

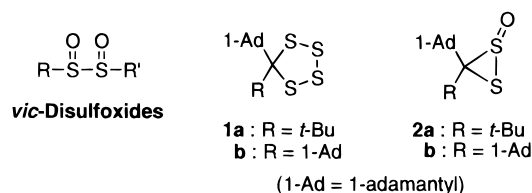
1-Adamantyl-*tert*-butyltetraathiolane 2,3-Dioxide: First Isolable *vic*-Disulfoxide and Efficient Precursor of S₂O

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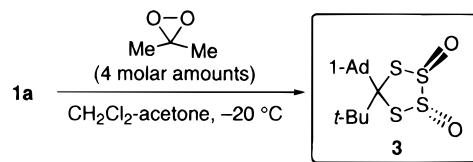
vic-Disulfoxides (α -disulfoxides) are one of the important intermediates in the oxidation of oligosulfides and have been drawing considerable attention.^{1–3} Nevertheless, most of them are still elusive and only a few were detected by NMR spectroscopy.³ We recently reported that the oxidation of tetraathiolanes (**1**)



yielded the corresponding dithiirane 1-oxides (**2**),⁴ and have now discovered that the intermediate, giving **2a**, is the corresponding tetraathiolane 2,3-dioxide (**3**), a *vic*-disulfoxide, which can be isolated as crystals at room temperature. In addition, we also disclosed that the decomposition of **3** provides **2a** and S₂O, which disproportionates to SO₂ and S₃. S₂O and S₃ are sulfur analogues of O₃ and have been drawing much attention in inorganic chemistry,⁵ coordination chemistry,⁶ physical chemistry,⁷ com-

putational chemistry,⁸ and space science⁹ but not in organic chemistry.^{10,11} We report here the structure determination of the tetraathiolane 2,3-dioxide **3** and satisfactory trapping experiments of SO₂ and S₃.

A solution of **1a**¹² in dichloromethane was treated with an acetone solution of dimethyldioxirane (DMD)¹³ (4 molar amounts) at –20 °C and then the solvent was removed in vacuo at –20 °C.¹⁴ Recrystallization of the pale-yellow residue from a mixed solvent of dichloromethane and hexane at –20 °C led to the two polymorphic crystals; pale-yellow plates (major, mp 74–76 °C dec) and yellow prisms (minor, mp 67–68 °C dec), which are separable mechanically and gave the same ¹H NMR spectrum at –10 °C.¹⁵ The infrared spectrum of the crystals, which showed two strong absorptions due to the S=O stretching vibrations (1109 and 1135 cm^{–1}), and elemental analysis results are indicative of the compound being a disulfoxide derivative of **1a**. Finally, its structure was determined to be the (2*RS*,3*RS*)-2,3-dioxide **3** by



X-ray crystallographic analysis.^{16,17} Figure 1 depicts an ORTEP drawing of **3** obtained from a yellow prism (minor) with the relevant bond lengths and bond angles. Both oxygen atoms in **3** occupy axial orientations and are trans to each other with respect to the S(2)–S(3) bond. The length of the bond S(2)–S(3) (2.301 Å) is approximately 12% longer than that of the corresponding S–S bond of **1a** (2.052 Å)¹² and the value is comparable to that of a calculated S–S bond length of *meso*-MeS(O)S(O)Me (2.303 Å) reported recently.¹⁸ The pale-yellow plates (major) were disordered in the crystals and X-ray crystallographic analysis of the mixture, which consisted of 86% of one enantiomer (2*R*,3*R* or 2*S*,3*S*) and 14% of the other, led to unsatisfactory results.¹⁶

The 2,3-dioxide **3** was stable in the crystalline state even at room temperature for several hours but in solution decomposed above –10 °C cleanly to the corresponding diastereomeric dithiirane 1-oxides, (1*RS*,3*SR*)- and (1*RS*,3*RS*)-**2a** (53 and 39%, respectively), the tetraathiolane **1a** (8%) (¹H NMR), and elemental

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(14) Repeated recrystallization (3 times) of the residue at –20 °C from CH₂Cl₂–EtOH gave pure **3** in 25–30% yield as pale-yellow, fine plates.

(15) **3**: ¹H NMR (400 MHz, CDCl₃, 263 K) δ 1.45 (br s, 9H, *t*-Bu), 1.65 (br s, 6H), 2.09 (br s, 9H); ¹³C NMR (100.6 MHz, CDCl₃, 263 K) δ 29.2 (CH), 33.4 (br s, CH₃), 35.9 (CH₂), 42.2 (CH₂), 44.5 (C), 46.9 (C), 153.9 (C).

(16) X-ray data for **3**: For yellow prisms: monoclinic, space group *P2₁/n*, *a* = 6.4150(3) Å, *b* = 18.878(1) Å, *c* = 13.7410(9) Å, β = 97.349(4)°, *V* = 1650.4(2) Å³, *Z* = 4, μ (Mo K α) = 5.54 mm^{–1}, temperature of data collection 153 K. *R* (*R_w*) = 0.077 (0.086) and GOF = 3.761; max/min residual electron density = 2.06/–1.97 e Å^{–3} for 3683 reflections [*I* \geq 2 σ (*I*)] (286 parameters). For pale-yellow plates: orthorhombic, space group *P2₂₂*, *a* = 6.5200(6) Å, *b* = 13.970(1) Å, *c* = 18.386(2) Å, *V* = 1665.6(3) Å³, *Z* = 4, μ (Mo K α) = 5.49 mm^{–1}, temperature of data collection 153 K. *R* (*R_w*) = 0.090 (0.094) and GOF = 3.422; max/min residual electron density = 2.37/–0.83 e Å^{–3} for 1992 reflections [*I* \geq 2 σ (*I*)] (210 parameters). For more details of the X-ray single-crystal analyses, see Supporting Information.

(17) The structure of the precursor for **2** was previously⁴ assumed to be the tetraathiolane 1-oxide and now should read the *vic*-disulfoxide **3**.

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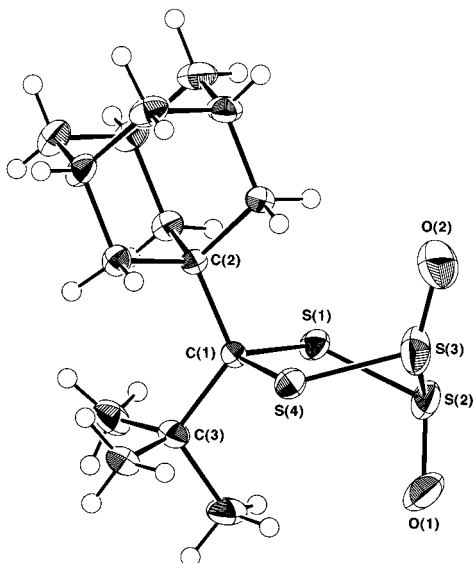
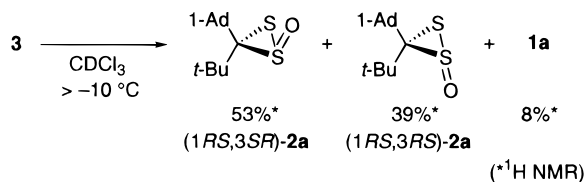


Figure 1. ORTEP drawing (50% ellipsoids) of 1-adamantyl-*tert*-butyltetrathiolane 2,3-dioxide (**3**). Relevant bond lengths (Å) and bond angles (deg): C1–S1 1.868(2); S1–S2 2.054; S2–S3 2.301(1); S3–S4 2.052(1); S4–C1 1.861(2); C1–C2 1.606(3); C1–C3 1.599(3); S2–O1 1.461(2); S3–O2 1.409(2); C1–S1–S2 109.3(1); S1–S2–S3 94.4(1); S2–S3–S4 93.0(1); C1–S4–S3 109.6(1); S1–C1–S4 107.8(1); C1–S1–S2–S3 39.6(1); S1–S2–S3–S4 45.5(1); S2–S3–S4–C1 42.6(1).

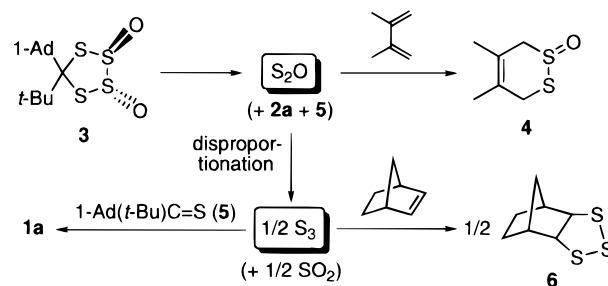
sulfur (detected by TLC); *vide infra*, for the formation mechanism of **1a**. The decomposition of **3** obeyed the first-order kinetics with a half-life of approximately 15 min at 25 °C in CDCl₃ ($k = 6.8 \times 10^{-4} \text{ s}^{-1}$, $c = 2.75 \times 10^{-2} \text{ M}$). The thermal stability of **3** in solution is much larger than that of acyclic *vic*-disulfoxides, RS(O)S(O)R,^{3a–c} which could be observed below –40 °C, and a little larger than or comparable to that of bridged bicyclic *vic*-disulfoxides, 8-substituted 6,7-dithiabicyclo[3.2.1]octane 6,7-dioxides.^{3d} The dioxide **3** showed no tendency to rearrange to the *OS*-sulfonyl sulfinate [R–S(O)OS–R] in contrast to the behavior of other *vic*-disulfoxides.^{1a,d,2a,3} Rearrangement–ring expansion would widen the S(1)–C(1)–S(4) angle increasing the unfavorable steric interaction between the two bulky substituents and the neighboring sulfur atoms S(1) and S(4).



Trapping experiments were done to verify the formation of S₂O and S₃ during the decomposition of **3**. The results are summarized in Scheme 1. Thus, 2,3-dioxide **3** was allowed to decompose in the presence of 2,3-dimethyl-1,3-butadiene (8 molar amounts) at room temperature to give the 3*H*,6*H*-1,2-dithiin 1-oxide **4**¹⁹ in 87% yield along with (1*RS*,3*SR*)- and (1*RS*,3*RS*)-**2a** (53 and 33%, respectively), 1-adamantyl *tert*-butyl thioketone (**5**)¹⁹ (11%), and **1a** (3%), whereas in the presence of norbornene (10 molar amounts), the trithiolane **6**^{19,20} was obtained in high

(19) The yields of **4** and **6** were determined by ¹H NMR with dibenzyl as the internal standard. See Supporting Information for **4** and **5**.

Scheme 1



yield (85%) along with (1*RS*,3*SR*)- and (1*RS*,3*RS*)-**2a** (50 and 38%, respectively), **5** (10%), and **1a** (2%). The formation of **4** and **6** can be explained as the results of the reaction of 2,3-dimethyl-1,3-butadiene with S₂O and that of norbornene with S₃, respectively.¹¹ The decomposition of **3** in the presence of both 2,3-dimethyl-1,3-butadiene and norbornene furnished **4** overwhelmingly (72%) as the trapping product. In addition, the decomposition rate of **3** and yields of **2a** were independent of the presence of the trapping reagents. Therefore, we conclude that **3** splits into **2a** and S₂O (and **5** as the byproduct) initially and S₂O reacts quickly with 2,3-dimethyl-1,3-butadiene in a [4+2] manner¹⁰ to give **4**, whereas the reaction of S₂O with norbornene does not take place or is sluggish allowing S₂O to disproportionate to S₃ and SO₂; the S₃ thus formed reacts with norbornene effectively to give **6**. Such a disproportionation was observed in an argon matrix by Raman spectroscopy.²¹ The reaction of S₃ with the thioketone **5** also explains the formation of **1a** in the absence of the trapping reagents.

Formation of the trithiolane **6** at elevated temperatures^{11,20,22} was reported previously in reactions of norbornene with reactive sulfur species, which were unspecified or proposed to be S₃ or S₂. In the above trapping experiments no adducts²³ between S₂ and 2,3-dimethyl-1,3-butadiene were observed.

In summary, we have succeeded in the unambiguous structure determination of the tetrathiolane 2,3-dioxide **3**, the first isolable *vic*-disulfoxide. In addition, we revealed that **3** releases S₂O, which disproportionates to S₃ and SO₂, almost stoichiometrically at ambient temperature.

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Supporting Information Available: Characterization data (¹H and ¹³C NMR, IR, MS, and elemental analyses) for **3**, **4**, and **5**, and structure determination summaries and tables of X-ray structure data for **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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