# The Chemistry of Alkylsulfenyl Alkylsulfinyl Thioanhydrides.[1] The Mechanism of Decomposition

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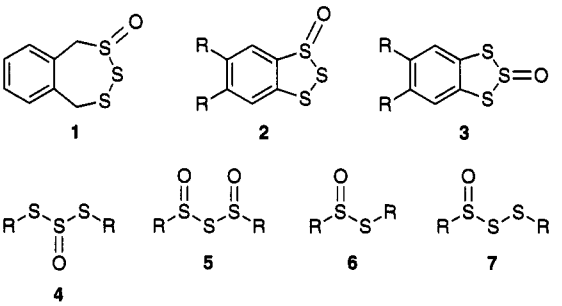
The decomposition mechanism of alkylsulfenyl alkylsulfinyl thioanhydrides has been investigated. Although the product mixture is complex in most cases, a detailed decomposition study as well as a careful analysis of the products allows for a proposal for a general mechanism which is interesting and not simple. We find, however, that the decomposition process is consistent with that of related systems.

Thiosulfinate esters have been extensively studied;[2] however, very little is known about the chemistry of their trisulfide analogs. Trisulfides are known to undergo oxidation, leading to the corresponding oxidized trisulfide derivatives. The 1 equiv peracid oxidation of 2,3,4-benzotrithiepin[3] regiospecifically gives the 1-oxide **1**. Similar results were reported using linear alkyl trisulfides.[4] However, the oxidation of certain cyclic trisulfides[5] (trithiolanes) has been found not to be regiospecific, the oxidation taking place on the terminal as well as the central sulfur atom and affording the corresponding trithiole 1-oxide **2** and trithiole 2-oxide **3**. Linear dithiosulfites **4** are generally prepared by a nonoxidative synthetic procedure.[6] Using 2 equiv of oxidizing agent, the two end sulfur atoms are oxidized, giving thioanhydride **5**.[4]

In contrast to the thiosulfinates **6**, linear sulfenyl sulfinyl thioanhydrides **7** were found to have a relatively low stability at room temperature; the stability increased with the degree of substitution (tertiary > secondary > primary).[4] To our knowledge, no extensive study of this class of compounds has been reported, although various decomposition products have been determined by different groups of researchers.[4,7] The decomposition of linear dithiosulfites **4** is clean.[6] Even here, however, parts of the proposed mechanism remain somewhat unclear. It was decided to further investigate the decomposition of this class of compounds focusing on the di-*tert*-butyl derivatives.




**Decomposition Products of *tert*-Butylsulfenyl *tert*-Butylsulfinyl Thioanhydride (8).** Oxide **8** was obtained in moderate yield and high purity by direct oxidation of the corresponding trisulfide **9**. The purification of **8** was difficult because of its low stability. Its decomposition has been investigated under various conditions and afforded contradictory complex mixtures of products that could not be completely rationalized.[4,7] In the present study, the decomposition of **8** is further investigated under standardized conditions.

The first part of this work focused on the determination of the identity and amounts of the decomposition products of **8**. Many attempts using pure **8** (>96% by proton NMR) have shown that the mixture is complex but afforded as major compounds di-*tert*-butyl tetrasulfide (**10**), *tert*-butylsulfenyl *tert*-butylsulfonyl thioanhydride (**11**), and di-*tert*-butyl thiosulfinate (**12**). The reaction was carried out at different temperatures (rt, 50 °C, and 100 °C), in different solvents (benzene-$d_6$, chloroform-$d$, acetone-$d_6$, and acetonitrile-$d_3$), at different concentrations (5–50 mg/mL), and under various decomposition conditions (dark, inert atmosphere). Although the relative concentration of the final products varied somewhat according to the purity of the starting material and the solvent used (*vide infra*), the reaction mixtures were found in most cases to be close to an equimolar mixture of the three products (**10**–**12**) (Scheme 1).

The relative concentrations of the final products were determined after separation by silica gel chromatography or by the relative integrals observed on $^{13}C$ NMR. A satisfactory integral could not be obtained by proton NMR owing to overlapping peaks. However, calibration experiments have shown that the relative $^{13}C$ integral of this specific mixture corresponds to their respective relative molar concentrations within *ca.* 7%. The deviation from the average 1:1:1 mixture of the three decomposition products can be rationalized by the fact that the reaction is not completely clean (*ca.* 10% of other derivatives), the inherent error of the NMR calculations, or the inevitable loss of compound by chromatography. The

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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 a trithiolane 2-oxide derivative (ref 5a). We have used the thioanhydride approach, even though there are less correct but clearer names available. For instance, the title compounds could be named as dialkylsulfenyl thiosulfinates in keeping with the structural relationship with the well-known thiosulfinates.

(2) (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. In *The Chemistry of Sulfinic Esters and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1990; Chapter 4.

(3) Milligan, B.; Swan, J. M. *J. Chem. Soc.* **1965**, 2901.

(4) (a) Steudel, R.; Latte, J. *Chem. Ber.* **1977**, *110*, 423. (b) Steudel, R. *Phosphorus Sulfur* **1985**, *23*, 33. (c) Freeman, F.; Ma, X.-B.; Lin, R. I.-S. *Sulfur Lett.* **1993**, *15*, 253. (d) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1995**, *18*, 167.

(5) (a) Ghosh, F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499. (b) Yomoji, N.; Takahashi, S.; Chida, S.-I.; Ogawa, S.; Sato, R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1995.

(6) Field, L.; Lacefield, W. B. *J. Org. Chem.* **1966**, *31*, 3555.

(7) Bleeker, I. P.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 459.

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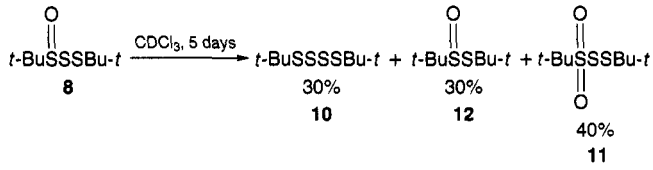
**Scheme 1**




quantification of the decomposition products has been attempted using GC analysis; unfortunately, the compounds decompose readily on the capillary column used.

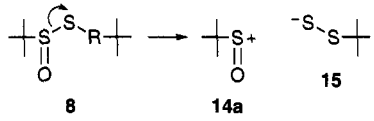
Although small amounts of di-*tert*-butyl trisulfide (**9**) (*t*-BuSSSBu-*t*) and di-*tert*-butyl thiosulfonate (**13**) (*t*-BuS(O)$_2$SBu-*t*) have been detected in some cases, the results observed here are somewhat in contrast with the literature[4,7] where reaction conditions were different from ours.

**Kinetic Study.** Kinetic experiments were carried out on oxide **8** employing $^{13}C$ and $^{1}H$ NMR; however, most of the proton NMR kinetic experiments could not be interpreted owing to overlapping peaks. The concentrations of **8** were approximately 0.3 mol $L^{-1}$ for $^{13}C$ kinetic experiments and 0.01 mol $L^{-1}$ for proton experiments. The NMR tubes were filled under a nitrogen atmosphere and sealed. These experiments were carried out at 45 °C, and the time between acquisitions was set to 1 h. In order to determine if there was any influence of solvent polarities upon the rates of the decomposition, the kinetic experiments were carried out in benzene-$d_6$, chloroform-*d*, acetone-$d_6$, and acetonitrile-$d_3$. In all cases, the decomposition was completed within 12 h at this temperature (45 °C). The rate constants were calculated from the slope of ln(rel conc) *vs* time plots, assuming first order kinetics (Figure 1). The relative concentrations (rel conc) of starting material and products were calculated by comparing their signal intensities to *tert*-butyl chloride which was used as an internal standard. In all the cases studied, no reaction with the internal standard could be detected. Following this procedure, reasonably good agreement with first order kinetics was obtained. A typical rate profile of the decomposition of **8** is shown in Figure 1.

The use of four different solvents did not afford completely consistent results. Although most of the plots of the ln(rel conc) *vs* time were linear and while the rates of decomposition generally increased with increasing solvent polarities, it was difficult to obtain fully consistent rates of decomposition; hence, the calculations of the enthalpy and the entropy of the decomposition of oxide **8** are not reported. Most of the data reasonably agreed with first order kinetics, and by analogy with other studies,[6] we believe that the decomposition of **8** can be postulated to follow a first order process with the cleavage of the sulfenyl sulfinyl thioanhydride **8** as the rate-determining step.

The use of solvents of different polarities did not afford a clear answer on whether the cleavage was homolytic or heterolytic. Parallel experiments have shown, however, that, in the presence of radical inhibitors (benzoquinone or 4-*tert*-butylcatechol) or light/dark effects, the decomposition was still taking place at similar rates and afforded the same decomposition products. Therefore, we conclude that the cleavage of oxide **8** is heterolytic.

According to previous reports[8] and considering the decomposition products formed, the ionic cleavage of **8** should certainly occur at one of the S–S bonds. Due to the presence of an oxygen atom on the sulfur chain and considering that crystallography studies[9] have shown that the S(O)–S bond is longer than the S–S and S(O)$_2$–S bonds, it is reasonable to suggest that the rate-determining step is the ionization of the S(O)–S bond; this cleavage should afford a cation and an anion, and by analogy with previous reports,[8] the ionic cleavage of **8** is believed to afford the *tert*-butylsulfinyl cation[10] (**14**) and the *tert*-butyl disulfide anion (**15**, eq 1a).




(1a)

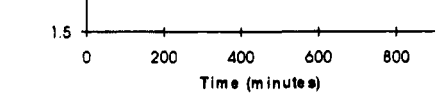
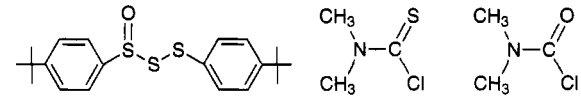



**Figure 1.** First order rate plot for the decomposition of **8** at 45 °C in $CDCl_3$. × = *t*-BuS(O)SSBu-*t*; — = first order.

Several attempts to confirm the postulated cleavage of **8** were carried out by decomposing it in the presence of a wide variety of trapping agents. Using analog **16**, excess di-*tert*-butyl trisulfide (**9**), dimethyl sulfoxide, phenylacetylene, 2,3-dimethyl-1,3-butadiene, dimethylthiocarbamoyl chloride (**17**), and dimethylcarbamyl chloride (**18**) was unsuccessful in our hands.




Under these specific conditions, normal decomposition of **8** occurred in most cases, implying that the trapping agents used were not reactive enough. In the rare cases where the trapping agents (dimethyl sulfoxide and 2,3-dimethyl-1,3-butadiene) participated in the decomposition, the reaction mixture was very complex and could not be analyzed using available techniques. However, using isopropylsulfinyl chloride[11] (**19**) as a trapping agent, significant amounts of *tert*-butylsulfinyl chloride (**20**) (~20%) could be easily detected (the $^{1}H$ and $^{13}C$ NMR chemical shifts of the trapped intermediate **20** were compared to those of a pure sample of *tert*-butylsulfinyl chloride (**20**)).

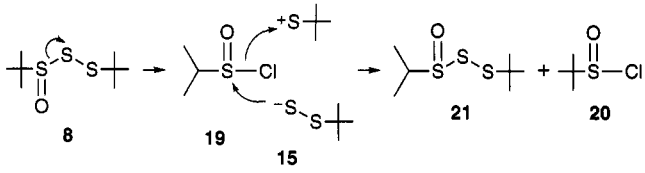
(8) (a) Freeman, F. *Chem. Rev.* **1984**, *84*, 117. (b) Oae, S.; Takata, T.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2484. (c) Freeman, F.; Lee, C. *J. Org. Chem.* **1988**, *53*, 1263.

(9) (a) Wahl, G. H., Jr.; Bordner, J.; Harpp, D. N.; Gleason, J. G. *J. Chem. Soc., Chem. Commun.* **1972**, 985. (b) Wahl, G. H., Jr.; Bordner, J.; Harpp, D. N.; Gleason, J. G. *Acta Crystallogr., Sect. B* **1973**, *28*, 2272.

(10) The existence of this cation has recently been discussed: (a) Schreiner, P. R.; Schleyer, P. V. R.; Hill, R. K. *J. Org. Chem.* **1993**, *58*, 2822. (b) Schreiner, P. R.; Schleyer, P. V. R.; Hill, R. K. *J. Org. Chem.* **1994**, *59*, 1849.

(11) Douglass, I. B.; Norton, R. V. *J. Org. Chem.* **1968**, *33*, 2104.

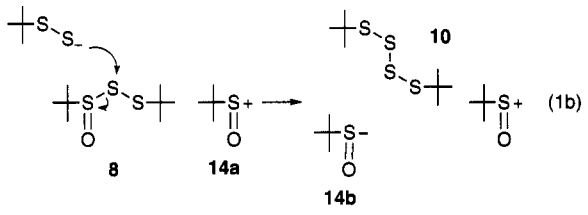
**Scheme 2**



The formation of **21** confirms the proposed cleavage because it involves the formation of the *tert*-butylsulfinyl cation **(14a)** which reacts with chloride anion. In addition, careful analysis of the other decomposition products also gives clear evidence of the reaction of the *tert*-butyl disulfide anion **(15)** with isopropylsulfinyl chloride **(19)** to form mixed oxide **21** (Scheme 2); all of its likely decomposition products were detected in the final reaction mixture (*vide infra*). In addition, when pure **21** was subjected to the above reaction conditions, no scrambling of the alkyl groups took place.

**Proposed Decomposition Mechanism.** The main features of the decomposition of *tert*-butylsulfenyl *tert*-butylsulfinyl thioanhydride **(8)**, which must be accounted for by any mechanism, are as follows. (1) The decomposition of **8** affords a 1:1:1 mixture of di-*tert*-butyl tetrasulfide **(10)**, di-*tert*-butyl thiosulfonate **(11)**, and di-*tert*-butyl thiosulfinate **(12)**. (2) The decomposition is approximated by first order kinetics. (3) The reaction is significantly influenced by heat but not by light and even takes place in the presence of radical inhibitors. (4) No scrambling of the alkyl groups is observed when an unsymmetric sulfenyl sulfinyl thioanhydride **21** is employed. (5) The decomposition is not completely clean, implying that competing rearrangements take place.

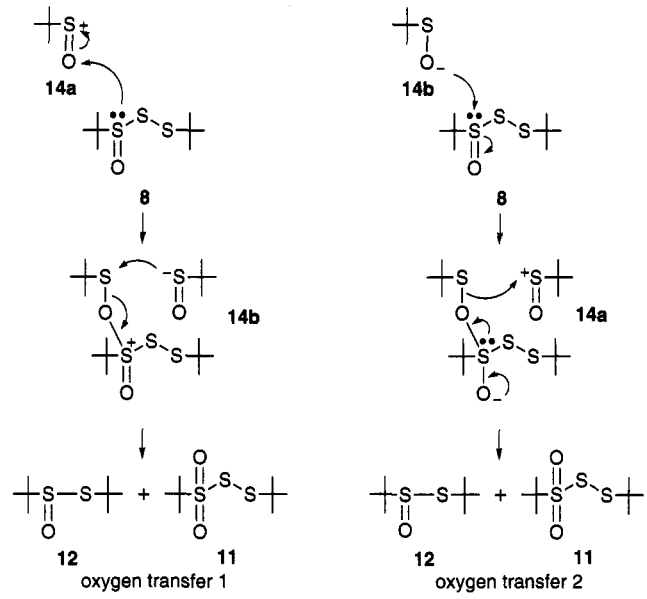
First, the rate-determining cleavage of oxide **8** into an ion pair is suggested, leading to the formation of the *tert*-butylsulfinyl cation **(14a)** and the *tert*-butyl disulfide anion **(15)** (eq 1a). This pair of ions can react with a second molecule of **8**. Attack on the central sulfur would cleave the weakest bond (S–S(O)), giving one decomposition product, di-*tert*-butyl tetrasulfide **(10)**, as well as the *tert*-butylsulfinyl anion **(14b)**. The existence of **14b** is supported by literature precedent[10] (eq 1b).

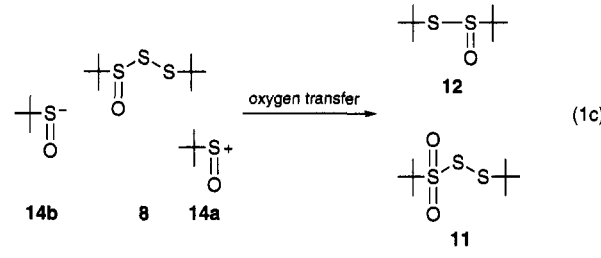


This pair of interesting ambident ions **14a,b** has been shown to not easily recombine to give the expected di-*tert*-butyl thiosulfonate **(13)**, likely because of steric effects.[12] As a consequence, they react faster with a third molecule of starting material **8** by an oxygen transfer mechanism that rationalizes the formation of the two other decomposition products (eq 1c).

Various oxygen transfer mechanisms can be proposed to explain the decomposition of oxide **8**. There are two reasonable possibilities; one involves the nucleophilic attack of **8** on the electrophilic sulfinyl ion **14a** and the other one the nucleophilic attack of **14b** on **8**. Both are illustrated in Scheme 3. Although neither of them can be unambiguously ruled out, mechanism 1 is less likely to happen because the 1 equiv electrophilic peracid oxidation of **8** affords exclusively the di-*tert*-butylsulfinyl thioanhydride **22** (*t*-Bu(S=O)$_2$S);[4] therefore, the reaction of **8** with the *tert*-butylsulfinyl cation **14a** (electrophilic mechanism, 1) should take place at the 3 position which is the most nucleophilic, but no trace of **22** has ever been detected in these decomposition experiments. The reaction at position 1 does however afford the thermodynamically favored product, namely *tert*-butylsulfenyl *tert*-butylsulfonyl thioanhydride **(11)**.

**Scheme 3**





Mechanism 2 is more likely to explain the formation of the decomposition products of oxide **8** because it suggests a nucleophilic oxygen atom attacking an electrophilic sulfur. According to the respective electronegativities of sulfur and oxygen, the ionic charge of the sulfinyl anion is believed to be substantially on the oxygen atom (*t*-BuS–O$^-$).[13]

In our hands, the nucleophilic oxidation of oxide **8** ($KMnO_4$, $KO_2$, $H_2O_2$/1 N NaOH, and *t*-BuOOH/1 N NaOH) did not afford any trace of dioxide **11**.

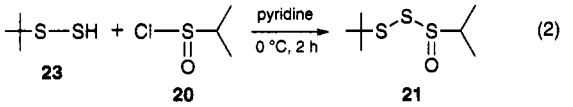
We believed that the analysis of the decomposition products of an unsymmetrical oxide (R–S(O)SS–R′) could help to confirm the likelihood of this rather complex decomposition mechanism (bond cleavage, formation of tetrasulfide, and oxygen transfer rearrangement).

The synthesis of *tert*-butylsulfenyl isopropylsulfinyl thioanhydride **(21)** was achieved by reaction of *tert*-butyl

(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) Oae, S.; Takata, T. *Tetrahedron Lett.* **1980**, *21*, 3213.

hydrodisulfide[14] (**23**) with isopropylsulfinyl chloride (**19**) in the presence of pyridine[7] (eq 2).




**23** **20** **21** (2)

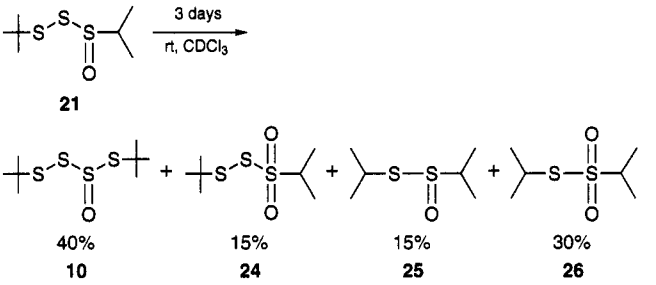
To our knowledge, this is the first synthesis of an unsymmetrical sulfenyl sulfinyl thioanhydride. Compound **21** was found to be even less stable than its analog **8** but could still be purified by column chromatography.

According to the mechanism suggested for the decomposition of oxide **8**, the decomposition products from **21** should be di-*tert*-butyl tetrasulfide (**10**), *tert*-butylsulfenyl isopropylsulfonyl thioanhydride (**24**), and diisopropyl thiosulfinate (**25**). No scrambling of the alkyl groups should be observed if the mechanism proposed is valid. The actual products of the reaction are indeed **10**, **24** and **25**. In addition, 30% of diisopropyl thiosulfonate (**26**) was detected. This is to be expected, considering that the oxidation of thiosulfinate **25** gives a high yield of the corresponding thiosulfonate **26** in contrast with the oxidation of di-*tert*-butyl thiosulfinate (**12**).[15] Direct combination of the two isopropylsulfinyl ambident ions should be more sterically favored than in the *tert*-butyl case;[15] rearrangement of this *vic*-disulfoxide would give thiosulfonate **26**.[16] It should be noted that the yields of products **10** and **24**–**26** give an overall excellent mass balance (Scheme 4).

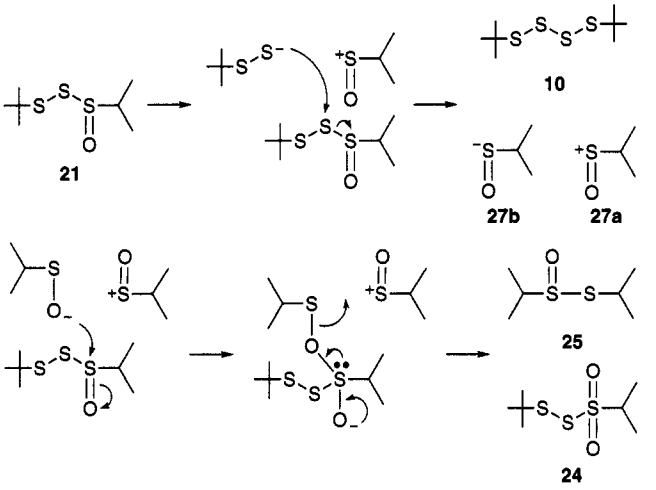
The relative concentration of each of the final products was estimated from the $^{13}C$ NMR as the proton NMR presented considerable overlapping and clear separations could not be obtained by silica gel chromatography. However, it is clear that di-*tert*-butyl tetrasulfide (**10**) is the only polysulfide formed and is the major decomposition product (no unsymmetrical tetrasulfide could be detected by NMR and GC analysis). The unique formation of tetrasulfide **10** implies the formation of the ambident isopropyl ions **27a,b**. In this case, the recombination of ions **27a,b** to form diisopropyl thiosulfonate (**26**) is in competition with their reaction with another molecule of oxide **21**. This latter reaction was previously proposed to be an oxygen transfer that only delivers *tert*-butylsulfenyl *tert*-butylsulfonyl thioanhydride (**24**) and diisopropyl thiosulfinate (**25**). Any mechanism other than oxygen transfer should give scrambling of the alkyl groups. A careful analysis of the NMR spectra ($^{13}C$ and $^{1}H$) as well as the separation of part of the reaction mixture by silica gel chromatography gives clear evidence of the sole formation of **24** and **25**. Moreover, the relative concentration of the final products of the oxygen transfer reaction was estimated to be a 1:1 mixture of **24** and **25** by comparing the intensities of the secondary carbon signals (CH). These results are consistent with the oxygen transfer mechanism as portrayed in Scheme 5.

Finally, the competition between the recombination of the pair of ions **27a,b** that gives diisopropyl thiosulfonate **26** and the oxygen transfer mechanism was estimated to be *ca.* 50/50 by comparing the relative intensities of the secondary carbon signals of diisopropyl **26** with those of **25** and **24** (Scheme 6). *tert*-Butyl isopropyl dithiosulfite

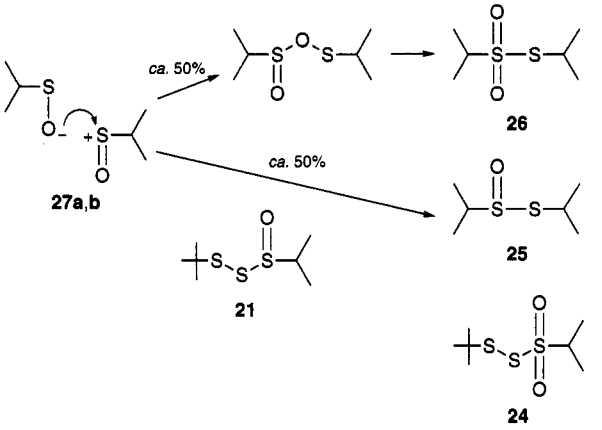
**Scheme 4**




**Scheme 5**




**Scheme 6**




(**32**) was independently prepared and had properties different from those of isomer **21**.

When this mechanism is applied to the decomposition of di-*tert*-butyl dithiosulfite (**28**), it provides consistent results and completely adheres to the general features reported by Field and Lacefield.[6] Compound **28** was prepared in high yield according to Field's procedure,[6] and its structure was confirmed by X-ray crystallography (Figure 2, Table 1). The two S–S bonds are slightly different from one another.

The first step of the breakdown of oxide **28** involves an ionic cleavage at the S(O)–S bond to cation **29** and *tert*-butylsulfenyl anion (**30**). In the presence of another molecule of **28**, the oxygen transfer reaction would afford the di-*tert*-butyl disulfide (**9**) and compound **31**. Compound **31** is believed to decompose immediately to an equimolar mixture of di-*tert*-butyl trisulfide (**9**) and sulfur dioxide which are the two final decomposition products (Scheme 7).

(14) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1992**, *14*, 199.
(15) Derbesy, G. Ph.D. Thesis, McGill University, Montreal, Canada, 1994. Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 1044.
(16) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039.

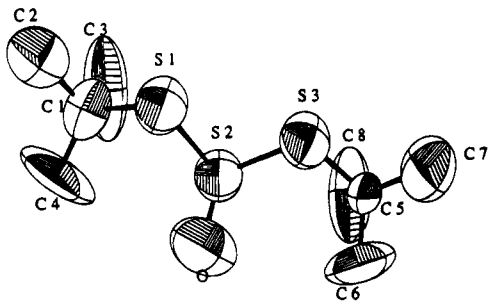



**Figure 2.** ORTEP drawing of di-*tert*-butyl dithiosulfite (**28**).

**Table 1. Atomic Coordinates ($x$, $y$, and $z$) and Temperature Factors ($B_{eq}$) for Compound 28**[a]

| | $x$ | $y$ | $z$ | $B_{eq}$[b] |
|---|---|---|---|---|
| S−2 | 0.1453(5) | 0.9012(5) | 0.0022(5) | 9.1(4) |
| S−1 | 0.1341(6) | 0.7465(5) | −0.0044(5) | 10.0(5) |
| S−3 | 0.2144(6) | 0.8891(5) | 0.1251(4) | 10.1(5) |
| O | 0.2217(18) | 0.9394(16) | −0.0685(12) | 15.3(17) |
| C−1 | 0.0394(21) | 0.7311(23) | −0.0968(21) | 9.0(17) |
| C−2 | 0.0355(24) | 0.615(3) | −0.1052(18) | 12.9(23) |
| C−3 | −0.051(3) | 0.768(3) | −0.0666(24) | 20.8(34) |
| C−4 | 0.072(4) | 0.778(3) | −0.1829(6) | 20.3(36) |
| C−5 | 0.2347(22) | 1.0248(20) | 0.1554(15) | 7.9(15) |
| C−6 | 0.301(4) | 1.076(3) | 0.0926(23) | 21.7(34) |
| C−7 | 0.269(3) | 1.0263(23) | 0.2437(21) | 18.0(31) |
| C−8 | 0.147(3) | 1.085(3) | 0.143(3) | 18.0(30) |

Calculated Hydrogen Atom Parameters

| | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| H−2C | 0.096 | 0.570 | −0.132 | 13.4 |
| H−2A | 0.018 | 0.577 | −0.043 | 13.4 |
| H−2B | −0.027 | 0.589 | −0.145 | 13.4 |
| H−3C | −0.055 | 0.720 | −0.008 | 22.0 |
| H−3A | −0.040 | 0.847 | −0.051 | 22.0 |
| H−3B | −0.103 | 0.738 | −0.115 | 22.0 |
| H−4C | 0.082 | 0.858 | −0.176 | 21.0 |
| H−4A | 0.140 | 0.749 | −0.212 | 21.0 |
| H−4B | 0.015 | 0.766 | −0.234 | 21.0 |
| H−6C | 0.374 | 1.043 | 0.093 | 22.6 |
| H−6A | 0.274 | 1.075 | 0.024 | 22.6 |
| H−6B | 0.311 | 1.155 | 0.107 | 22.6 |
| H−7C | 0.220 | 0.987 | 0.289 | 18.7 |
| H−7A | 0.336 | 0.981 | 0.240 | 18.7 |
| H−7B | 0.294 | 1.098 | 0.269 | 18.7 |
| H−8C | 0.114 | 1.086 | 0.076 | 18.0 |
| H−8A | 0.087 | 1.050 | 0.182 | 18.0 |
| H−8B | 0.147 | 1.159 | 0.170 | 18.0 |

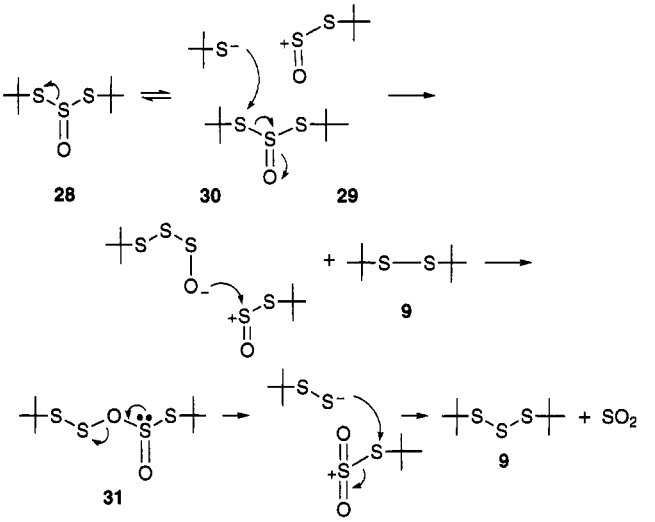
[a] Estimated standard deviations refer to the last digit. [b] $B_{eq}$ is the mean of the principal axes of the thermal ellipsoid. [c] Hydrogen positions are calculated assuming a C−H bond length of 1.08 Å. $B_{iso}$(H) is from $U_{iso}$(H) = 0.01 + $U_{eq}$(C).

The results presented here clearly show that the decompositions of *tert*-butylsulfenyl *tert*-butylsulfinyl thioanhydride (**8**) and the corresponding dithiosulfite **28** follow a logical but somewhat complicated pathway. This mechanism is consistent with the experimental data and has been supported by parallel experiments on related molecules.[15]

## 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. 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 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.[17] Dimethyldioxirane (DMD) was prepared according

**Scheme 7**




to the literature procedure.[18] 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 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[19] 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 instruments), at 270 MHz (Jeol 270-CPF instrument), and at 300 MHz (Varian XL-300 instrument) 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 spectra were recorded on the same instruments (50.3, 67.9, 75.4 MHz). In both cases, the chemical shifts ($\delta$) are reported in parts per million relative to the deuterated solvent. Low-resolution electron impact (EI) and chemical ionization (CI) mass spectra were obtained using a Dupont instrument 21-492B equipped with a 70 eV ionizing energy source and used in direct-inlet mode. 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 28.** Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer using graphite-monochromated Cu K$\alpha$ ($\lambda$ = 1.540 56 Å) radiations using the $\theta/2\theta$ scan mode. Structures were solved by direct methods.[20] Hydrogens were calculated. Solution and refinement was done using NRCVAX system programs.[21] Crystal data, collection, and refinement parameters are given in Table 2.[22] Crystal **28** decomposed in the beam, and data were collected from four crystals.

(17) Shartz, N. N.; Blumberg, J. H. *J. Org. Chem.* **1976**, *41*, 1496.
(18) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Singh, M.; Murray, R. W. *J. Org. Chem.* **1992**, *57*, 4263.
(19) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(20) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, M., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175−189.
(21) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

**Table 2. Crystal Data for the Structure Determination of 28**

| | |
|---|---|
| chemical formula | $C_8H_{18}OS_3$ |
| formula weight | 226.41 |
| X-ray crystal dimension (mm)[a] | 0.50 × 0.40 × 0.30 |
| crystal system | tetragonal |
| space group | $P4_32_12$ |
| lattice constants | |
| $a$ (Å) | 13.301(3)[a] |
| $b$ (Å) | |
| $c$ (Å) | 14.800(3) |
| $V$ (Å$^3$) | 2619.3(8) |
| $Z$ | 8 |
| $F$ (000) | 985.35 |
| density (calcd) (g cm$^{-3}$) | 1.149 |
| 2$\theta$ maximum (deg) | 90.0 |
| $h, k, l$ ranges | $0 < h$ 12, $0 < k < 8$, $0 < l < 13$ |
| no. of reflections with $I_{net} > 2.5\sigma(I_{net})$ | 679 |
| for significant reflections | $R_f = 0.076$[b], $R_w = 0.086$[c], GOF = 2.92[d] |
| maximum shift/$\sigma$ ratio | 0.035 |
| deepest hole in D-map (e/Å$^3$) | −0.240 |
| highest peak in D-map (e/Å$^3$) | 0.270 |
| drop of standard intensities | 1.7% for each crystal |

[a] Cell dimensions were obtained from 25 reflections with 2$\theta$ angle in the range 48.00−60.00°. [b] $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$. [c] $R_w = (\Sigma[w(F_o - F_c)^2/\Sigma(wF_o^2)])^{1/2}$. [d] GOF = $(\Sigma[w(F_o - F_c)^2/$(no. of reflections − no. of parameters)$])^{1/2}$.

**General Oxidation Procedures. Procedure 1: *m*-CPBA Oxidation.** A typical experimental procedure is the *m*-CPBA oxidation of di-*tert*-butyl trisulfide **(9)** to *tert*-butylsulfenyl *tert*-butylsulfinyl thioanhydride **(8)**. 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 di-*tert*-butyl trisulfide **(9)** (1.09 g, 5.19 mmol) in $CH_2Cl_2$ (15 mL) during 0.5 h under nitrogen. After 3 h of stirring at 0 °C, the mixture was concentrated to 10 mL by rotoevaporation. The solution was cooled to −78 °C, and the *m*-CPBA 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 **8** (1.08 g, 4.77 mmol, 92%) as a white solid: mp 61−63 °C (lit.[4] 63−65 °C); $^1$H NMR ($CDCl_3$) $\delta$ 1.385 (s, 9H), 1.390 (s, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 60.67, 48.73, 29.80, 23.79; MS (EI, 70 eV, 30 °C) *m/z* (relative intensity) 226 ($M^{\bullet+}$, 1.1), 178 ($M^{\bullet+}$ − S=O, 3.5), 170 (*t*-BuS(O)SS$^{\bullet+}$, 6.0), 106 (*t*-BuS(O)$^{\bullet+}$, 20.8), 90 ($C_4H_{10}^{\bullet+}$, 18.4), 57 (*t*-Bu$^+$, 100), 41 ($C_3H_5^+$, 62.1). In the following *m*-CPBA oxidations, the reaction temperature, the time, and the number of equivalents of *m*-CPBA may vary and are reported. The method of separation can also differ, depending on the compound prepared.

**Procedure 2: Peracetic Acid ($CH_3CO_3H$) Oxidation.** A typical experimental procedure is the $CH_3CO_3H$ oxidation of di-*tert*-butyl trisulfide **(9)** to oxide **8**. A solution of peracetic acid (40%) (0.97 g, 5.13 mmol, 1.1 equiv) in methylene chloride (25 mL) was added dropwise to an ice-cooled solution of di-*tert*-butyl trisulfide **(9)** (0.98 g, 4.66 mmol) in $CH_2Cl_2$ (15 mL) during 0.5 h under nitrogen. After 5 h of stirring at 0 °C, 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 **8**. Spectral data were consistent with samples previously prepared.

**Procedure 3: DMD Oxidation.** A typical experimental procedure is the DMD oxidation of di-*tert*-butyl trisulfide **(9)** to oxide **8**. 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 di-*tert*-butyl trisulfide **(9)** (0.5 g, 2.38 mmol) in acetone (10 mL) during 30 min under nitrogen. After 1 h of stirring at −78 °C, the solvent was removed *in vacuo* to give **8** (0.53 g, 2.33 mmol, 98%) as a solid. Analytical data were identical to the data of the one previously reported. 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.

**Preparation of 8 by Reaction of *tert*-Butyl Hydrodisulfide (23) with *tert*-Butylsulfinyl Chloride (20).**[7] A solution of *tert*-butylsulfinyl chloride[11] **(20)** (0.481 g, 3.44 mmol, 1 equiv) in methylene chloride (25 mL) was added dropwise to an ice-cooled solution of *tert*-butyl hydrodisulfide **(23)** (0.42 g, 3.44 mmol) and pyridine (0.28 g, 3.44 mmol, 1 equiv) in $CH_2Cl_2$ (20 mL) during 0.5 h under nitrogen. After 12 h of stirring at 0 °C, the reaction mixture was washed with 2 × 25 mL portions of water, 3 × 25 L portions of 1 N NaOH solution, and 25 mL portions of water until the mixture was neutral to pH paper. The organic phase was separated, dried with $MgSO_4$, filtered, and evaporated. The solvent was removed *in vacuo* to give an oily residue that was chromatographed on alumina using a 13% ethyl acetate/hexanes solution to give **8** as a solid (0.528 g, 2.34 mmol, 68%), the remaining compound being di-*tert*-butyl tetrasulfide **(10)**. Spectral data were identical to those previously reported.

**Preparation of Di-*tert*-butyl Dithiosulfite (28) by Reaction of *tert*-Butyl Mercaptan with Thionyl Chloride.** Di-*tert*-butyl dithiosulfite **(28)** was prepared using the procedure of Field and Lacefield.[6] Compound **28** was isolated as a colorless solid (90%): mp 50−52 °C (lit.[6] 51−51.5°C); $^1$H NMR ($CDCl_3$) $\delta$ 1.545 (s, 18H); $^{13}$C NMR ($CDCl_3$) $\delta$ 52.10, 31.80; MS (EI, 70 eV, 30 °C) *m/z* (relative intensity) 226 ($M^{\bullet+}$, 1.3), 210 ($M^{\bullet+}$ − O, 1.2), 178 ($M^{\bullet+}$ − S=O, 3.8), 170 (*t*-BuSS(O)S$^{\bullet+}$, 11.1), 154 (*t*-BuSSS$^{\bullet+}$, 2.0), 90 ($C_4H_{10}^{\bullet+}$, 19.0), 57 (*t*-Bu$^+$, 100), 41 ($C_3H_5^+$, 42.1).

**Preparation of *p-tert*-Butylphenylsulfenyl *p-tert*-Butylphenylsulfinyl Thioanhydride (16).** The oxidation of bis(*p-tert*-butylphenyl) trisulfide (0.82 g, 2.26 mmol) using *m*-CPBA (0 °C, 2 h, 1.1 equiv) or DMD (−78 °C, 1 h, 1 equiv) afforded **16** (87% and 88%, respectively) by crystallization from hexanes according to procedures 1 and 3: mp 128−130 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.29 (q, 4H), 7.43 (q, 4H), 1.32 (s, 9H), 1.30 (s, 9H); $^{13}$C NMR ($CDCl_3$) $\delta$ 157.52, 154.98, 140.11, 136.27, 127.38, 126.42, 125.63, 124.53, 35.21, 34.89, 31.09, 31.00; MS (CI, 70 eV, 180°C) *m/z* (relative intensity) 380 (M, $NH_4^+$ − O, 54.4), 362 ($M^+$ − O, 51.3), 330 ($M^+$ − S=O, 33.5), 315 ($M^+$ − S=O − $CH_3$, 18.8), 197 (*t*-Bu$C_6H_4SS^+$, 25.6), 181 (*t*-Bu$C_6H_4SO^+$, 100.0), 166 (*t*-Bu$C_6H_4S^+$, 30.3), 151 (*t*-Bu$C_6H_4S^+$ − $CH_3$, 33.0), 134 (*t*-Bu$C_6H_4^+$, 14.7), 119 (*t*-Bu$C_6H_4^+$ − $CH_3$, 31.3).

**Attempted Preparation of Dioxide 31 by Nucleophilic Oxidation of Di-*tert*-butyl Dithiosulfite (28).** The oxidation of **28** (0.4−0.5 g, 1.77−2.21 mmol) was attempted using $H_2O_2$/1 N NaOH,[23] *t*-BuOOH/1 N NaOH,[23] $KO_2$,[23] $KMnO_4$,[5] and $NaIO_4$[24] under the experimental conditions described in the literature. The reactions were followed by TLC and GC. When no reaction had taken place under the reported conditions, the mixture was refluxed until partial decomposition of the starting material took place. In all cases, the final products were a mixture of di-*tert*-butyl di-, tri-, and tetrasulfides that were characterized by NMR spectroscopy and GC analysis.

**Preparation of Di-*tert*-butylthiosulfinate (12).** Compound **12** was obtained according to a known procedure.[8c]

**Preparation of Diisopropyl Thiosulfinate (25) and Diisopropyl Thiosulfonate (26).** Compounds **25** and **26** were obtained using *m*-CPBA according to the known procedure[15] (similar to procedure 1). The oxidation was also achieved using 1 and 2 equiv of DMD according to procedure 3. **25** (oil, quant.): $^1$H NMR ($CDCl_3$) $\delta$ 3.51 (h, 1H), 3.09 (h, 1H), 1.38 (dd, 6H), 1.27 (dd, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.08, 38.11, 24.45, 24.24, 16.38, 15.53. **26** (oil, 93%): $^1$H NMR ($CDCl_3$) $\delta$ 3.62 (h, 1H), 3.31 (h, 1H), 1.42 (d, 6H), 1.48 (d, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 63.48, 42.92, 24.24, 16.28.

**Preparation of *tert*-Butylsulfenyl Isopropylsulfinyl Thioanhydride (21).** The synthesis of **21** was achieved by a slightly modified version of the procedure reported by Bleeker.[7]

(22) The authors have deposited atomic coordinates for **28** 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, UK.

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

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

A solution of isopropylsulfinyl chloride **(19)** (0.631 g, 5 mmol)[11] in 25 mL of ether was added dropwise over a 1 h period under nitrogen to an ice-cooled solution of *tert*-butyl hydrodisulfide[14] **(23)** (0.610 g, 5 mmol) and pyridine (0.400 g, 5 mmol) in 50 mL of ether. A heavy white precipitate formed during addition. After an additional 5 h of stirring at 0 °C, the reaction mixture was washed with 2 × 25 mL portions of water, 3 × 25 mL portions of 1 N NaOH solution, and 25 mL portions of water until the mixture was neutral to pH paper. The organic phase was separated, dried with $MgSO_4$, filtered, and evaporated. The solvent was removed *in vacuo* to give an oily residue that was chromatographed on silica gel using a 13% ethyl acetate/hexanes solution. The first fraction was di-*tert*-butyl tetrasulfide **(10)** (10%). The second fraction was *tert*-butylsulfenyl isopropylsulfonyl thioanhydride **(24)** (8%) (*vide infra*). The third fraction was *tert*-butylsulfenyl isopropylsulfinyl thioanhydride **(21)** (0.795 g, 3.75 mmol, 75%) as a liquid. The last fraction was diisopropyl thiosulfinate **(25)** (oil, 7%). **21**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.05 (h, 1H), 1.40 (s, 9H), 1.32 (dd, 6H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 55.45, 48.12, 29.56, 16.17, 15.35; MS (CI, 70 eV, 70 °C) *m/z* (relative intensity) 213 (M, $H^+$, 47.4), 200 (**25**, $NH_4^+$, 100.0), 183 (**25**, $H^+$, 38.7).

**Preparation of *tert*-Butyl Isopropyl Dithiosulfite (32).** Compound **32** was prepared according to Field's procedure[6] and was purified by column chromatography using a 13% ethyl acetate/hexanes solution as eluent to give a colorless oil (82%). **32**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.49 (m, 1H), 1.45 (s, 9H), 1.37 (dd, 6H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 51.54, 39.84, 31.62, 24.05, 23.25. Compound **32** was found to be too unstable to give consistent results on MS but was clearly identified by NMR and gave one spot on TLC.

**Preparation of *tert*-Butylsulfenyl Isopropylsulfonyl Thioanhydride (24).** Isopropylsulfonyl chloride **(33)** was most conveniently prepared according to the Douglass procedure[11] using 4 equiv of acetic anhydride. A solution of isopropylsulfonyl chloride **(33)** (0.257 g, 1.81 mmol)[14] in 15 mL of ether was added dropwise over a 1 h period under nitrogen to an ice-cooled solution of *tert*-butyl hydrodisulfide **(23)** (0.221 g, 1.81 mmol) and pyridine (0.160 g, 2 mmol) in 25 mL of ether. After an additional 5 h of stirring at room temperature, the reaction mixture was washed with 2 × 25 mL portions of water, 3 × 25 mL portions of 1 N NaOH solution, and 25 mL portions of water until the mixture was neutral to pH paper. The organic phase was separated, dried with $MgSO_4$, filtered, and evaporated. The solvent was removed *in vacuo* to give an oily residue that was chromatographed on silica gel using a 13% ethyl acetate/hexanes solution to give **24** (0.090 g, 0.39 mmol, 22%) as a liquid. The first fraction was di-*tert*-butyl tetrasulfide **(10)** (65%). **24**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.52 (h, 1H), 1.42 (d, 6H), 1.38 (s, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 61.85, 50.17, 30.34, 17.02; MS (CI, 70 eV, 100 °C) *m/z* (relative intensity) 246 (M, $NH_4^+$, 100.0). All the other peaks have an intensity less than 3%.

**NMR Rate Measurements.** The kinetic experiments were performed on a XL300 spectrometer at 45 °C using *tert*-butyl chloride (0.5 equiv) as internal standard. A 5 mm NMR tube containing a solution of *tert*-butylsulfenyl *tert*-butylsulfinyl thioanhydride **(8)** and the internal standard (*tert*-butyl chloride) in various solvents (benzene-$d_6$, chloroform-*d*, acetone-$d_6$, and acetonitrile-$d_3$) was allowed to equilibrate at 45 °C in the NMR probe for 15 min. $^1H$ or $^{13}C$ NMR spectra were acquired (32 or 1024 transients, respectively) at various intervals over a period of 12 h. The rates were calculated by measuring the peak heights of product formed or reactant consumed and the peak height of the internal standard. Considering that the concentration of *tert*-butyl chloride was known and constant, the concentrations of the different products and reagent were easily obtained at any time. When ln(rel conc) *vs* time was plotted, the first order rate could be calculated from the slope of the linear plots obtained.

Some of these experiments were repeated using traces of radical inhibitors (benzoquinone or 4-*tert*-butylcatechol). In both cases, normal decomposition of **8** was observed.

**Trapping Experiments. Decomposition of *tert*-Butylsulfenyl *tert*-Butylsulfinyl Thioanhydride (8) in the Presence of 0.5 Equiv of Isopropylsulfinyl Chloride (19).** The decomposition of a solution of **8** (300 mg, 1.33 mmol) and isopropylsulfinyl chloride **(19)** (84 mg, 0.66 mmol, 0.5 equiv) in 10 mL of $CHCl_3$ was carried out at room temperature for a week or at 50 °C for 12 h. The $^1H$ and $^{13}C$ NMR spectra of the crude mixtures were similar in both cases. The partial separation of the reaction mixtures by silica gel chromatography and the careful analysis of the crude NMR spectra allowed for the detection of the decomposition products of **8**, *i.e.* **21** and the mixed decomposition[15] as well as *tert*-butylsulfinyl chloride **(20)**. Pure samples of **20** were prepared according to literature procedures.[2c,7] **20**: $^1H$ NMR ($CDCl_3$) $\delta$ 1.36 (s, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 64.24, 22.23.

**Decomposition of *tert*-Butylsulfenyl Isopropylsulfinyl Thioanhydride (21).** The decomposition of **21** (70 mg, 0.33 mmol) in $CDCl_3$ was followed by $^1H$ and $^{13}C$ NMR at room temperature. After 4 days under these conditions, no traces of **21** could be detected. The decomposition products were identified by $^1H$ and $^{13}C$ NMR to be *tert*-butyl tetrasulfide **(10)** (40%), *tert*-butylsulfenyl isopropylsulfonyl thioanhydride **(24)** (15%), diisopropyl thiosulfinate **(25)** (15%), and diisopropyl thiosulfonate **(26)** (30%). The decomposition was repeated at 45 °C for 12 h using 300 mg of **21**. The reaction mixture was partially separated by silica gel chromatography using a 10% ethyl acetate/hexanes solution. The results obtained were similar to the one previously reported at room temperature.

**Decomposition of *tert*-Butyl Isopropyl Dithiosulfite (32).** The decomposition of **32** (65 mg, 0.31 mmol) in $CCl_4$ was achieved by reflux for 12 h until no traces of **32** could be detected by TLC. The decomposition products were identified by $^1H$ and $^{13}C$ NMR to be a scrambled mixture of the possible symmetrical and unsymmetrical di- and trisulfides. These results were confirmed by GC analysis.

**Decomposition of *tert*-Butylsulfenyl *tert*-Butylsulfinyl Thioanhydride (8).** The decomposition of **8** (34 mg, 0.15 mmol) in $CDCl_3$ was followed by $^1H$ and $^{13}C$ NMR at room temperature. After 5 days, no traces of **8** could be detected. The decomposition products were identified as **10**[15] (30%), **12**[15] (30%), and **11**[15] (40%); these quantities were calculated from the intensity observed on $^{13}C$ NMR because the $^1H$ NMR presented too much overlap of signals. A reference solution of **10** (33 mg, 0.14 mmol), **12** (31 mg, 0.16 mmol), and **11** (27 mg, 0.11 mmol) confirmed that the intensity of the signals on $^{13}C$ NMR were proportional to the ratio of each compound of the sample at ±7%. Other similar calibration experiments using different derivatives were carried out. In all cases, a good agreement between the $^{13}C$ NMR intensity and the relative concentrations of the derivatives employed was found within 5−10%. Parallel accuracies in related decompositions have been reported.[8]

**Decomposition of Di-*tert*-butyl Dithiosulfite (28).** The decomposition of **28** (41 mg, 0.18 mmol) in $CDCl_3$ was followed by $^1H$ and $^{13}C$ NMR at room temperature. After 5 months, no traces of **28** could be detected. The decomposition products were identified by $^1H$ NMR and GC as an equimolar mixture of di-*tert*-butyl trisulfide **(9)** (50%) and the disulfide analog **9** (50%). The decomposition of **28** (145 mg, 0.64 mmol) at 100°C in $CCl_4$ gave the same decomposition mixture within 19 h (identity by NMR and GC). The condenser employed was equipped with a trap of wet pH paper. Clear evidence of sulfur dioxide evolution was given by the strongly acidic coloration of the pH paper by the end of the decomposition.

**Acknowledgment.** We thank Elf Aquitaine (France) and Atochem North America, King of Prussia, and the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

**Supplementary Material Available:** NMR spectra of compounds **16** and **21** as well as X-ray data of compound **28** (5 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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