JOC Article

Oxidation of *cis*- and *trans*-3,5-Di-*tert*-butyl-3,5-diphenyl-1,2,4-trithiolanes: Isolation and Properties of the 1-Oxides and the 1,2-Dioxides

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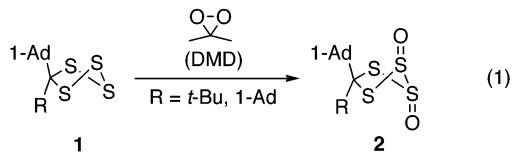
Oxidation of *trans*-3,5-di-*tert*-butyl-3,5-diphenyl-1,2,4-trithiolane with dimethyldioxirane (DMD) or *m*-chloroperbenzoic acid (MCPBA) gave two stereoisomeric (1*S**,3*S**,5*S**)- and (1*R**,3*S**,5*S**)-1-oxides (**16** and **17**, respectively). Oxidation of **16** with DMD gave the (1*S**,2*R**,3*S**,5*S**)-1,2-dioxide (**18**) and the 1,1-dioxide **19**, and that of **17** yielded the (1*R**,2*R**,3*S**,5*S**)-1,2-dioxide (**20**) mainly along with **18** and **19**. The structures of the 1,2-dioxides **18** and **20** were determined by X-ray crystallography. 1,2-Dioxides **18** and **20** isomerized to each other in solution, and the equilibrium constant *K* (**20**/**18**) is 19 in $CDCl_3$ at 295 K. The kinetic study suggested a biradical mechanism for the isomerization. Isomerization of **16** and **17** to *cis*-3,5-di-*tert*-butyl-1,2,4-trithiolane 1-oxides by treatment with $Me_3O^+BF_4^-$ is also described.

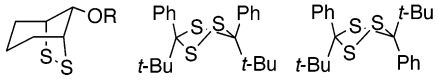
Introduction

The chemistry of *vic*-disulfoxides [RS(O)S(O)R′] has been drawing much attention.[1−6] Recently, we succeeded in the first isolation and structure determination of compounds bearing a −S(O)−S(O)− linkage by the oxidation of tetrathiolanes **1** with an acetone solution of dimethyldioxirane (DMD) (eq 1).[7] The two oxygen atoms



1 **2** (1)

CHART 1



3 ***cis*-4** ***trans*-4**

of the tetrathiolane 2,3-dioxides **2** take the diaxial orientations characteristically, where the anomeric effect by adjacent sulfur atoms[7b,8,9] at both ends seems to contribute to the stability of **2**. Naturally, our attention was turned to the synthesis of *vic*-disulfoxides not having such a special stabilization effect, that is, those which have a C−S(O)−S(O)−C linkage. The above-mentioned study, as well as the study by Folkins and Harpp on the oxidation of 4,5-dithiabicyclo[3.2.1]octanes **3** (Chart 1),[3] suggests that *vic*-disulfoxides derived from cyclic disulfides possess fair stability compared with those derived from acyclic disulfides,[4] thus leading us to investigate the oxidation of 1,2,4-trithiolanes.[10] In our recent communication,[11] we reported that the oxidation of tetrasubstituted 1,2,4-trithiolane ***cis*-4** with DMD furnished the two diastereomeric 1-oxides and the desired 1,2-

(1) For reviews, see: (a) Freeman, F. *Chem. Rev.* **1984**, *84*, 117−135. (b) Lacombe, S. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; Myu: Tokyo, 1999; Vol. 21, pp 1−41.

(2) For recent papers on *vic*-disulfoxides, see: (a) Freeman, F.; Lee, C. *J. Org. Chem.* **1988**, *53*, 1263−1266. (b) Block, E.; Bayer, T. *J. Am. Chem. Soc.* **1990**, *112*, 4584−4585. (c) Gu, D.; Harpp, D. N. *Tetrahedron Lett.* **1993**, *34*, 67−70. (d) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952−7954. (e) Nakayama, J.; Mizumura, A.; Yokomori, Y.; Krebs, A.; Schütz, K. *Tetrahedron Lett.* **1995**, *36*, 8583−8586. (f) Clennan, E. L.; Stensaas, K. L. *J. Org. Chem.* **1996**, *61*, 7911−7917 and references therein.

(3) Folkins, P. L.; Harpp, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 8998−9000.

(4) (a) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232−6235. (b) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1982**, *104*, 5766−5774. (c) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039−4049.

(5) (a) Lacombe, S.; Loudet, M.; Dargelos, A.; Robert-Banchereau, E. *J. Org. Chem.* **1998**, *63*, 2281−2291. (b) Gregory, D. D.; Jenks, W. S. *J. Phys. Chem. A* **2003**, *107*, 3414−3423.

(6) (a) Steudel, R.; Drozdova, Y. *Chem.—Eur. J.* **1996**, *2*, 1060−1067. (b) Clenann, E. L.; Stensaas, K. L. *Org. Prep. Proced. Int.* **1998**, *30*, 551−600.

(7) (a) Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc.* **1999**, *121*, 7959−7960. (b) Ishii, A.; Nakabayashi, M.; Jin, Y.-N.; Nakayama, J. *J. Organomet. Chem.* **2000**, *611*, 127−135.

(8) Harpp, D. N.; Gleason, J. G. *J. Org. Chem.* **1971**, *36*, 1314−1316.

(9) (a) Juaristi, E.; Ordoñez, M. In *Organosulfur Chemistry*; Page, P., Ed.; Academic Press: San Diego, CA, 1998; Vol. 2, Chapter 3. (b) Kleinpeter, E. In *Conformational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH Publishers: New York, 1995; Chapter 6.

(10) For oxidation of 1,2,4-trithiolanes, see: (a) Wratten, S. J.; Faulkner, D. J. *J. Org. Chem.* **1976**, *41*, 2465−2467. (b) Weigand, W.; Wünsch, R.; Polbrn, K.; Mloston, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1518−1522. (c) Bräutigam, S.; Wünsch, R.; Weigand, W.; Majchrzak, A.; Mloston, G. *Book of Abstracts*, The Sixth International Conference on Heteroatom Chemistry (ICHAC-6), Lodz, Poland, 2001; S4-O-2, p 108. (d) Majchrzak, A.; Mloston, G.; Ostycharz, E.; Skarzewski, J.; Weigand, W. *Book of Abstracts*, The Sixth International Conference on Heteroatom Chemistry (ICHAC-6), Lodz, Poland, 2001; P-25, p 153.

(11) Oshida, H.; Ishii, A.; Nakayama, J. *Tetrahedron Lett.* **2002**, *43*, 5033−5037.

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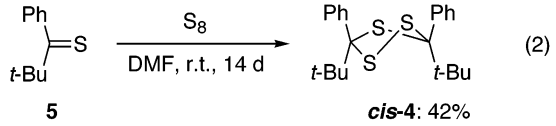
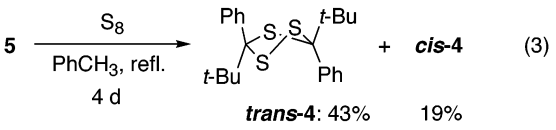
dioxide depending on the amount of DMD. In this paper, after a short summary of the oxidation of ***cis*-4**, we report the oxidation of ***trans*-4** that yields the two isomeric 1-oxides and the two isomeric 1,2-dioxides and the properties of these oxides.

Results and Discussion

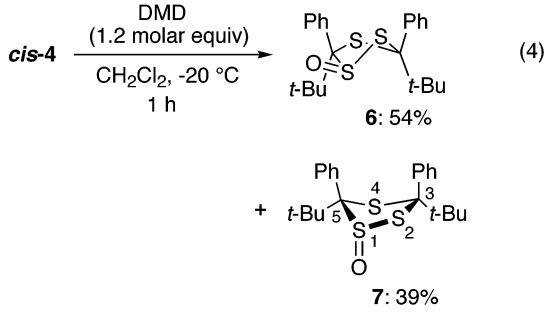
Preparation of *cis*- and *trans*-1,2,4-Trithiolanes *cis*-4 and *trans*-4. 1,2,4-Trithiolanes ***cis*-4** and ***trans*-4** were prepared by reaction of thiopivalophenone **(5)** with elemental sulfur (eqs 2 and 3).[12] Thus, treatment of **5**





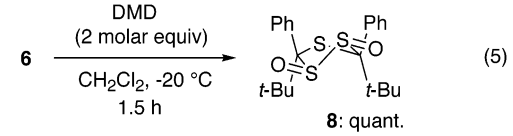
with elemental sulfur in *N*,*N*-dimethylformamide (DMF) at room temperature for 14 days gave a mixture of 1,2,4-trithiolane ***cis*-4** and **5**, from which ***cis*-4** was isolated in 42% yield as the only isomer. In contrast, the reaction in refluxing toluene yielded 1,2,4-trithiolanes ***trans*-4** (43%) and ***cis*-4** (19%). The synthesis of cis- and trans-substituted 3,5-di-*tert*-butyl-3,5-diaryl-1,2,4-trithiolanes by the reaction of the corresponding ketones with P_2S_5 has also been reported.[13]

Oxidation of 1,2,4-Trithiolane *cis*-4. Oxidation of ***cis*-4** with 1.2 mol equiv of DMD[14] gave two stereoisomeric monoxides **6** and **7** in 54% and 39% yields, respectively (eq 4). These two isomers were separated by



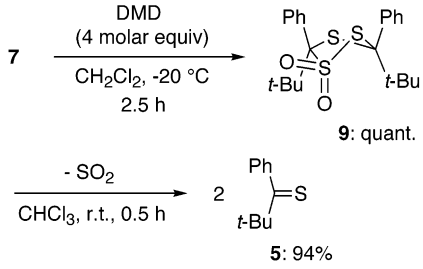
silica gel column chromatography, and their structures were determined by X-ray crystallographic analyses.[11] In the solid state, 1-oxide **6** takes a half-chair conformation with the oxygen atom being cis to the phenyl group and occupying the equatorial orientation, while the other 1-oxide **7** takes an envelope conformation [∠S(1)−S(2)−C(3)−S(4) of 3.07(12)°] with the oxygen atom trans to the phenyl group and occupying the axial orientation. The S−S bond in **7** [2.052(2) Å] is significantly shorter than that in **6** [2.1133(9) Å], which is the result of an anomeric effect in **7** ($n_S \rightarrow \sigma^*_{S-O}$ orbital interaction[7b,8,9]). Recently, it was reported that the oxidation of 3,3,5,5-tetraphenyl-1,2,4-trithiolane with *m*-chloroperbenzoic acid (MCPBA) yielded the 1-oxide with the oxygen atom possessing the axial orientation in the solid state.[10b] Incidentally, no formation of 4-oxides of ***cis*-4** was observed in the present reaction, in contrast to the case of the oxidation of the parent[10a,d] and 3,3,5,5-tetramethyl-1,2,4-trithiolanes which gives the corresponding 1- and 4-oxides.[10c]

Trithiolane 1-oxides **6** and **7** thus obtained were allowed to react with DMD in CH_2Cl_2 at −20 °C. Oxidation of **6** with an excess of DMD (2 mol equiv) yielded the desired 1,2-dioxide **8** quantitatively (eq 5).

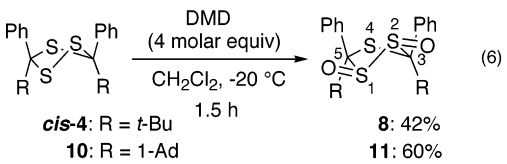


In contrast, the reaction of **7** with DMD was so slow that a large excess of DMD (4 mol equiv) and a longer reaction time were required for the complete consumption of **7** to give 1,1-dioxide **9** (Scheme 1). Although **9** was unstable in solution at room temperature and decomposed to quickly form 2 mol equiv of thioketone **5** (94%), the yield of **9** was quantitative, judging from the ^{1}H NMR spectrum of the reaction mixture measured at −20 °C. The lower reactivity of **7** compared with **6** might be attributed to a lowering of the energy level of the lone pair of electrons on the S(2), owing to the anomeric effect described above.

SCHEME 1



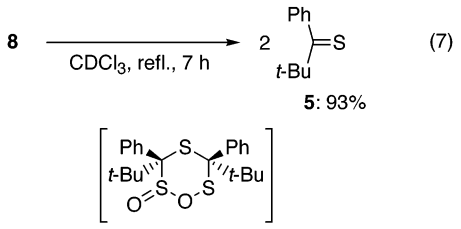
1,2-Dioxide **8** was also obtained directly by oxidation of ***cis*-4** with 4 mol equiv of DMD in 42% yield. Oxidation of (1-adamantyl)-substituted 1,2,4-trithiolane **10** with DMD proceeded similarly to give the 1,2-dioxide **11** in 60% yield (eq 6). The structure of **11** was determined by



X-ray crystallography.[11] In the crystalline state, the trithiolane ring of **11** takes a near-envelope conformation [∠C(5)−S(4)−C(3)−S(2) of 11.4(3)°]. The S(1)−S(2) bond length of 2.249(2) Å is elongated by ∼10% compared with the usual S−S bond lengths.[15] For reference, the S−S bond length of ***cis*-4** is 2.024(2) Å.[12]

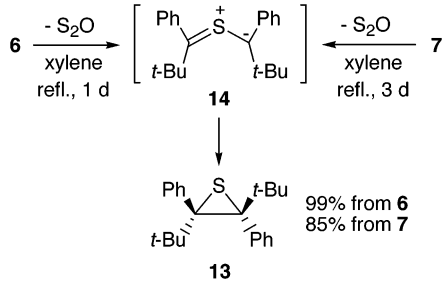
(12) Ishii, A.; Oshida, H.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 319−328.
(13) Okuma, K.; Shibata, S.; Shioji, K.; Yokomori, Y. *J. Chem. Soc., Chem. Commun.* **2000**, 1535−1536.
(14) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377. Adam, W.; Hadjiarapoglou, L.; Smerz, A. *Chem. Ber.* **1991**, *124*, 227−232.
(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

In relation to the unexpected instability of 1,1-dioxide **9** compared with 1,2-dioxide **8**, thermal reactions of **8** and monoxides **6** and **7** were examined. Heating of **8** in refluxing $CDCl_3$ yielded 2 mol equiv of thioketone **5** (93%) (eq 7). The formation of 2 mol equiv of **5** is explained in

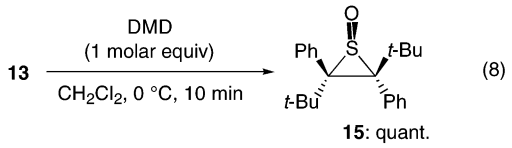


terms of the extrusion of SO_2 from a rearrangement product **9** or the *O*,*S*-sulfenyl sulfinate **12**.[1] Elemental sulfur was not detected by TLC in this thermolysis.

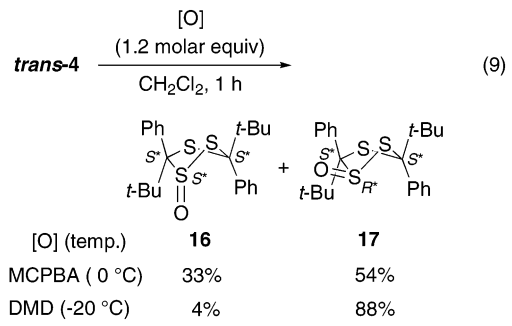
SCHEME 2



On the other hand, thermal reactions of **6** and **7** in refluxing xylene gave the identical *trans*-episulfide **13** in high yields (Scheme 2). The stereoselective reactions of **6** and **7** would proceed through the common thiocarbonyl ylide intermediate **14** in a manner similar to that in the N_2-extrusion reaction of 1,3,4-thiadiazolines reported by Kellogg and Wassenaar.[16] The trans stereochemistry of **13** was verified by the oxidation of **13** to give a single episulfoxide **15** having spectroscopically nonequivalent *tert*-butyl groups (eq 8).



Oxidation of 1,2,4-Trithiolane *trans*-4. Oxidation of 1,2,4-trithiolane ***trans*-4** with 1.2 mol equiv of MCPBA in CH_2Cl_2 at 0 °C gave two monoxides **16** and **17** in 33% and 54% yields, respectively (eq 9). The structures of **16**



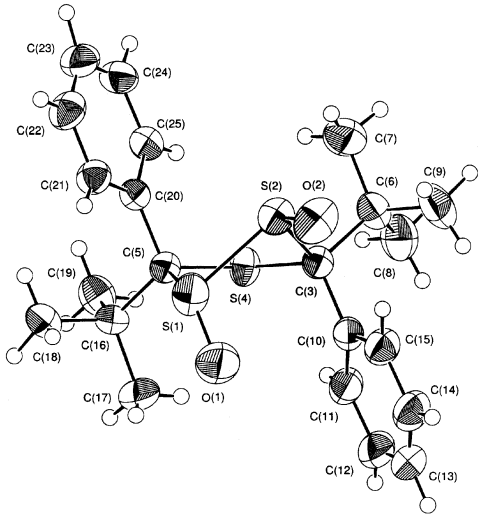
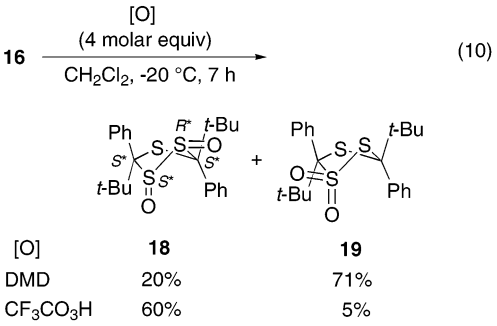


FIGURE 1. ORTEP drawing of 1,2-dioxide **18**.

and **17** were confirmed by X-ray crystallography. When DMD (1.2 mol equiv) was employed as the oxidant, the oxide **17** (88%) was obtained preferably together with a small amount of **16** (4%). The preferred formation of **17** is interpreted by the steric repulsion between the oxidant and the substituents of ***trans*-4**. Thus, sterically more demanding DMD approaches the sulfur atom to be oxidized from the less hindered phenyl group side. The lower reaction temperature might serve as an additional factor for the high selectivity.

Oxidation of trithiolane 1-oxide **16** with 4 mol equiv of DMD in CH_2Cl_2 at −20 °C for 7 h gave 1,2-dioxide **18** and 1,1-dioxide **19** in 20% and 71% yields, respectively (eq 10). In the IR spectrum of **18**, two strong absorptions



due to the S=O stretching vibrations (1075 and 1129 cm^{-1}) were observed, and the ^1H and ^{13}C NMR spectra showed that the 1,2-dioxide did not have C_2-symmetry. The definitive assignment provided by X-ray crystallography showed it to be the (1*S**,2*R**,3*S**,5*S**)-1,2-dioxide **18** (Figure 1). Thus, in the solid state, 1,2-dioxide **18** takes a half-chair conformation with an S(1)−S(2) bond length of 2.241(1) Å and a torsional angle ∠C(5)−S(1)−S(2)−C(3) of −62.3(1)°. The two oxygen atoms in **18** are cis with respect to the S(1)−S(2) bond, and the dihedral angle ∠O(1)−S(1)−S(2)−O(2) is −62.2(2)°. Interestingly, the oxidation of **16** with trifluoroperacetic acid (4 mol equiv) yielded 1,2-dioxide **18** as the main product in 60% yield. Hydrogen bonding at the oxygen

(16) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045−4060.

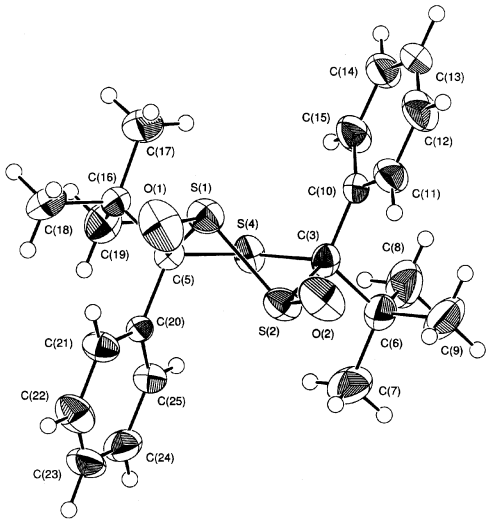
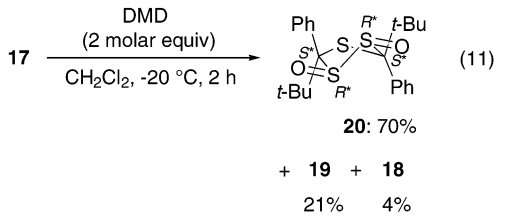


FIGURE 2. ORTEP drawing of 1,2-dioxide **20**.

atom of **16** would increase the positive charge at the sulfinyl sulfur atom[17] to change the selectivity.

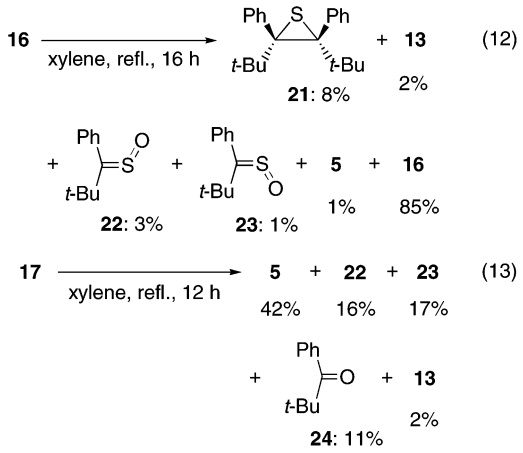
The other 1-oxide **17** was also treated with 2 mol equiv of DMD in CH_2Cl_2 at −20 °C for 2 h to give an alternative 1,2-dioxide, (1*R**,2*R**,3*S**,5*S**)-**20**, in 70% yield along with **19** (21%) and **18** (4%) (eq 11). The two *tert*-butyl



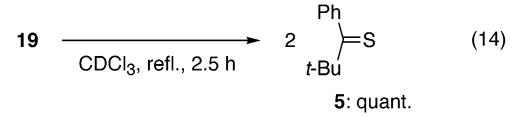
groups, as well as the phenyl groups, in dioxide **20** are equivalent to each other in the ^1H and ^{13}C NMR spectra, indicating the C_2-symmetry of the structure. An X-ray analysis showed that **20** has a half-chair form with an S(1)−S(2) bond length of 2.237(1) Å and a torsional angle ∠C(5)−S(1)−S(2)−C(3) of 72.4(1)° (Figure 2). The two oxygen atoms of **20** occupy equatorial orientations with a dihedral angle ∠O(1)−S(1)−S(2)−O(2) of 59.8(2)°. In both **18** and **20**, the *tert*-butyl groups possess the pseudoequatorial orientations to reduce steric hindrance.

As described later, because neither 1,2-dioxide **18** nor **20** isomerizes to 1,1-dioxide **19** under ambient conditions, **19** is considered to be formed directly from **16** and **17**. Generally, in the multistep oxidation of disulfides with electrophilic oxidants, the initial oxidation products, *S*-substituted thiosulfinates (1-oxides), are further oxidized at the sulfenyl sulfur atoms to give the corresponding *vic*-dioxides (1,2-dioxides) predominantly, and then the *vic*-dioxides isomerize to the thiosulfonates (1,1-dioxides),[1−6] whereas the oxidation of thiosulfinates with nucleophilic oxidants such as $NaIO_4$ takes place at the sulfinyl sulfur atoms.[18] In this respect, the direct, predominant formation of **19** from **16** in the oxidation with DMD (eq 10) is noteworthy. This exceptional regioselectivity is also discussed later.

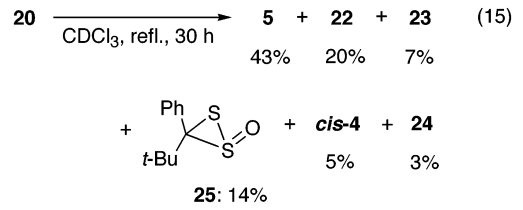
Thermolysis of 1-oxides **16** and **17** was examined with the expectation of the stereoselective formation of *cis*-episulfide **21** through the corresponding thiocarbonyl ylide intermediate. Thus, heating of **16** in refluxing xylene for 16 h gave the expected *cis*-episulfide **21**[19] (8%) and *trans*-episulfide **13** (2%) with 85% recovery of **16** (eq 12). Elongated heating led to decomposition of the



products to give mainly ketone **24** along with a small amount of **13**. The thermal decomposition of **17** was rather complex to yield thioketone **5**, sulfines **22** and **23**, and ketone **24** as the main products along with a small amount of *trans*-episulfide **13** (eq 13).



Thermolysis of 1,1-dioxide **19** in refluxing $CDCl_3$ yielded 2 mol equiv of thioketone **5** quantitatively (eq 14). 1,2-Dioxide **20** mainly decomposed to thioketone **5** (eq 15).



DFT calculations were performed on trithiolane 1-oxides **6**, **7**, **16,** and **17** and 1,2-dioxides **8**, **18**, and **20** at the B3LYP/6-31G* level.[20] Table 1 summarizes relevant bond length and torsion angle data of their experimental and calculated structures. Compound **16** is, however, not included in the discussion because its oxygen atom is disordered in the X-ray analysis. Except that the calculated S−S and C−S bond lengths are slightly longer than the experimental ones, the optimized structures were quite similar to those in the solid state. The calculations reproduced the tendency that the S−S bond lengths of

(17) For example: Drago, R. S.; Wayland, B.; Carlson, R. L. *J. Am. Chem. Soc.* **1963**, *85*, 3125−3128.

(18) (a) Kim, Y. H.; Takata, T.; Oae, S. *Tetrahedron Lett.* **1978**, 2305−2308. (b) Oae, S.; Takata, T. *Tetrahedron Lett.* **1980**, *21*, 3213−3216. (c) Takata, T.; Kim, Y. H.; Oae, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1443−1147.

(19) *cis*-Episulfide **21** isomerizes to *trans*-episulfide **13** by an unknown mechanism under the present conditions.

TABLE 1. Observed and Calculated Bond Lengths (Å) and Torsion Angles (deg) of 1,2,4-Trithiolane 1-Oxides 6, 7, 16, and 17 and 1,2-Dioxides 11/8, 18, and 20

	6 obsd[a]/calcd[b]	**7** obsd[a]/calcd[b]	**16** obsd[a]/calcd[b]	**17** obsd[a]/calcd[b]	**11/8** obsd[a]/calcd[b]	**18** obsd[a]/calcd[b]	**20** obsd[a]/calcd[b]
S1−S2	2.113(1)/2.197	2.052(2)/2.142	*c*/2.147	2.104(2)/2.185	2.249(2)/2.342	2.241(1)/2.355	2.237(1)/2.337
S2−C3	1.838(2)/1.871	1.858(3)/1.893	*c*/1.865	1.825(3)/1.924	1.860(6)/1.935	1.876(3)/1.905	1.863(3)/1.907
C3−S4	1.855(2)/1.903	1.832(4)/1.878	*c*/1.893	1.881(3)/1.923	1.862(6)/1.893	1.847(3)/1.876	1.868(3)/1.898
S4−C5	1.814(2)/1.854	1.818(3)/1.844	*c*/1.865	1.831(3)/1.868	1.829(5)/1.868	1.855(3)/1.897	1.869(3)/1.898
C5−S1	1.880(2)/1.927	1.897(3)/1.944	*c*/1.938	1.881(3)/1.854	1.838(5)/1.906	1.868(3)/1.910	1.848(3)/1.907
S1−O1	1.457(2)/1.504	1.460(4)/1.500	*c*/1.499	1.464(3)/1.504	1.468(5)/1.509	1.434(3)/1.502	1.463(2)/1.507
S2−O2					1.455(5)/1.508	1.471(2)/1.509	1.475(2)/1.507
C5−S1−S2−C3	45.82(9)/−47.1	−32.0(2)/37.4	*c*/51.4	−60.2(2)/61.8	−57.3(2)/−54.6	−62.3(1)/−60.4	72.4(1)/70.4
O1−S1−S2−O2[d]					73.6(3)/78.0	−62.2(2)/−63.6	−59.8(1)/−63.5

[a] X-ray. [b] Structure optimizations were made by DFT calculations at the B3LYP/6-31G* level. [c] The oxygen atom is disordered. [d] O1···O2 distances (obsd/calcd) [Å]: **11/8**, 3.500(8)/3.672; **18**, 3.49(6)/3.761; **20**, 3.427(4)/3.633.

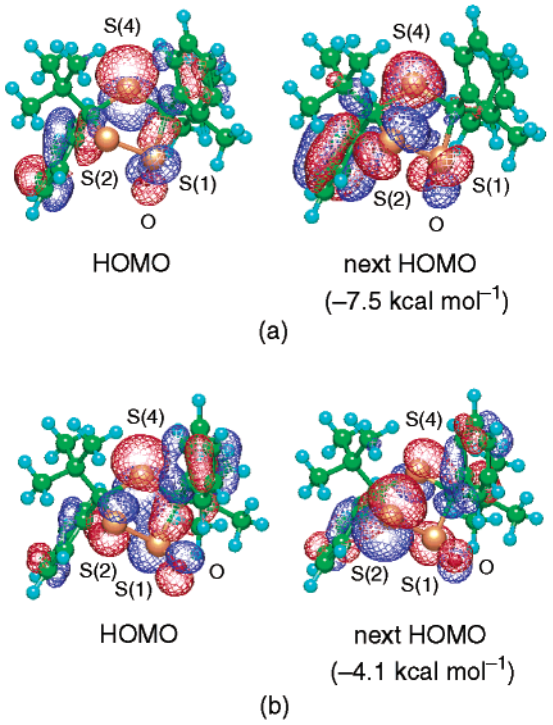
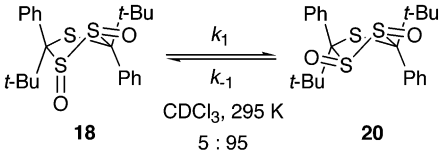


FIGURE 3. HOMOs and next-HOMOs of (a) **16** and (b) **17**.

the axial-*O* monoxides **7** (obsd 2.052(2)/calcd 2.142 Å) and **16** (calcd 2.147 Å) are shorter than those of the equatorial-*O* monoxides **6** (obsd 2.113(1)/calcd 2.197 Å) and **17** (obsd 2.104(2)/calcd 2.185 Å).

Figure 3 depicts the HOMOs and the next-HOMOs of monoxides **16** and **17**. In the HOMO of **16**, the lobes at S(4) and S(1) are the main contributors, and there is no contribution of the lone pair of S(2) (Figure 3a). The lobe of the lone pair of S(2) appears in the next-HOMO, which is 7.5 kcal mol^{-1} lower in energy than the HOMO, where the lobe is a little smaller than that at S(4) and comparable to that at S(1). In contrast, in the HOMO of **17**, the lobe at S(2) is comparable to that at S(1) though smaller than that at S(4), and in the next-HOMO, 4.1 kcal mol^{-1} lower in energy than the HOMO, the lobe at S(2) has the greatest contribution (Figure 3b). A straightforward interpretation for the above calculations is as follows. In **16**, the energy level of the S(2) lone pair is energetically below that of S(4) probably because of a stereoelectronic interaction ($n_{S(2)} \rightarrow \sigma^*_{S(1)-O}$[9]). In **17**, since the stereoelectronic effect is negligibly small, the lone pair on S(2) is kept at a high energy level, comparable to those of S(4) and S(1).[21] In the actual oxidation of **16**, DMD, an electrophilic oxidant, is unable to approach the sterically congested S(4); therefore, as the second choice, it attacks at S(1) to give the 1,1-dioxide **19** as the main product (eq 10). In the case of **17**, the oxidation occurs at S(2) preferably to give the 1,2-dioxide **20** as the main product, where the S(4) resists oxidation because of the same reason as that in the case of **16**. The above considerations, based on ground-state frontier orbitals and steric effects, provide reasonable explanations for the regioselectivities shown in eqs 10 and 11. This is also true for the regioselective oxidations of **6** (eq 4) and **7** (Scheme 2).

Isomerization between 1,2-Dioxides 18 and 20. 1,2-Dioxides **18** and **20** isomerized to each other in solution at room temperature, whereas they did not in the crystalline state. Both **18** and **20** gave the equilibrium mixture after several days in $CDCl_3$ at 295 K, and the ratio of **20**/**18** was determined to be 95/5 by ^{1}H NMR spectroscopy (eq 16). This value corresponds to ΔG_{295}



(16)

[G_{295}(**18**) − G_{295}(**20**)] = 1.7 kcal mol^{-1}. DFT calculations on the 1,2-dioxides **18** and **20** at the B3LYP/6-31G* level indicated that C_2-symmetric **20** is more stable than nonsymmetric **18** by 1.5 kcal mol^{-1} in Gibbs free energy (Table 2).

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) For more sophisticated and quantitative consideration on stereoelectronic effects with the natural bond orbital (NBO) analysis, see the following recent papers and references therein: (a) Sproviero, E. M.; Burton, G. *J. Phys. Chem. A* **2003**, *107*, 5544−5554. (b) Alabugin, I. V. *J. Org. Chem.* **2000**, *65*, 3910−1919.

TABLE 2. Calculated Electronic Energies (E_{elec}), Thermal Corrections to Gibbs Free Energies (TCG), Gibbs Free Energies (G), and Differences of G (ΔG) of 1,2-Dioxides 18, 20, and 8 and 1-Oxides 6, 7, 16, and 17 at the B3LYP/6-31G* Level

	E_{elec}[a]	TCG[a−c]	G[a,b]	ΔG[b,d]
1,2-dioxides				
18	−2200.101 637	0.389 829	−2199.711 808	1.5
20	−2200.104 298	0.390 046	−2199.714 252	0.0
8	−2200.106 386	0.391 091	−2199.715 295	−0.7
1-oxides				
6	−2124.931 943	0.387 646	−2124.544 297	1.5
7	−2124.935 617	0.388 967	−2124.546 650	0.0
16	−2124.931 577	0.388 111	−2124.543 466	2.0
17	−2124.930 399	0.388 040	−2124.542 359	2.7

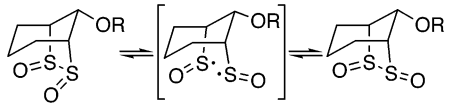
[a] In hartrees. [b] At 298.15 K and 1.00 atm. [c] After scaling by the factor 0.9804.[22] [d] In kcal mol^{-1}.

TABLE 3. Rate Constants of the Isomerizations of 18 to 20 (k_1) and 20 to 18 (k_{-1}) at 295 K

run	solvent	additive	k_1 (10^{-5} s^{-1})	k_{-1} (10^{-6} s^{-1})
1	$CDCl_3$	none	3.94 ± 0.01	2.08 ± 0.01
2	CD_3CN	none	4.44 ± 0.02	2.34 ± 0.01
3	CD_3OD	none	5.51 ± 0.03	2.90 ± 0.02
4	$CDCl_3$	DPPH	4.89 ± 0.01	2.58 ± 0.01
5	$CDCl_3$	CF_3CO_2H	1.43 ± 0.01	0.75 ± 0.04

The instability of *vic*-disulfoxides is attributed to low dissociation energies of the S−S bonds.[1−5] Folkins and Harpp observed the isomerization between *vic*-disulfoxides **26** and **27** by ^{1}H and ^{13}C NMR spectroscopies, and they proposed intervention of a biradical intermediate **28** for the isomerization (Scheme 3).[3]

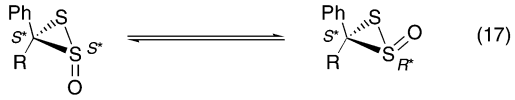
SCHEME 3



26 **28** **27**

The isomerization starting with **18** obeyed reversible first-order kinetics very well at least over a period of 3 half-lives of **18**. The results of several kinetic runs are summarized in Table 3. The equilibrium constants K (k_1/k_{-1}) were the same in all cases examined (K = 95/5 = 19) (runs 1−5). Runs 1−3 showed clearly that the rate constants were almost independent of the solvent polarity, indicating that the polarity change of the reactant is small in the rate-controlling step.

We have previously reported the isomerization between dithiirane 1-oxides **29** and **30** (eq 17).[23] The isomerization



(17)

29 **30**

R = $CMe_2CH_2CMe_2C(O)Ph$

between **29** and **30** did not take place in the presence of a radical scavenger such as diphenylpicrylhydrazyl (DPPH), so we concluded that the isomerization is catalyzed by a radical contaminant.[23] In the present case, the rate of the isomerization between **18** and **20** was not influenced by DPPH (run 4), indicating the operation of a mechanism different from that of isomerization between **29** and **30**. In addition, even when a solution of **18** in $CDCl_3$ was contained in a Teflon vessel, the isomerization proceeded at a rate similar to that in a glass vessel, indicating that the rough surface of a glass vessel does not catalyze the isomerization and the surface acidic SiOH groups on glass also do not affect the rate of isomerization, unlike the case of CF_3CO_2H (vide infra).

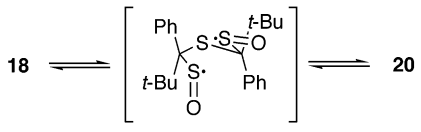
When an excess amount of CF_3CO_2H (10 mol equiv) was added to a $CDCl_3$ solution of **18**, the isomerization became about 3 times slower, probably because of the stabilization of the ground state of **18** and **20** by the hydrogen bonding at the sulfoxide oxygen (run 5).[17]

The isomerization of **18** was followed by ^{1}H NMR spectroscopy in the temperature range 295−318 K in $CDCl_3$ to obtain activation parameters. Because the exact equilibrium constants could not be determined in the higher temperature range, owing to the partial decomposition of the 1,2-dioxides, the approximate rate constants (k_1') were estimated from decreasing rates of **18** over a half-life period where the contribution of the reverse reaction to the rates is negligible (Table 4). The activation parameters thus obtained are $\Delta E^{\ddagger}$ = 29.6 ± 0.2 kcal mol^{-1}, $\Delta H^{\ddagger}$ = 29.0 ± 0.2 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = 19.8 ± 0.7 eu.

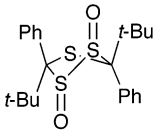
TABLE 4. Approximate Rate Constants (k_1') of the Isomerization of 18 to 20

temp (K)	k_1' (10^{-5} s^{-1})
295	3.93 ± 0.02
303	15.4 ± 0.01
308	34.4 ± 0.2
313	75.2 ± 0.4
318	150 ± 1

SCHEME 4



31



32

The large positive $\Delta S^{\ddagger}$ for the isomerization is in harmony with a biradical mechanism (Scheme 4).[1−5] The isomerization would involve homolysis of the S−S bond to give the biradical intermediate **31** with loss of stereochemistry. Rotation about the C−S(O) bond followed by recombination completes the isomerization. Sulfinyl radicals have been recognized as π radicals.[24] The difference of the spin densities does not appear to be large for the sulfur 3p and the oxygen 2p orbitals, although it is a

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(23) Ishii, A.; Nakamura, S.; Yamada, T.; Nakayama, J. *Tetrahedron* **1997**, *53*, 12203−12214.
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CHART 2

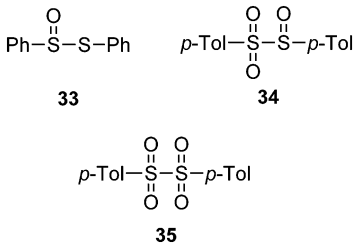


TABLE 5. Yields of Products of the Reactions of 1-Oxides 6, 7, 16, and 17 with $Me_3O^+BF_4^-$

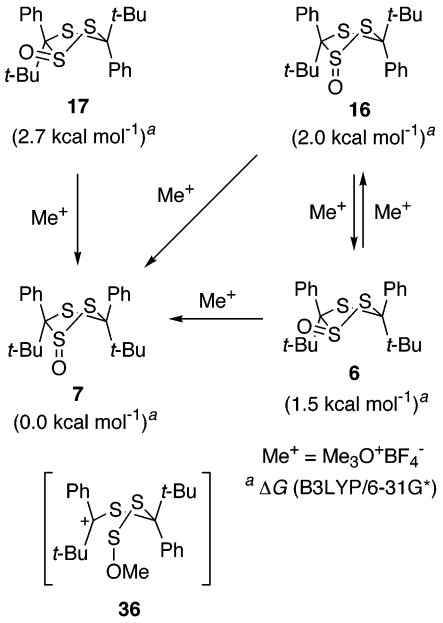
			products[a] (isolated yield (%))			
entry	substrate	time (d)	**6**	**7**	**16**	**17**
1	**6**	1	21	6	24	
2	**7**	3		76		
3	**16**	3	15	3	54	
4	**17**	1		64		8

[a] In all cases, ketone **24** and sulfine **22** were formed as decomposition products.

matter of some argument.[24] The formation of six-membered *O*,*S*-sulfenyl sulfinates, which correspond to **12**, and another 1,2-dioxide **32** was not observed in the isomerization.[25] Compound **32** would prefer to take a conformation with pseudoequatorial *tert*-butyl groups, similar to those of 1,2-dioxides **18** and **20**, leading to the diaxial 1,2-dioxide structure. Compound **32** is estimated to be 1.1 kcal mol^{-1} less stable than **20** by DFT calculations at the B3LYP/6-31G* level.[26] In homolytic dissociation of S−S bonds, aromatic thiosulfinate **33**[27] ($\Delta S^{\ddagger} = 12.6$ eu, $\Delta H^{\ddagger} = 34.5$ kcal mol^{-1}), sulfinyl sulfone **34**[28] ($\Delta S^{\ddagger} = 11.2$ eu, $\Delta H^{\ddagger} = 27.6$ kcal mol^{-1}), and α-disulfone **35**[29] ($\Delta S^{\ddagger} = 16.6$ eu, $\Delta H^{\ddagger} = 40.9$ kcal mol^{-1}) are known to have similar $\Delta S^{\ddagger}$ values, although they are acyclic compounds (Chart 2).

Reactions of 1-Oxides 6, 7, 16, and 17 with $Me_3O^+BF_4^-$. Trithiolane 1-oxides **6**, **7**, **16**, and **17** did not isomerize to each other by either heating or treatment with CF_3CO_2H. However, isomerization was observed when they were treated with $Me_3O^+BF_4^-$ in CH_2Cl_2 at room temperature (Table 5 and Scheme 5). Treatment of cis-substituted 1-oxide **6** with $Me_3O^+BF_4^-$ for 1 day gave **7** (6%) and, unexpectedly, trans-substituted 1-oxide **16** (24%), along with **6** (21%) and some decomposition products (entry 1). Similarly, trans-substituted **16** provided cis-substituted 1-oxides **6** (15%) and **7** (3%) (entry 3), and **17** gave **7** in 64% yield (entry 4). While **7** was always formed in the above three reactions, the 1-oxide

SCHEME 5



7 itself did not isomerize to the other oxides (entry 2). Mutual isomerization was observed only between **6** and **16**. The isomerization among the four 1-oxides would take place by way of the carbocation intermediate **36** that is formed by *O*-methylation followed by C−S(OMe) bond cleavage. Rotations about the C^+−S and S−S bonds in **36** lead to the cis−trans isomerization and the inversion of the S=O group, respectively. It has been established that the inversion of the S=O group in sulfoxides takes place by treatment with $R_3O^+BF_4^-$ followed by alkaline hydrolysis, where the intermediate alkoxysulfonium salts are isolable.[30] In the present case, the corresponding sulfonium salts were not observed by NMR spectroscopies. Incidentally, calculations at the B3LYP/6-31G* level showed that 1-oxide **7** is more stable than **6**, **16**, and **17** by 1.5, 2.0, and 2.7 kcal mol^{-1}, respectively (Table 2).

Conclusion

We succeeded in the isolation and the structure determination of 1,2,4-trithiolane 1,2-dioxides in addition to those of the 1-oxides. The 1,2-dioxides are the first isolable compounds having the C−S(O)−S(O)−C linkage. Furthermore, we observed isomerization between 1,2-dioxides **18** and **20** in solution and proposed the biradical mechanism based on a kinetic study.

Experimental Section

Preparation of 1,2,4-Trithiolane *cis*-4. A mixture of *tert*-butyl phenyl thioketone **5**[31] (0.996 g, 5.59 mmol) and elemental sulfur (179 mg, 5.58 mmol) in DMF (15 mL) under argon was stirred for 14 d at room temperature. The mixture was diluted with aq NH_4Cl and then extracted with ether. The extract was dried, and the solvent was evaporated. The residue was subjected to column chromatography (SiO_2, hexane) to give ***cis*-4**[12] (455 mg, 42%).

(25) In the oxidation of **16** (eq 10), the initial formation of **32** followed by isomerization to **19** cannot be ruled out. However, the hypothetical **32**, if formed, would isomerize not to **19** but to **18** and **20** through the common intermediate **31**.

(26) **32**: $E_{elec} = -2200.101\ 141$ hartrees, TCG = 0.388 571 hartrees, $G = -2199.712\ 57$ hartrees, $\Delta G = 1.1$ kcal mol^{-1} (see Table 2). The calculated dipole moments of **18**, **20**, and **32** are 3.9813, 4.4293, and 1.3753, respectively. The relative stability of **32** compared to **18** and **20** in a polar solvent may be lowered due to the small dipole moment or by solvation on the oxygen atoms, leading to an increase in the bulkiness around the axial-oxygen atoms. Incidentally, 1-oxides **18** and **20** do not dissolve in nonpolar solvents such as hexane.

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(28) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898−4904.

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Preparation of 1,2,4-Trithiolane *trans*-4. A mixture of **5** (1.99 g, 11.2 mmol) and elemental sulfur (358 mg, 11.2 mmol) in toluene (15 mL) under argon was heated at reflux for 4 d. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (hexane) and then HPLC (SiO_2, hexane/CH_2Cl_2 97/3) to give ***trans*-4** (985 mg, 43%) and ***cis*-4** (409 mg, 19%).

Oxidation of *cis*-4 with DMD (1.2 mol equiv). To a solution of ***cis*-4** (52.4 mg, 0.135 mmol) in CH_2Cl_2 (7 mL) was added DMD[14] (0.10 M, 1.6 mL, 0.16 mmol) at −20 °C under argon, and the mixture was stirred for 1 h. The resulting mixture was evaporated to dryness, and the residue was subjected to HPLC (hexane/Et_2O 95/5) to give **6**[11] (29.4 mg, 54%) and **7**[11] (21.3 mg, 39%).

Oxidation of 6 with DMD. To a solution of **6** (51.8 mg, 0.128 mmol) in CH_2Cl_2 (8 mL) was added DMD (0.058 M, 4.4 mL, 0.26 mmol) at −20 °C under argon, and the mixture was stirred for 1.5 h. The solvent was removed in vacuo below −20 °C. The ^{1}H NMR spectrum of the residue showed the quantitative formation of 1,2-dioxide **8**.[11]

Oxidation of 7 with DMD. To a solution of **7** (25.2 mg, 0.0623 mmol) in CH_2Cl_2 (7 mL) was added DMD (0.080 M, 3.1 mL, 0.25 mmol) at −20 °C under argon, and the mixture was stirred for 2.5 h. The solvent was removed in vacuo below −20 °C. The ^{1}H NMR spectrum of the residue measured at −20 °C showed the exclusive formation of 1,1-dioxide **9**.[11]

The crude **9**, thus obtained, rearranged to give **5** (20.9 mg, 94%), when it was dissolved in $CHCl_3$ (5 mL) and the solution was stirred for 0.5 h at room temperature. After removal of the solvent, the residue was purified by HPLC (hexane) to give **5**.

Oxidation of *cis*-4 with DMD (4 mol equiv). To a solution of ***cis*-4** (32.9 mg, 0.0846 mmol) in CH_2Cl_2 (7 mL) was added DMD (0.10 M, 3.2 mL, 0.32 mmol) at −20 °C under argon. The mixture was stirred for 1.5 h, and then the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2) to give crude 1,2-dioxide **8**, which was recrystallized from $CHCl_3$ to give pure **8** (14.8 mg, 42%).

Oxidation of 10 with DMD (4 mol equiv). In a manner similar to the one above, **10**[12] (29.9 mg, 0.0549 mmol) was oxidized with DMD (0.058 M, 3.8 mL, 0.22 mmol) at −20 °C for 1.5 h. The mixture obtained after removal of the solvent under reduced pressure was subjected to HPLC (hexane/Et_2O 90/10) to give 1,2-dioxide **11**[11] (18.9 mg, 60%).

Thermal Decomposition of 8. A solution of **8** (5.1 mg, 0.012 mmol) in $CDCl_3$ (5 mL) was heated at reflux for 7 h. The mixture obtained after removal of the solvent under reduced pressure was subjected to HPLC (hexane) to give **5** (4.0 mg, 93%).

Thermal Decomposition of 6. A solution of **6** (21.0 mg, 0.0519 mmol) in xylene (7 mL) was heated at reflux for 1 d. The residue obtained after removal of the solvent under reduced pressure was subjected to HPLC (hexane) to give episulfide **13**[11] (16.6 mg, 99%).

Thermal Decomposition of 7. A solution of **7** (17.2 mg, 0.0425 mmol) in xylene (5 mL) was heated at reflux for 3 d. The residue obtained after removal of the solvent under reduced pressure was subjected to HPLC (hexane) to give **13** (11.7 mg, 85%).

Oxidation of 13. To a solution of **13** (10.4 mg, 0.0320 mmol) in CH_2Cl_2 (7 mL) was added DMD (0.080 M, 0.45 mL, 0.036 mmol) at 0 °C under argon. The mixture was stirred for 10 min and evaporated to dryness. The ^{1}H NMR spectrum of the residue showed the quantitative formation of **15**.

Oxidation of *trans*-4 with MCPBA. To a solution of ***trans*-4** (55.6 mg, 0.143 mmol) in CH_2Cl_2 (7 mL) was added a solution of MCPBA (purity of 91%, 32.6 mg, 0.172 mmol) in CH_2Cl_2 (3 mL) at 0 °C under argon. The mixture was stirred for 1 h, and then aq Na_2SO_3 was added. The mixture was neutralized with aq $NaHCO_3$. The organic layer was washed with water, dried, and evaporated to dryness. The residue was subjected to HPLC (hexane/Et_2O 96/4) to give **16** (19.1 mg, 33%) and **17** (31.2 mg, 54%).

Oxidation of *trans*-4 with DMD. To a solution of ***trans*-4** (103 mg, 0.265 mmol) in CH_2Cl_2 (15 mL) was added DMD (0.10 M, 3.2 mL, 0.32 mmol) at −20 °C under argon, and the mixture was stirred for 1 h. The mixture was evaporated to dryness, and the residue was subjected to HPLC (hexane/Et_2O 96/4) to give **16** (4.3 mg, 4%) and **17** (94.3 mg, 88%).

Oxidation of 16 with DMD. To a solution of **16** (61.7 mg, 0.152 mmol) in CH_2Cl_2 (10 mL) was added DMD (0.096 M, 6.3 mL, 0.61 mmol) at −20 °C under argon, and the mixture was stirred for 7 h. The solvent was removed in vacuo below −20 °C, and the residue was subjected to HPLC (hexane/Et_2O 90/10, 10−12 °C) to give **18** (12.8 mg, 20%) and **19** (45.1 mg, 71%). The fraction containing **18** was evaporated below −20 °C to prevent **18** from isomerization.

Oxidation of 16 with CF_3CO_3H. To a mixture of **16** (51.1 mg, 0.126 mmol) and H_2O_2 (30%, 57.7 mg, 0.509 mmol) in CH_2Cl_2 (10 mL) under argon was added $(CF_3CO)_2O$ (0.21 mL, 1.5 mmol) at −20 °C, and the mixture was stirred for 7 h at this temperature. The solvent was removed in vacuo below −20 °C, and the residue was subjected to HPLC (hexane/Et_2O 90/10, 10−12 °C) to give **18** (31.6 mg, 60%) and **19** (2.7 mg, 5%).

Oxidation of 17 with DMD. To a solution of **17** (50.5 mg, 0.125 mmol) in CH_2Cl_2 (10 mL) under argon was added DMD (0.11 M, 2.3 mL, 0.25 mmol) at −20 °C, and the mixture was stirred for 2 h. The solvent was removed in vacuo below −20 °C, and the residue was subjected to HPLC (hexane/Et_2O 90/10, 10−12 °C) to give **20** (36.8 mg, 70%), **19** (11.0 mg, 21%), and **18** (2.1 mg, 4%).

Thermal Decomposition of 16. A solution of **16** (10.7 mg, 0.0264 mmol) in xylene (6 mL) was heated at reflux for 16 h. Yields of the products were calculated to be 8% *cis*-episulfide **21**, 2% *trans*-episulfide **13**, 3% (*Z*)-sulfine **22**,[32] 1% (*E*)-sulfine **23**,[32] 1% thioketone **5**, and 85% **16**, on the basis of the integral ratio of the ^{1}H NMR spectrum of the mixture.

Thermal Decomposition of 17. A solution of **17** (17.7 mg, 0.0437 mmol) in xylene (6 mL) was heated at reflux for 12 h. Yields of products were calculated to be 42% thioketone **5**, 16% (*Z*)-sulfine **22**, 17% (*E*)-sulfine **23**, 11% ketone **24**, 2% episulfide **13**, and 2% unidentified compounds, on the basis of the integral ratio of the *tert*-butyl groups in the ^{1}H NMR spectrum of the mixture.

Thermal Decomposition of 19. A solution of **19** (16.0 mg, 0.0380 mmol) in $CDCl_3$ (3 mL) was heated at reflux for 2.5 h. The ^{1}H NMR spectrum of the reaction mixture showed the quantitative formation of thioketone **5**.

Thermal Decomposition of 20. A solution of **20** (6.2 mg, 0.015 mmol) in $CDCl_3$ (1.5 mL) was heated at reflux for 30 h. Yields of products were calculated to be 43% thioketone **5**, 20% (*Z*)-sulfine **22**, 7% (*E*)-sulfine **23**, 14% dithiirane 1-oxide **25**,[33] 5% 1,2,4-trithiolane ***cis*-4**, 3% ketone **24**, and 8% unidentified compounds, on the basis of the integral ratio of the *tert*-butyl groups in the ^{1}H NMR spectrum of the mixture.

Isomerization of 18 and 20. The isomerizations were carried out in a 14 mM solution of **18** under argon. Progress of the reaction was monitored by ^{1}H NMR spectroscopy. The yields were estimated by integral ratios.

Reaction of 1-Oxide 6 with $Me_3O^+BF_4^-$. 1-Oxide **6** (24.7 mg, 0.0610 mmol) and $Me_3O^+BF_4^-$ (97%, 11.0 mg, 0.0721 mmol) were dissolved in CH_2Cl_2 (5 mL) under argon, and the mixture was stirred for 1 d at room temperature. The solvent was removed under reduced pressure, and the residue was subjected to HPLC (hexane/Et_2O 95/5) to give **6** (5.1 mg, 21%), **7** (1.5 mg, 6%), and **16** (5.9 mg, 24%). The ^{1}H NMR spectrum of the reaction mixture indicated the formation of ketone **24** (33%), thioketone **5** (6%), and sulfine **22** (5%) along with **6**, **7**, and **16**.

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Reaction of 1-Oxide 7 with $Me_3O^+BF_4^-$. In a manner similar to the one above, a solution of **7** (22.9 mg, 0.0566 mmol) and $Me_3O^+BF_4^-$ (10.6 mg, 0.0695 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 d to give **7** (17.5 mg, 76%). Formation of ketone **24** (13%) and sulfine **22** (4%) was detected by ^{1}H NMR spectroscopy of the reaction mixture.

Reaction of 1-Oxide 16 with $Me_3O^+BF_4^-$. In a manner similar to the one above, a solution of **16** (23.3 mg, 0.0576 mmol) and $Me_3O^+BF_4^-$ (10.5 mg, 0.0689 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 d to give **6** (3.5 mg, 15%), **7** (0.8 mg, 3%), and **16** (12.6 mg, 54%). Formation of ketone **24** (18%) and sulfine **22** (5%) was detected by ^{1}H NMR spectroscopy of the reaction mixture.

Reaction of 1-Oxide 17 with $Me_3O^+BF_4^-$. In a manner similar to the one above, a solution of **17** (30.8 mg, 0.0761 mmol) and $Me_3O^+BF_4^-$ (14.2 mg, 0.0931 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1 d to give **17** (19.7 mg, 64%) and **7** (2.5 mg, 8%). Formation of ketone **24** (16%) and sulfine **22** (7%) was detected by ^{1}H NMR spectroscopy of the reaction mixture.

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Supporting Information Available: General experimental methods, analytical and spectroscopic data for ***trans*-4** and **15**−**21**, X-ray data for compounds **16**, **17**, **18**, and **20**, and optimized coordinates and thermochemical corrections of **6**, **7**, **8**, **16**, **17**, **18**, **20**, and **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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