur Chem.* **1967**, *8*, 307. (b) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3921. (c) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3929. (d) Hoyle, J. J. *The Chemistry of Sulfinic Esters and Their Derivatives*; Patai, S., Ed.; New York: John Wiley and Sons Ltd., 1990; Chapter 4.

(2) For a recent review see: Zefirov, N. F.; Zyk, N. V.; Beloglazkina, E. K.; Kutateladze, A. G. *Sulfur Rep.* **1993**, *14*, 223 and references cited therein.

(3) Highlights of current findings 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. (d) For a recent review on reactive, naturally occuring *vic*-disulfoxides see: Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135.

(4) (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.; Favstristky, N. *J. Org. Chem.* **1970**, *35*, 114. (k) Farng, L.-P. O.; Kice, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1137. (l) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1982**, *47*, 4194.

(5) (a) Freeman, F.; Angeletakis, C. N.; Maricichi, T. J. *Tetrahedron Lett.* **1981**, *22*, 1867. (b) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1981**, *46*, 3981. (c) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232. (d) Freeman, F.; Angeletakis, C. N.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 1161. (e) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1982**, *104*, 5766. (f) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039.

(6) (a) Asakawa, H.; Takey, K. S. *Takeda Kenkyusho Ho* **1970**, *29*, 610; *Chem. Abstr.* **1971**, *74*, 125603. (b) Kice, J. L.; Lee, T. W. S. *J. Am. Chem. Soc.* **1978**, *100*, 5094. (c) Kice, J. L.; Lee, T. W. S.; Pan, S. *J. Am. Chem. Soc.* **1980**, *102*, 4448.

(7) (a) Bass, F. W.; Evans, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 710. (b) Freeman, F.; Lee, C. *J. Org. Chem.* **1988**, *53*, 1263.

(8) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.

0022-3263/95/1960-1044$09.00/0

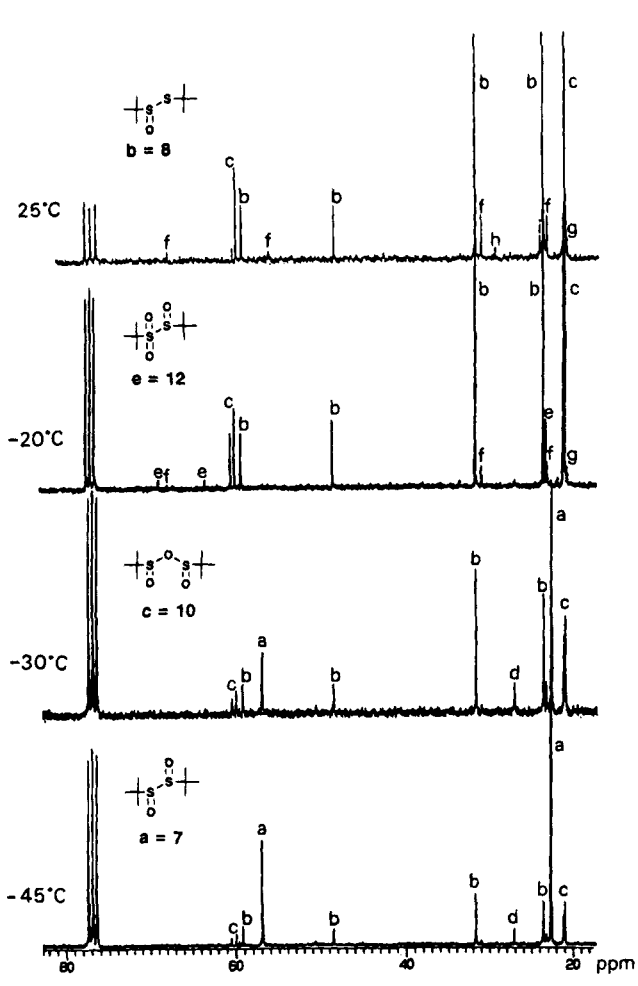
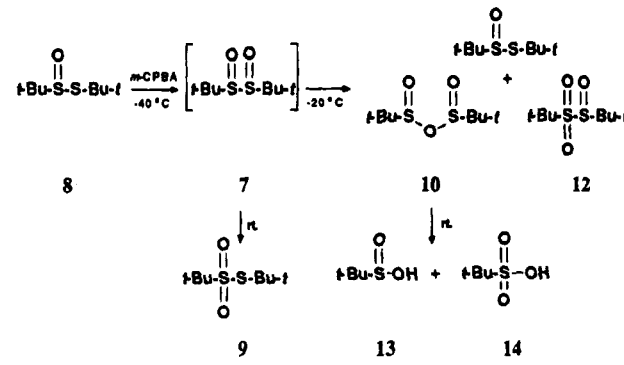


Figure 1. ^{13}C NMR spectra at several temperatures of the product mixture from the *m*-CPBA oxidation of **8**.

reported by Freeman and Angeletakis.[5] The oxidation of **8** has been carried out using *exactly* 1 equiv of *m*-CPBA (>99% as opposed to commercially available 80–85% as reported in the related papers). Considering that the di-*tert*-butyl *vic*-disulfoxide (**7**) formed should be stable at −40 °C,[5c] the reaction was stirred for 4 days at −55 °C. In contrast, Freeman and Angeletakis waited only 1 h before filtration. This is surprising because all the other experiments conducted at warmer temperatures were carried out for at least 3 h before completion.[5a,b,d,6,7] Working at a lower temperature, the oxidation should be slower. In our work, the reaction was conducted in deuterated chloroform, and most of the unreacted *m*-CPBA and *m*-CBA formed were not soluble at this temperature. The reaction mixture was then filtered using a customized device (described in the Experimental Section) that permits the filtration to take place at temperatures lower than −40 °C. Under the same

Scheme 1



conditions, the solution was transferred into a 5 mm NMR tube which was stored in dry ice. The spectrometer (Jeol 270) was cooled to −100 °C and the sample was kept in dry ice. The transfer of the NMR tube from the dry ice to the probe of the spectrometer was done in 30–60 s, the probe temperature remained below −60 °C, and the sample was still frozen (mp of $CDCl_3$ = −64 °C). Then, the temperature of the spectrometer was set to −45 °C, the sample was allowed to stabilize for 30 min, and the ^1H and ^{13}C NMR spectra were recorded at various temperatures (Figure 1).

Analysis of the NMR Spectra. The ^1H and ^{13}C NMR spectra obtained at −45 °C show the presence of di-*tert*-butyl *vic*-disulfoxide (**7**) as the major product (>80%) as well as an equimolar mixture of di-*tert*-butyl thiosulfinate (**8**), di-*tert*-butylsulfinic anhydride (**10**), and small amounts of *tert*-butylsulfenic acid (**11**). On warming to −30 °C, the *vic*-disulfoxide **7** slowly decomposed to an equimolar mixture of **8** and **10**. At −20 °C, the disulfoxide **7** and the sulfenic acid **11** had completely disappeared, and small amounts of *tert*-butylsulfinyl *tert*-butyl sulfone (**12**) could be detected. Finally, after 10 min at room temperature, the product mixture was composed of di-*tert*-butyl thiosulfinate (**8**) (45%), one of the two diastereoisomers of di-*tert*-butylsulfinic anhydride (**10**) (30%), di-*tert*-butyl thiosulfonate (**9**) (7%), and small amounts of *tert*-butylsulfinic acid (**13**), *tert*-butylsulfonic acid (**14**), as well as traces of undefined compounds (Scheme 1). All these results can be seen on the spectra presented in Figure 1, and the chemical shifts of all the compounds identified in this low temperature experiment have been reported in Table 1 and were derived from parallel synthesis or consistent literature reports.

The ratios of the intermediates were determined from the integration of the various proton NMR spectra as well as from the intensity of the carbon signals that were shown by calibration experiments to correspond to their relative molar concentration (within 10%) when simple acyclic disulfide–polyoxides bearing the same alkyl group are compared.

Table 1: ^{13}C and ^1H NMR Chemical Shifts of the Related di-*t*-butyl derivatives[a]

entry	compd	spectra	C	CH_3	H	C′	CH_3′	H′
11	*t*-BuSOH[8]	d	50.85	27.39	1.31			
13	*t*-BuS(O)OH	g	57.46	21.42	1.19			
14	*t*-BuS(O)$_2$OH[b]	i	58.07	24.49	1.43			
6	*t*-BuSSBu-*t*		45.87	30.54	1.28			
8	*t*-BuS(O)SBu-*t*	b	59.35	24.18	1.53	48.65	32.21	1.35
7	*t*-BuS(O)S(O)Bu-*t*[c]	a	57.08	22.95	1.29			
9	*t*-BuS(O)$_2$SBu-*t*	f	68.01	23.65	1.59	56.31	31.45	1.44
12	*t*-BuS(O)$_2$S(O)Bu-*t*[d]	e	69.28	23.74	1.50	63.68	23.80	1.47
10a	*t*-BuS(O)OS(O)Bu-*t*[d]		60.52	21.37	1.28			
10b	diastereoisomers	c	60.07	21.53	1.26			

[a] All the spectra were recorded in $CDCl_3$. [b] Partially soluble in $CDCl_3$. [c] The spectra were obtained at-45 °C. [d] The spectra were obtained at −20 °C.

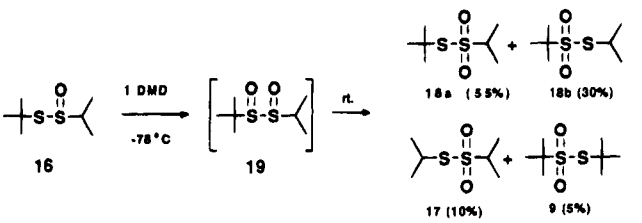
Determination of the Influential Parameters. The low-temperature oxidation of di-*tert*-butyl thiosulfinate (**8**) was repeated several times using excess *m*-CPBA or commercially available 80−85% *m*-CPBA, for different reaction times (1 h to 4 days), in anhydrous conditions and in the presence of water; the spectra were recorded at slightly different temperatures (stepwise by 5 °C). Finally, different decomposition studies have been examined (stepwise from − 40 to 25 °C and direct decomposition −40 to 25 °C).

It is unnecessary to detail each of these experiments (a typical procedure is described above), but a general behavior as well as the influential parameters can be highlighted. While results can be obtained with 80−85% *m*-CPBA as reported by Freeman and Angeletakis,[5] we feel it is preferable to use a pure oxidizing agent in order to add exactly 1 equiv and be sure that the conditions are anhydrous. The use of excess *m*-CPBA (2 equiv) for a relatively long period of time (12 h) does not affect the reaction products. A study of the reaction time has shown that the reaction was almost completed after 2 h at −45 °C. Carrying out the reaction over 4 days showed that *vic*-disulfoxide **7** was very stable under these low-temperature conditions. The formation of **7** does not seem to be affected by the presence of water. However, more *tert*-butylsulfenic acid (**11**) has been detected under aqueous conditions, although some **11** was also found when the reaction was carried out under an inert atmosphere. The formation of *tert*-butyl sulfenic acid (**11**) seems to be independent of the decomposition of *vic*-disulfoxide **7** as it is present at −45 °C, its low concentration remaining relatively constant until it decomposes (see spectra above). Compound **7** seems to be stable up to temperatures ranging from −40 to −35 °C. The decomposition is very fast above −25 °C (<5 min). No real difference was observed between the stepwise decomposition and the direct one but the presence of water as well as the presence of residual *m*-CPBA or *m*-CBA substantially altered the ratios of decomposition products and no general behavior could be found.

Mechanistic Study. The above results permit the determination of the optimum conditions for this reaction now defined as 1 equiv of pure *m*-CPBA, a temperature lower than −40 °C at all times, reaction times greater than 12 h, and an anhydrous, inert medium. Under these specific conditions, the results obtained are explicable in terms of exclusive formation of one of the two possible diastereoisomers of di-*t*-butyl *vic*-disulfoxide (**7**) as shown on the spectrum recorded at −45 °C. According to the procedure employed and the spectrum obtained at −45 °C, the conversion of thiosulfinate **8** to *vic*-disulfoxide **7** was at least 90%. In addition, no trace of *m*-CPBA, *m*-CBA, or water could be detected in the spectrum. The decomposition of **7** afforded an equimolar mixture of **8** and **10** as well as small amounts of **12**. A possible explanation would be the complete formation of **7** followed, at warmer temperatures, by its disproportionation into one part of thiosulfinate **8** and one part of sulfinic anhydride **10**. As a consequence, the spectrum obtained at −20 °C only presents an equimolar mixture of **8** and **10** as well as traces of **12**. The other products observed at room temperature come from the decomposition of the reactive *tert*-butyl sulfinic anhydride[7b] **10** (Scheme 1).

These overall results agree well with those reported by Freeman and Angeletakis.[5c] However, the spectra reported[5c] were misinterpreted and led to the proposal of inconsistent decomposition mechanisms because the reaction was incomplete after 1 h and the temperature chosen (−40 °C) was too close to the decomposition temperature of the *vic*-disulfoxide **7**. As a result, their reaction mixtures always included significant amounts of sulfinic anhydride **10** and thiosulfinate **8** reported as the decomposition products of **7** as well as unreacted **8**. These side products seriously complicated the analysis of the reaction path.

Scheme 2



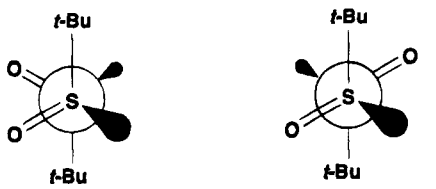
The decomposition study reported here was clarified by the almost complete formation of the di-*t*-butyl *vic*-disulfoxide (**7**). The previous results have clearly shown that the disproportionation of **7** afforded mainly the corresponding thiosulfinate **8** and sulfinic anhydride **10**. However, the detailed decomposition mechanism is not clear because only one of the two possible diastereoisomers of **7** is formed and no di-*tert*-butyl thiosulfonate (**9**) can be observed at −20 °C.

In a separate experiment, the unsymmetrical thiosulfinate (**15**) was oxidized using 1 equiv of dimethyldioxirane (DMD) at low temperature. The reaction products were a mixture of the four possible dialkyl thiosulfonates **9**, **16**, **17**, and (Scheme 2).

Considering that there is exclusive formation of the corresponding *vic*-disulfoxide (**19**), the analysis of the reaction products (mixed thiosulfonates) clearly implies the cleavage of **19**. In addition, the percentages of each product presented in Scheme 2 are very different and are representative of preferred cleavage and recombination. This observation is more in favor of a heterolytic cleavage rather than a homolytic one. Similar studies[9] provided the same conclusion.

As stated earlier, the low-temperature oxidation of other alkyl thiosulfinates[3] always afforded the two diastereoisomers of the corresponding *vic*-disulfoxides; their decompositions gave the thiosulfonates as the major products. However, the oxidation of di-*tert*-butyl thiosulfinate (**8**) affords only one of the two possible diastereoisomers of the *vic*-disulfoxide **7**, and its decomposition gives almost none of the expected thiosulfonate **9**, but rather a clean mixture of products that cannot be rationalized by a straightforward mechanism.

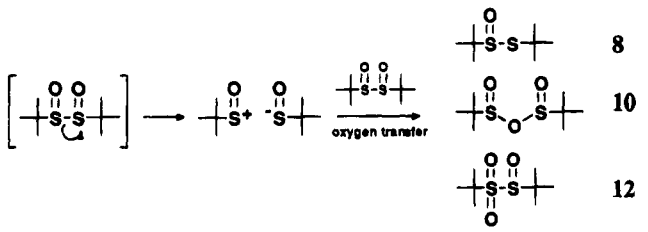
In the case of the di-*tert*-butyl derivative, the oxidation of di-*tert*-butyl thiosulfinate (**8**) is believed to only afford the kinetically favored *vic*-disulfoxide **7a** or **b**. This



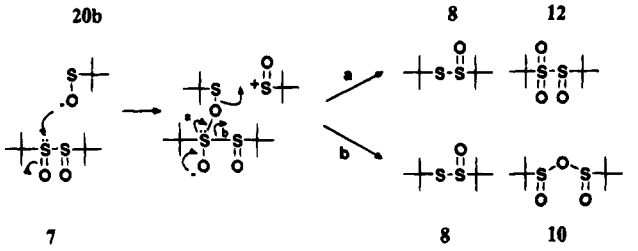
7a: d,l **7b: meso**

(9) (a) Oae, S.; Takata, T.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2484. (b) Oae, S.; Kim, Y. H.; Takata, T.; Fukushima, D. *Tetrahedron Lett.* **1977**, 1195.

Scheme 3



Scheme 4



possibility is supported by the results observed for the di-*tert*-butylsulfinyl thioanhydride.[10]

On warming, heterolytic cleavage of the *vic*-disulfoxide **7** should afford two very interesting ambident species (*t*-BuS$^+$(=O) (**20a**) and *t*-BuS$^-$(=O) (**20b**)) whose existence is supported by literature evidence[11] (Schleyer and coworkers reported clear evidence of a sulfinyl cation and anion in different systems). In contrast with the other alkyl derivatives, the *t*-butylsulfinyl ions **20a,b** are so sterically hindered that their recombination apparently is slower than their reaction with another molecule of *vic*-disulfoxide **7** which is less hindred under these specific conditions[12] (*vide infra*). As a consequence, the formation of the second diastereoisomer of **7** does not occur and, thus, there is no formation of di-*tert*-butyl thiosulfonate (**9**). Another possible explanation could be that the kinetically favored product is also the thermodynamic compound. Due to the steric hinderance of the *tert*-butyl groups, only one of the diastereomeric *vic*-disulfoxides **7** is formed, and if it is the thermodynamic diastereoisomer, the other one will not be observed. The formation of thiosulfinate **8** as well as the diastereomeric sulfinic anhydride **10** or the sulfinyl sulfone **12** can be explained by an oxygen transfer mechanism between one molecule of *vic*-disulfoxide **7** and the *tert*-butyl sulfinyl ions **20a,b** (Scheme 3). This mechanism is similar to the one advanced for the decomposition of oxidized trisulfide derivatives.[13]

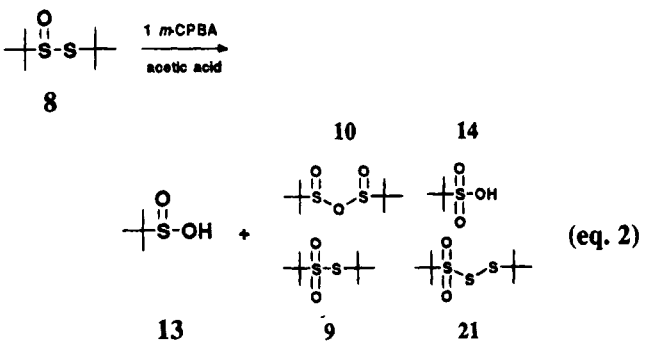
The rationalization of the oxygen transfer reaction led us to the proposal of several possible mechanisms.[13] Considering the lifetimes of the ions present and the likelihood of the intermediates formed, the nucleophilic attack of the sulfinyl anion **20b** at the electrophilic center of **7** appears to be the preferred oxygen transfer mechanism.[13] This attack is supported by the resonance forms of the sulfinyl anion (*t*-BuS$^-$(=O) ↔ *t*-BuSO$^-$). Rearrangement of the intermediate formed according to path a and b rationalizes the expected decomposition products **8**, **10**, and **12** (Scheme 4).

In the present decomposition, path b is favored over path a probably because in the related intermediate the S–S bond is weaker than the corresponding S–O or because the product formed in path b is thermodynamically favored compared to the one formed by path a. A possible mechanism (ionic cleavage, steric hindrance in the recombination, and oxygen transfer) is suggested and accounts for the results observed here.

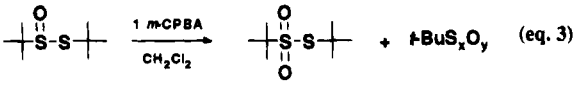
Synthesis of Di-*tert*-butyl Disulfide 1,1-Dioxide (9). As stated earlier, the synthesis of di-*tert*-butyl thiosulfonate (**9**) by direct oxidation of the corresponding thiosulfinate **8** or disulfide under various conditions has always been reported as a very complicated reaction.[5-7] However, the oxidation of the less substituted dialkyl thiosulfinates[2] such as diisopropyl thiosulfinate affords a high yield of the corresponding thiosulfonate. The careful analysis of the reported results as well as the reinvestigation of part of our studies led us to the conclusion that the formation of the di-*tert*-butyl thiosulfonate (**9**) is solvent and reagent concentration dependent. Although a termolecular or a concerted unimolecular process could also explain such dependency, the following mechanism proposed is fully consistent with the overall behavior of polysulfide polyoxides.[13]

Solvent Effects. The solvent effect study presented here has been carried out using standard conditions that are similar to the one reported by Freeman and Lee.[7b] In all cases, pure di-*tert*-butyl thiosulfinate (**8**) was oxidized by 1 equiv of 99% *m*-CPBA under an inert atmosphere at 0 °C until no starting material could be detected on TLC (1 h to 3 days depending on the solvent used). The dilution factor was always about 0.5 g of **8** for 15 mL of solvent ([**8**] ≈ 0.2 M).

Using acetic acid as solvent, no trace of **8** could be detected after 1 h of reaction under the above conditions. The analysis of the reaction mixture by ^{1}H and ^{13}C NMR revealed the presence of *tert*-butylsulfinic acid (**13**) (>90%) as the major product and small amounts of **9**, **10**, **21**, and **14** and other undefined polysulfide polyoxides (eq 2).



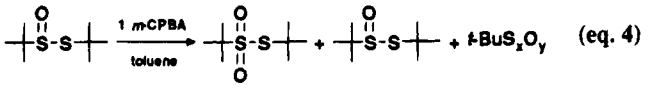
When methylene chloride was used as solvent, results similar to those reported by Freeman and Lee[7b] were recorded after 5 h of reaction. Only 19% of the expected thiosulfonate **9** could be detected, the remaining 81% being the complex mixture reported earlier (eq 3).



When toluene was used as solvent, 37% of thiosulfonate **9** was detected after 7 h of reaction. The other reaction products were similar to the ones reported

(10) Derbesy, G.; Harpp, D. N. *Sulfur Lett.*, in press.
(11) (a) Schreiner, P. R.; Schleyer, P. v R.; Hill, R. K. *J. Org. Chem.* **1993**, *58*, 282. (b) Schreiner, P. R.; Schleyer, P. v R.; Hill, R. K. *J. Org. Chem.* **1994**, *59*, 1849 and references cited therein.
(12) (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.
(13) Derbesy, G.; Ph.D. Thesis, 1994, McGill University.

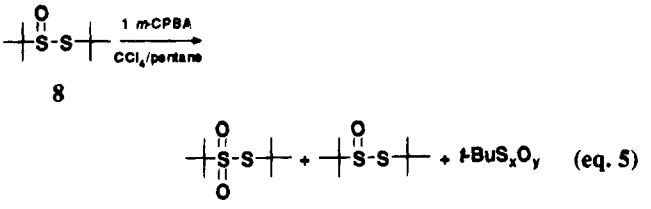
earlier in slightly different ratios plus *ca.* 10% of unreacted thiosulfinate **8** (eq 4).



(eq. 4)

8 **9 (37%)** **8 (10%)**

Finally, when a 50/50 carbon tetrachloride/*n*-pentane solution was used as solvent, close to 50% of **9** was obtained, the remaining reaction mixture being the usual byproducts. However, 90% conversion of the thiosulfinate **8** resulted only after 3 days at room temperature and 2 h at reflux (eq 5).



(eq. 5)

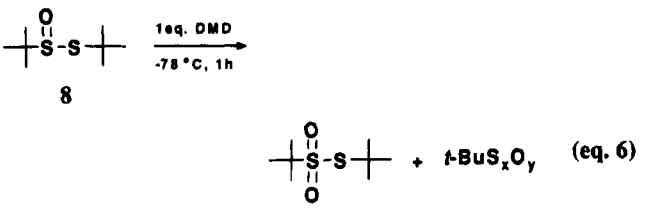
8 **9 (50%)** **8 (10%)**

The solvents were chosen according to their empirical polarities[14] ($E_{T(30)}$) in order to represent a range of polarity. These results clearly show that the less polar the solvent is, the more di-*tert*-butyl thiosulfonate (**9**) is formed and the slower the oxidation reaction is. The *m*-CPBA oxidation is believed to proceed through a heterolytic mechanism, and the rate of oxidation is then directly correlated to the polarity of the solvent.[15] However, considering the mechanism proposed earlier for the decomposition of *vic*-disulfoxides **3**, the cleavage of **7** into sulfinyl ions is postulated. The solvation of the ions formed is directly correlated to the polarity of the solvent.[14,15] In the case of the di-*tert*-butyl derivative,[12] the solvation is apparently such that it creates hindrance that retards the two ions from reacting together. In contact with another molecule of *vic*-disulfoxide **7**, the oxygen transfer reaction described previously can take place because **7** would be much less solvated than an ionic species. However, when less polar solvents are used, the solvation should decrease implying less overall hindrance, and thus, the formation of thiosulfonate **9** should be significantly favored as observed.

Reagent Concentration Effects. Most of the oxidation reactions reported here have been carried out using *m*-CPBA as well as DMD. As stated earlier, the use of DMD considerably simplified the procedure employed but no major difference was found in terms of oxidative results. However, the oxidation of di-*tert*-butyl thiosulfinate (**8**) using *m*-CPBA or DMD afforded very different reaction mixtures for no apparent reason.

The 1 equiv DMD oxidation of thiosulfinate **8** was carried out at −78 °C in acetone and anhydrous conditions until no trace of **8** could be detected by TLC. This reaction afforded a relatively high yield (83%) of the expected di-*tert*-butyl thiosulfonate (**9**) (eq 6) while a typical *m*-CPBA oxidation of **8** in methylene chloride always gives a low yield of **9**.

In all the DMD oxidation experiments reported here, the oxidizing agent was a 0.04−0.08 M solution of

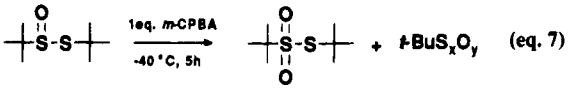


(eq. 6)

8 **9 (83%)**

dimethyldioxirane in acetone. Thus, the DMD oxidation reactions were always carried out at low concentration ([**8**] ≈ 0.02 M) compared to the one reported here and by others[5−7] using other oxidizing agents ([**8**] ≈ 0.2 M). For the specific case reported here, the reagent concentration of the DMD oxidation is about 10 times that of a typical *m*-CPBA oxidation. According to the mechanism reported earlier, the DMD oxidation should give the exclusive formation of the corresponding *vic*-disulfoxide **7** (the low-temperature experiment could not be carried out because of the dilution problem and inevitable presence of acetone). On warming to room temperature, the cleavage of **7** should afford the ambident *tert*-butylsulfinyl ions **20a-b** (*t*-BuS$^+$(=O) and *t*-BuS$^-$(=O)). At such reagent concentrations, these ions react together before they meet another molecule of *vic*-disulfoxide **7**. The recombination of these two sulfinyl ions affords the expected thiosulfonate probably *via* the formation of *O,S*-sulfenyl sulfinate **22** (Scheme 5).

Accordingly, in a separate experiment, the oxidation of di-*tert*-butyl thiosulfinate (**8**) was carried out using 1 equiv of *m*-CPBA under similar conditions (low concentration) to those reported for the DMD oxidation of **8** ([**8**] = 0.01 M, −78 °C, CH_2Cl_2). Analysis of the reaction mixture afforded a moderate yield (64%) of the expected di-*tert*-butyl thiosulfonate (**9**) (eq 7).



(eq. 7)

[**8**] = 0.01 M **9 (64%)**

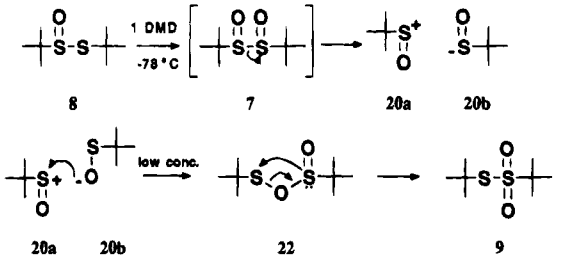
In contrast, Freeman and Angeletakis[5c] reported that only traces of di-*tert*-butyl thiosulfonate (**9**) were formed by the low-temperature *m*-CPBA oxidation of di-*tert*-butyl thiosulfinate (**8**). As stated earlier, the similar experiment reported here showed significant amounts of **9** (7%) at the end of the decomposition. A consistent explanation for such a difference lies in the fact that their reaction mixtures were much more concentrated than ours (5−10 times) as they were using 10 mm NMR tubes and obtained almost noiseless ^{13}C NMR spectra by only acquiring 200 transients.

The results presented in this section give clear evidence of the special behavior of the di-*tert*-butyl derivatives. Low-temperature experiments, use of unsymmetrical starting material as well as various solvents, and working at different concentrations allows the proposal of a mechanism that is consistent with the results observed for the low-temperature decomposition of di-*tert*-butyl *vic*-disulfoxide (**7**) as well as for the formation of di-*tert*-butyl thiosulfonate (**9**) by direct oxidation.

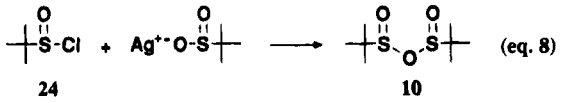
Characterization of Di-*tert*-butyl Disulfide Tri- and Tetraoxides. To our knowledge, *tert*-butylsulfinyl *tert*-butyl sulfone (**12**) and di-*tert*-butyl *vic*-disulfone (**23**) have never been isolated, detected, or characterized. The synthesis of other alkyl and aryl sulfinyl sulfones **4** was reported[4e,f,l] by reacting the corresponding sulfinyl chlo-

(14) Reichardt, C. *Solvent Effects in Organic Chemistry*; Ebel, H. F., Ed.; Verlag Chemie Weinheim: New York, 1979; Vol. 3, p 242.
(15) Sanderson, R. T. *Polar Covalence*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press, Inc.: New York, 1983; Chapters 1 and 2.

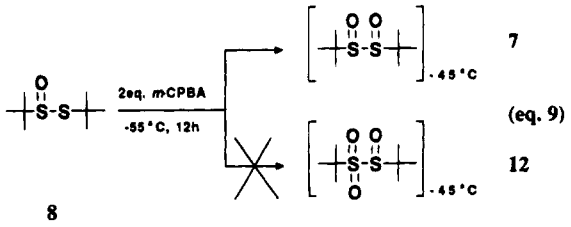
Scheme 5



ride with the sodium salt of the sulfinic acid. However, when *tert*-butylsulfinyl chloride (**24**) and silver *tert*-butylsulfinate were used, the only compound isolated[4h] was not the expected **12** but the corresponding anhydride **10** probably because of steric hindrance or thermodynamic control, i.e., **10** is more stable than **12** as suggested by Freeman[4l] (eq 8).

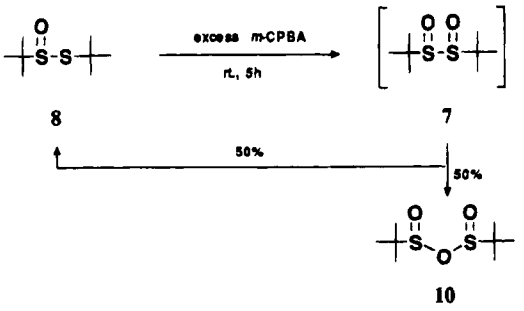


As stated earlier, small amounts of supposed sulfinyl sulfone **12** were detected in the low-temperature decomposition of the corresponding *vic*-disulfoxide **7**. The chemical shifts observed were tentatively assigned to **12** by analogy with the ones of other di-, tri-, and tetrasulfide derivatives as well as with the ones of the tri- and tetrasulfide analogs **25** and **26** (see Table 2). From these results, it was thought that trioxide **12** might be detected at low temperature. However, the low-temperature oxidation of di-*tert*-butyl thiosulfinate (**8**) using 2 equiv of *m*-CPBA only afforded the corresponding *vic*-disulfoxide **7**, and no trace of **12** could be detected at −45 °C as reported above. A possible explanation is the exclusive formation of **7** (Figure 1) that should then react with the other equivalent of *m*-CPBA. The formation of trioxide **12** would imply the attack of a sulfinyl sulfur at the electrophilic oxygen of the peracid. Considering that the electrophilic oxidation of a sulfinyl sulfur at −55 °C is slow and that the *vic*-disulfoxide **7** is rather sterically hindred, it is not surprising that no reaction takes place under these specific conditions (eq 9).



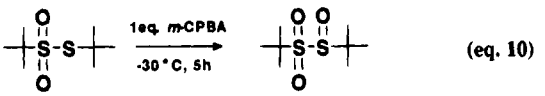
Direct oxidation of thiosulfinate **8** at higher temperature using more than 2 equiv of *m*-CPBA afforded only

Scheme 6



the sulfinic anhydride **10**. In this case, the *vic*-disulfoxide **7** formed is not stable at this temperature and decomposes to an equimolar mixture of **8** and **10** as seen previously. The thiosulfinate **8** present in the reaction mixture can then be reoxidized by the excess *m*-CPBA forming **7** which decomposes to **8** and **10**; this process could proceed until all the oxidizing agent has been used (Scheme 6).

Knowing that small amounts of trioxide **12** could be detected at −20 °C, and that sulfenyl sulfur atoms are usually much more nucleophilic than sulfinyl sulfur atoms, the synthesis of **12** was attempted by direct oxidation of di-*tert*-butyl thiosulfonate (**9**) using 1 equiv of pure *m*-CPBA at −30 °C for 5 h according to the low-temperature experiment procedure previously described (eq 10).



The ^1H and ^{13}C NMR spectra (Figure 2) were recorded at −30 °C and interpreted as a major conversion of di-*tert*-butyl thiosulfonate (**9**) to *tert*-butylsulfinyl *tert*-butyl sulfone (**12**) (85% conversion at the end of the oxidation). Small amounts of trisulfide analog **25** are also detected because the thiosulfonate **9** used contained some trisulfide analog **21** as well as very small quantities of **23** represented by the unlabeled proton resonance.

The chemcial shifts of the compounds detected in this low-temperature experiment are reported in Table 2.

The decomposition study of trioxide **12** was also investigated. Although *tert*-butylsulfinic acid (**13**) and *tert*-butylsulfonic acid (**14**) (known as the decomposition products of *tert*-butylsulfinic anhydride (**10**)) were detected, the stepwise (10 °C) decomposition of **12** from −30 °C to room temperature was complicated and did not allow the determination of a clear mechanism. However, significant amounts of di-*tert*-butyl *vic*-disulfone (**23**) were detected at various temperatures. The presence of **23** suggests that the mechanism proposed previously, ionic cleavage and oxygen transfer (steric hindrance in

Table 2. ^1H and ^{13}C NMR Chemical Shifts of the Compounds Observed in the Low-Temperature Detection of *tert*-Butylsulfinyl *t*-Butyl sulfone (12)[a,b]

entry	compd	spectra	C	CH_3	H	C′	CH_3′	H′
9	*t*-Bu$S(O)_2$S*Bu-t*	b	68.01	23.65	1.592	56.31	31.45	1.448
12[c]	*t*-Bu$S(O)_2$S(O)Bu-*t*	a	69.28	23.74	1.501	63.68	23.80	1.473
23	*t*-Bu$S(O)_2$S$(O)_2$Bu-*t*		72.67	24.60	1.633			
21	*t*-Bu$S(O)_2$SSBu-*t*		70.06	24.18	1.465	49.95	29.86	1.395
25	*t*-Bu$S(O)_2$SS(O)Bu-*t*	c	71.38	23.99	1.551	63.08	24.51	1.463
27	*t*-Bu$S(O)_2$SS$(O)_2$Bu-*t*		73.45	24.15	1.545			

[a] All the spectra were recorded in $CDCl_3$. [b] The chemical shifts reported here were obtained from pure samples at room temperature unless otherwise stated. [c] These spectra were obtained at −30 °C.

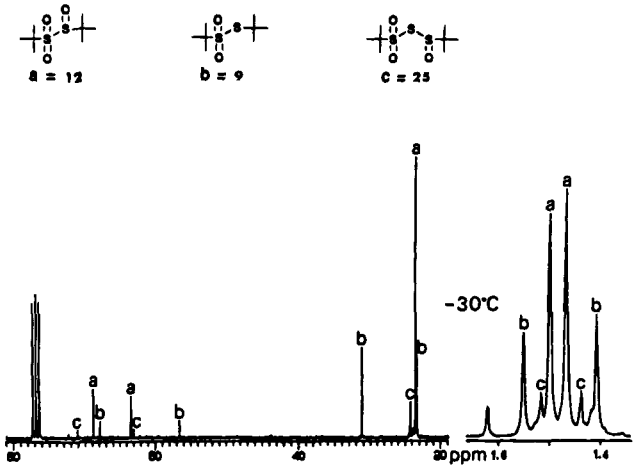
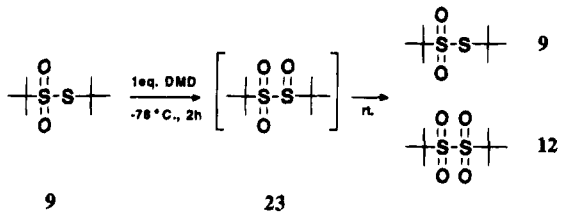


Figure 2. Low-temperature ^{13}C and ^{1}H NMR spectra of di-*tert*-butyl disulfide 1,1,2-Trioxide (**12**).

Scheme 7



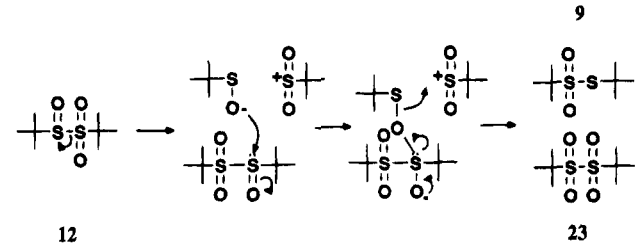
the recombination) could be extrapolated to the decomposition of trioxide **12**.

The possibility of such a decomposition mechanism was also supported by the results obtained from a separate experiment. The oxidation of pure di-*tert*-butyl thiosulfonate (**9**) was attempted using 1 equiv of DMD at −78 °C. The NMR analysis of the reaction mixture at room temperature gave a clean array of decomposition products, and no trace of **12** was detected. The reaction mixture presents a 60/40 mixture of di-*tert*-butyl *vic*-disulfone (**23**) and di-*tert*-butyl thiosulfonate (**9**) (Scheme 7).

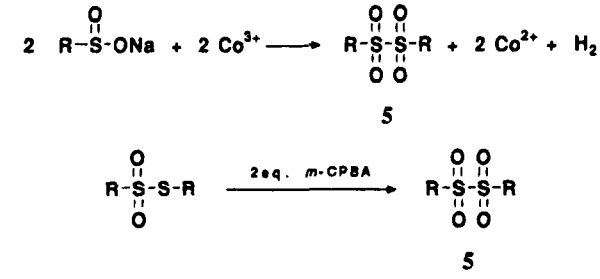
Considering that the low-temperature oxidation of **9** gave 85% of trioxide **12** (eq 10), that the sulfenic sulfur of **9** must be much more nucleophilic than the sulfinic sulfur of **12**, and that the steric effect is in favor of the formation of **12** rather than **23**, the oxidation of di-*tert*-butyl thiosulfonate (**9**) by DMD at low temperature should afford the exclusive formation of **12**. By analogy with the results obtained for the low-temperature oxidation of di-*tert*-butyl thiosulfinate (**8**), the trioxide **12** formed should cleave and give a pair of ions on warming. It is difficult to predict whether *tert*-butyl-sulfonyl cation **28a** and *tert*-butylsulfinyl anion (**20b**) or the reverse are formed. However, sulfinyl and sulfonyl groups are known to be good leaving groups,[4k] and under these dilute conditions, the reaction of the ions formed with another molecule of starting material should eventually give the products observed as the formation of trioxide **12** is not favored. The recombination of the sulfonyl ion **28** should be sterically very difficult with respect to the recombination of sulfinyl ions. As a consequence, the oxygen transfer mechanism[13] is still a good explanation for the formation of these decomposition products (disproportionation) (Scheme 8).

If the mechanism presented above is correct, only 50% of tetraoxide **23** should have been obtained. The 60% of **23** observed can be explained by the NMR integration errors which were earlier reported to be about 10%.

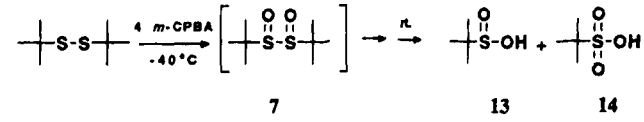
Scheme 8



Scheme 9



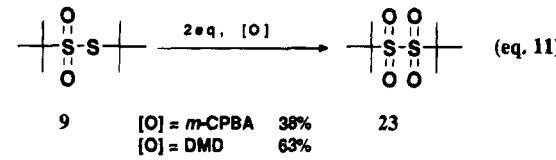
Scheme 10



Possibly the discrepancy could be related to an excess of oxidizing agent or a combination of both.

Although almost nothing is known about the chemistry of the alkyl *vic*-disulfones (**5**), the synthesis of a few aryl and alkyl *vic*-disulfones has been reported by oxidation of the corresponding sodium sulfinate with cobalt(III) sulfate[4g] or by direct peracid oxidation of the corresponding thiosulfonates[4k,l] (Scheme 9).

The oxidation of thiosulfonate **9** using 2 equiv of *m*-CPBA or DMD afforded a low to moderate yield of the corresponding tetraoxide **23** (eq 11).



When *m*-CPBA was used, the oxidation reaction was very slow, and after 8 days at −20 °C a low yield of tetraoxide **23** was isolated. However, the DMD oxidation afforded a fair yield (63%) of the desired **23** in less than 12 h from −78 °C to room temperature. Direct oxidation of di-*tert*-butyl disulfide (**6**) with 4 equiv of *m*-CPBA at −40 °C were unsuccessful and mainly afforded *tert*-butylsulfinic acid (**13**) and *tert*-butylsulfonic acid (**14**) for reasons stated earlier (Scheme 10).

Conclusions. The further investigation of the formation and decomposition of the di-*tert*-butyl disulfide polyoxides has allowed the characterization of new products, the explanation of inconsistent results,[3b,c,5c,7b] and the proposal of a consistent, general mechanism.[13] In comparison to the well-studied disproportionation of thiosulfinates,[1] clear evidence of a similar disproportionation for the decomposition of di-*tert*-butyl *vic*-disulfoxide (**7**) and *tert*-butylsulfinyl *tert*-butyl sulfone (**12**) is reported. In contrast with a previous report,[5c] the general mechanism proposed here accounts for most of the results observed (detection of only one diastereoisomer of **7**,

decomposition products, and intermediates). Finally, the use of DMD has been shown to present a considerable advantage in changing the oxidation process over peroxy acids in this case of the *tert*-butyl disulfide polyoxides where steric and electronic effects are very important.

Experimental Section

Chemical reagents were obtained from commercial sources and used directly unless otherwise stated. Di-*tert*-butyl trisulfide (99%) was provided by Elf Atochem N. A. Inc., King of Prussia, PA, and used as such. The *m*-CPBA used was purified by washing the commercial 80–85% or 50–60% material with a phosphate buffer, drying, filtering, and evaporating at reduced pressure. The solid was then recrystallized from methylene chloride to afford 99% *m*-CPBA.[16] Dimethyldioxirane was prepared according to the literature procedure.[17] It was stored in the freezer over 3Å 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 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 on Fisher Scientific Neutral Alumina (80–200 mesh) that had previously been dried. In both cases flash column procedures[18] were used. Gas chromatography was performed on a Varian Associates (VA) Model 3700 gas chromatograph equipped with a model 4270 printing integrator and an FID detector. Separation was achieved using a 15 m glass capillary column bonded with 3% silicone OV-101.

^{1}H NMR spectra were recorded at 200 MHz (Varian XL-200 and Varian Gemini 200), at 270 MHz (Jeol 270-CPF), and at 300 MHz (Varian XL-300) with the solvents noted. Multiplicity assignments are reported using the following abbreviations: s for singlet, d for doublet, t for triplet, q for quartet, h for heptet, and m for multiplet. ^{13}C NMR were recorded on the same instruments (50.3 MHz, 67.9 MHz and 75.4 MHz). In both cases, the chemical shifts (δ) are reported in parts per million relative to the deuterated solvent (δ $CDCl_3$ ^{13}C = 77.00ppm; ^{1}H = 7.24ppm).

Procedure 1: *m*-CPBA Oxidation. A typical experimental procedure as follows. A solution of *m*-CPBA (0.98 g, 5.71 mmol, 1.1 equiv) in methylene chloride (25 mL) was added dropwise to an ice-cooled solution of disulfide (5.19 mmol) in CH_2Cl_2 (15 mL) during 0.5 h under nitrogen. After being stirred for 3 h at 0 °C, the mixture was concentrated to 10 mL by rotoevaporation. The solution was cooled to −78 °C, and the *m*-CBA that crystallized (0.85 g, 5.48 mmol, 96%) was collected. 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 the corresponding thiosulfinate. In the following *m*-CPBA oxidations, the reaction temperature, the reaction time, and the number of equivalents of *m*-CPBA may vary and are reported. The method of separation can also be different depending on the compound prepared.

Procedure 2: DMD Oxidation. A typical experimental procedure is as follows. A 0.07 M solution of DMD in acetone (34 mL, 2.38 mmol, 1 equiv) was added dropwise to a cooled solution (−78 °C) of disulfide (2.38 mmol) in acetone (10 mL) during 30 min under nitrogen. After the solution was stirred for 1 h at −78 °C, the solvent was removed *in vacuo* to give the corresponding thiosulfinate. In the following DMD oxidations, the reaction time and the number of equivalents of DMD may vary and are reported. The method of separation is indicated when necessary.

Oxidation of Disulfides. Preparation of Di-*tert*-butyl Thiosulfinate (8). Compound **8** (oil) was prepared in almost quantitative yield by Freeman's[7b] procedure. Similar results were obtained using DMD following procedure 2: ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9H) 1.56 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 59.35, 48.56, 32.25, 24.19 ppm.

Preparation of Di-*tert*-butyl Thiosulfonate (9). Compound **9** was prepared in low yield by Freeman's[7b] procedure. However, the 1 equiv DMD (−78 °C, 6 h, 1 equiv) oxidation of **8** and the 2 equiv DMD (−78 °C, 6 h, 2 equiv) oxidation of di-*tert*-butyl disulfide gave a high yield of **9** (83% and 75%, respectively) under the conditions described in procedure 2. In both cases, compound **9** (oil) was purified by silica gel chromatography using benzene as solvent; anhydrous conditions were crucial: ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9H) 1.60 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 68.09, 56.39, 31.53, 23.73 ppm.

Attempted Preparation of *tert*-Butylsulfinyl *tert*-Butyl Sulfone (12). The preparation of trioxide **12** and tetraoxide **23** was attempted by oxidation of the corresponding disulfide (0.8–1.2 g, 4.49–6.74 mmol) using *m*-CPBA (0 to −40 °C, 1–8 days, 3–5 equiv) according to procedure 1. Evaporation of the solvent *in vacuo* and at low temperature (10 °C) gave the diastereomeric mixture of di-*tert*-butylsulfinic anhydride (**10**). **10a**: ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 18H) ppm; ^{13}C NMR ($CDCl_3$) δ 60.43, 21.51 ppm. **10b**: ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 18H) ppm; ^{13}C NMR ($CDCl_3$) δ 60.07, 21.37 ppm. After 2 h at room temperature **10** was converted to a mixture of *tert*-butylsulfinic acid (**13**), *tert*-butylsulfonic acid (**14**), *tert*-butyl *m*-chlorobenzoate (**29**), and di-*tert*-butyl sulfinate (**30**). Compounds **13** and **14** were identified by ^{1}H and ^{13}C NMR from the crude mixture and were characterized from parallel syntheses as well as literature reports.[5c] **13**: ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 57.46, 21.42 ppm. **14**: ^{1}H NMR ($CDCl_3$ partly soluble) δ 1.43 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 58.07, 24.49 ppm. Compounds **29** and **30** were obtained by silica gel column chromatography. Elution with 13% ethyl acetate/hexanes gave **29**, and further elution with 25% ethyl acetate/hexanes afforded **30**.[5c] **29** (9%): ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9H), 7.31 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 164.46, 134.30, 133.78, 132.40, 129.51, 129.48, 127.53, 81.67, 28.12 ppm. **30** (19%): ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9H), 1.15 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 82.55, 56.76, 29.40, 21.60 ppm.

Preparation of Di-*tert*-Butyl *vic*-Disulfone (23). The preparation of tetraoxide **23** was achieved by oxidation of **9** (0.82 g, 3.74 mmol) using *m*-CPBA (−20 °C, 8 days, 2.5 equiv) according to procedure 1. Evaporation of the solvent *in vacuo* and silica gel chromatography using a 25% ethyl acetate/hexanes solution afforded the desired **23** (0.53, 2.20 mmol, 58%) as a solid. The same experiment was repeated using DMD (−78 °C, 6 h, 2.5 equiv) and gave **23** (76%) according to procedure 2: mp compound **23** melted over a range of 63–92 °C, it is likely that it decomposed; ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 18H) ppm; ^{13}C NMR ($CDCl_3$) δ 72.67, 24.60 ppm. No parent peak could be observed using EI and CI mass spectrometry. However, **23** showed a single spot on TLC and its NMR data are consistent with those of other polysulfide polyoxide derivatives presented in Table 1 and elsewhere.[10,13,19]

Preparation of Diisopropyl Thiosulfinate (31) and Diisopropyl Thiosulfonate (16). Compounds **31** and **16** were obtained using *m*-CPBA according to the known procedure[4k] (similar to procedure 1). The oxidation was also achieved using 1 and 2 equiv of DMD according to procedure 2. **31** (quant): ^{1}H NMR ($CDCl_3$) δ 3.51 (h, 1H), 3.09 (h, 1H), 1.38 (dd, 6H), 1.27 (dd, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 55.08, 38.11, 24.45, 24.24, 16.38, 15.53 ppm. **16** (93%): ^{1}H NMR ($CDCl_3$) δ 3.62 (h, 1H), 3.31 (h, 1H), 1.42 (d, 6H), 1.48 (d, 6H) ppm; ^{13}C NMR ($CDCl_3$) δ 63.48, 42.92, 24.24, 16.28 ppm. These data are consistent with previously reported values.[4k]

Solvent Effect. *m*-CPBA Oxidation of Di-*tert*-butyl Thiosulfinate (8) in Acetic Acid. A solution of *m*-CPBA (0.487 g, 2.83 mmol, 1.1 equiv) in 10 mL of freshly distilled acetic acid was added dropwise to an ice-cooled solution of **8**

(16) Shartz, N. N.; Blumberg, J. H. *J. Org. Chem.* **1976**, *29*, 1496.
(17) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Singh, M.; Murray, R. W. *J. Org. Chem.* **1992**, *57*, 4263.
(18) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(19) (a) Freeman, F.; Angeletatkis, C. N. *J. Org. Chem.* **1982**, *47*, 4194. (b) Mieloszynski, J. L.; Weber, J. V.; Schneider, M.; Paquer, D.; Born, M.; Pare, G. *Sulfur Lett.* **1988**, *8*, 27. (c) Freeman, F.; Lee, C. *Magn. Reson. Chem.* **1988**, *26*, 813.

(0.5 g, 2.58 mmol) and *tert*-butyl chloride (0.120 g, 1.3 mmol) in 5 mL of acetic acid under anhydrous conditions. *tert*-Butyl chloride was used as an internal standard. After being stirred for 2 h, the reaction mixture was evaporated and the NMR of the crude mixture showed no trace of di-*tert*-butyl thiosulfonate (**9**) but *tert*-butyl sulfinic acid (**13**) as major compound (87%). The chemical shifts observed for **13** were essentially identical to those reported in the literature.[5c] **13**: ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$) δ 57.46, 21.42 ppm.

***m*-CPBA Oxidation of Di-*tert*-butyl Thiosulfinate (8) in Methylene Chloride.** A solution of *m*-CPBA (0.487 g, 2.83 mmol, 1.1 equiv) in 10 mL of anhydrous CH_2Cl_2 was added dropwise to an ice-cooled solution of **8** (0.5 g, 2.58 mmol) and *tert*-butyl chloride (0.120 g, 1.3 mmol) in 5 mL of anhydrous CH_2Cl_2 under nitrogen. *tert*-Butyl chloride was used as an internal standard. After being stirred for 5 h at 0 °C, the reaction mixture was kept at −78 °C for 30 min. The *m*-CBA that crystallized was collected, and the NMR of the crude mixture showed 19% of di-*tert*-butyl thiosulfonate (**9**) plus a complex mixture of compounds reported earlier. The chemical shifts observed for **9** were similar to those reported earlier as well as in the literature.[7]

***m*-CPBA Oxidation of Di-*tert*-butyl Thiosulfinate (8) in Toluene.** A solution of *m*-CPBA (0.487 g, 2.83 mmol, 1.1 equiv) in 10 mL of dried toluene was added dropwise to an ice-cooled solution of **8** (0.5 g, 2.58 mmol) and *tert*-butyl chloride (0.120 g, 1.3 mmol) in 5 mL of toluene under nitrogen. *tert*-Butyl chloride was used as an internal standard. After being stirred for 7 h at 0 °C, the reaction mixture was kept at −78 °C for 30 min. The *m*-CBA that crystallized was filtered, and the NMR of the crude mixture showed 73% of di-*tert*-butyl thiosulfonate (**9**), 10% of unreacted **8**, plus a complex mixture of compounds reported earlier. The chemical shifts observed for **9** were similar to those reported earlier as well as in the literature.[7]

***m*-CPBA Oxidation of Di-*tert*-butyl Thiosulfinate (8) in 50/50 Carbon Tetrachloride and *n*-Pentane.** A solution of *m*-CPBA (0.487 g, 2.83 mmol, 1.1 equiv) in 10 mL of dried CCl_4 was added dropwise to an ice-cooled solution of **8** (0.5 g, 2.58 mmol) and *tert*-butyl chloride (0.120 g, 1.3 mmol) in 5 mL of dried *n*-pentane under nitrogen. *tert*-Butyl chloride was used as an internal standard. After being stirred for 3 days at room temperature and 2 h at reflux, the reaction mixture was kept at −78 °C for 30 min. The *m*-CBA that crystallized was collected, and the NMR of the crude mixture showed 48% of di-*tert*-butyl thiosulfonate (**9**), 10% of unreacted **8**, plus a complex mixture of compounds reported earlier. The chemical shifts observed for **9** were similar to those reported earlier as well as in the literature.[7]

Concentration Effect. DMD Oxidation of Di-*tert*-butyl Thiosulfinate (8) in Acetone. A 0.05 M dried solution of DMD (20 mL, 1 eq) in acetone was added dropwise to an ice-cooled solution of **8** (0.2 g, 1.03 mmol) and *tert*-butyl chloride (0.046 g, 0.5 mmol) in 30 mL of dried acetone. *tert*-Butyl chloride was used as an internal standard and the relative concentration of **8** was 0.023 M. After being stirred for 1 h at −78 °C the solvent was evaporated and the NMR of the crude mixture showed 83% of di-*tert*-butyl thiosulfonate (**9**) plus a complex mixture of compounds reported above. The chemical shifts observed for **9** were similar to those reported earlier as well as in the literature.[7]

***m*-CPBA Oxidation of Di-*tert*-butyl Thiosulfinate (8) at Low Concentration in CH_2Cl_2.** A solution of *m*-CPBA (0.195 g, 1.13 mmol, 1.1 equiv) in 50 mL of anhydrous CH_2Cl_2 was added dropwise to an ice-cooled solution of **8** (0.2 g, 1.03 mmol) and *tert*-butyl chloride (0.046 g, 0.5 mmol) in 50 mL of anhydrous CH_2Cl_2 under nitrogen. *tert*-Butyl chloride was used as an internal standard, and the relative concentration of **8** was 0.01. The reaction mixture was stirred for 12 h at −78 °C. The *m*-CBA that crystallized was collected, and the NMR of the crude mixture showed 64% of di-*tert*-butyl thiosulfonate (**9**) plus a complex mixture of compounds reported earlier as well as significant quantities of residual *m*-CBA. The chemical shifts observed for **9** were similar to those reported earlier as well as in the literature.[7]

Low-Temperature Oxidation Experiments. General Procedure for the Low-Temperature *m*-CPBA Oxidation Experiments. A typical procedure is the detection of di-*tert*-butyl *vic*-disulfoxide (**7**). The oxidation of di-*tert*-butyl thiosulfinate (**8**) (150 mg, 0.77 mmol) dissolved in 0.5 mL of dry $CDCl_3$ was achieved by the slow addition of pure anhydrous *m*-CPBA (>99%) (133 mg, 0.77 mmol, 1 equiv) partially dissolved in 2 mL of $CDCl_3$. The reaction mixture was stirred for 4 days at −55 °C under nitrogen using a cooling system. The reaction was carried out in deuterated chloroform, and most of the *m*-CPBA and *m*-CBA formed were not soluble at this temperature. The reaction mixture was then filtered using a customized piece of equipment that allowed the filtration to take place at a temperature lower than −40 °C. The filtration equipment was a two-necked flask (5 mL) placed in the coolling bath. One outlet was connected to the vacuum hose and the other to a coarse filtration Schlenk device that was surrounded by a jacket filled with dry ice. Using a pipette that had previously been stored in dry ice, the reaction mixture was quickly transferred to the bottom of the Schlenk. Because of a moderate vacuum, the solution went through the filtrate before it froze. After removal of the jacket, Schlenk, and vacuum hose, the reaction mixture was transferred into a 5 mm NMR tube that was kept in dry ice (transfer by frozen pipette). The spectrometer (Jeol 270) was cooled to −100 °C, and the sample was kept in dry ice. The transfer of the NMR tube from the dry ice to the probe of the spectrometer was done in 30−60 s, the temperature of the probe remained below −60 °C, and the sample was still frozen (mp of $CDCl_3$ = −64 °C). Then, the temperature of the spectrometer was set to −45 °C, the temperature of the sample was allowed to stabilize for 0.5 h, and the ^{1}H and ^{13}C NMR spectra were recorded at various temperatures.

Low-Temperature Detection of *tert*-Butylsulfinyl *tert*-Butyl Sulfone (12). The oxidation of di-*tert*-butyl thiosulfonate (**9**) (200 mg, 0.95 mmol) dissolved in 0.5 mL of dry $CDCl_3$ was achieved by the slow addition of pure anhydrous *m*-CPBA (>99%) (164 mg, 0.95 mmol, 1 equiv) partially dissolved in 2 mL of $CDCl_3$. After 5 h at −30 °C the reaction mixture was treated as previously described.

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Supplementary Material Available: NMR spectra of compound **23** (1 page). 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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