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Oxidation of tetrathiolanes: isolation of a *vic*-disulfoxide, 5-(1-adamantyl)-5-*tert*-butyltetrathiolane 2,3-dioxide and its decomposition to the dithiirane 1-oxide and 'S_2O'

Akihiko Ishii *[1], Masaaki Nakabayashi, Yi-Nan Jin, Juzo Nakayama *[2]

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan

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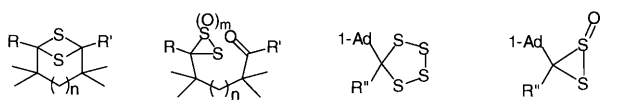
Abstract

Oxidation of 5-(1-adamantyl)-5-*tert*-butyltetrathiolane (**3a**) with dimethyldioxirane (DMD) at −78 or −20°C gave (1*R**,3*S**)- and (1*R**,3*R**)-3-(1-adamantyl)-3-*tert*-butyldithiirane 1-oxides (*cis*-**4a** and *trans*-**4a**, respectively) as the final products. The reaction was revealed to proceed through stepwise oxidation to the corresponding 2-oxide and then to the 2,3-dioxide **5**, a *vic*-disulfoxide; the latter is isolated in pure form by low-temperature recrystallization and is fairly stable at room temperature in the crystalline state. The structure of **5** was determined by X-ray crystallography. The 2,3-oxide **5** decomposes in solution above −10°C to *cis*-**4a**, *trans*-**4a**, and 'S_2O' as the principal products. The reactive sulfur species, S_2O, is trapped by 2,3-dimethyl-1,3-butadiene to give 4,5-dimethyl-3*H*,6*H*-1,2-dithiin 1-oxide. In the absence of the diene, S_2O disproportionates to SO_2 and 'S_3', which is trapped by norbornene to give *exo*-norbornane trithiolane (*exo*-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]decane).

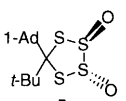
Keywords: Tetrathiolane; Oxidation; Dimethyldioxirane; *vic*-Disulfoxide; Dithiirane oxide; S_2O; S_3

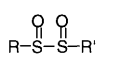
1. Introduction

We have reported the first synthesis of isolable dithiiranes **2** by the oxidative hydrolysis of bicyclic 1,3-dithietanes **1** [1]. Detailed examination of this synthesis has revealed it to be successfully applicable only to bicyclic 1,3-dithietanes, which inevitably yield carbonyl group-containing dithiiranes **2** [1d,e]. Although the carbonyl groups are considered to be independent of the stability of the dithiirane rings by inspection of the crystal structures of **2** ($n = 1$, $m = 0,1$) [1a,b,e], they take part in some reactions of **2** [1b,e,f]. In our continuing study to develop new and more general methods for the preparation of dithiirane derivatives, which do not possess other functional groups, we found that the oxidation of tetrathiolanes **3** [2] with dimethyldioxirane (DMD) leads to a new synthesis of dithiirane 1-oxides **4** [3].



Furthermore, we succeeded in the isolation of the corresponding tetrathiolane 2,3-dioxide **5** (Fig. 1), the first isolable *vic*-disulfoxide [4], as the intermediate giving **4a**. *vic*-Disulfoxides (α-disulfoxides), which possess an extremely weak sulfur–sulfur bond, are an important intermediate in the oxidation of oligosulfides and have been drawing considerable attention [5–7]. Nevertheless, most of them are still elusive and only a few were detected by NMR spectroscopy [7].





[1] *Corresponding author.

[2] *Corresponding author. Tel.: +81-48-8583390; fax: +81-48-8583700; e-mail: nakaj@post.saitama-u.ac.jp.

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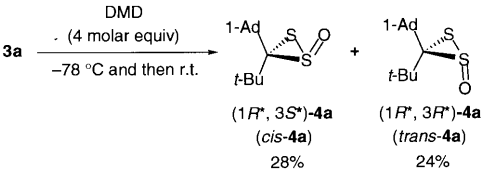
We report here a full account of the oxidation of tetrathiolanes **3** with DMD including the structure determination of intermediates, mono- and dioxides of **3**, and decomposition of the 2,3-dioxide **5** to the dithiirane 1-oxide **4** and a reactive sulfur species, S_2O.

2. Results and discussion

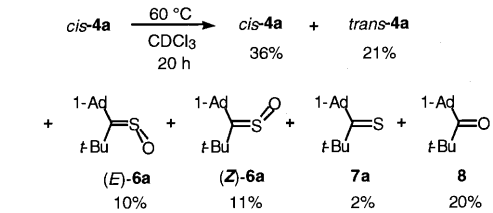
2.1. Oxidation of tetrathiolane *3a* with DMD: formation of dithiirane 1-oxide *4a*

A solution of 1-adamantyl-*tert*-butyltetrathiolane (**3a**) in dichloromethane was treated with DMD [8] (four molar equivalents) at −78°C, and the mixture was stirred for 1 h at −78°C and then for 4 h at room temperature. Removal of the solvent and careful purification of the residue by gel-permeation chromatography (GPC) gave a mixture of (1*R**,3*S**)- and (1*R**,3*R**)-dithiirane 1-oxides **4a** (*cis*-**4a** and *trans*-**4a**, respectively) in 62% combined yield. The use of the optimized equivalent of DMD improved the yield of **4a** compared with that given in our preliminary report [4]. The *cis*–*trans* mixture of **4a** was separated by HPLC with a silica-gel column to give *cis*-**4a** and *trans*-**4a** in 28 and 24% isolated yields, respectively (Eq. (1)). Their stereochemistry could be elucidated by ^{1}H-NMR spectroscopy: the *tert*-butyl signal of *cis*-**4a** (δ 1.09) appears at a 0.35 ppm higher field than that of *trans*-**4a** (δ 1.44), whereas three broad signals due to the adamantyl of *cis*-**4a** appear at 0.08–0.23 ppm lower fields than those of *trans*-**4a**, because of the anisotropy of the SO group [9]. The above assignment was further supported by aromatic solvent-induced shift studies [10]. Optical resolution of (1*R**,3*R**)-**4a** (*trans*-**4a**) was performed by HPLC equipped with a chiral column, and the enantiomer with a shorter retention time was assigned as (1*R*, 3*R*)-**4a** by X-ray crystallography [11].



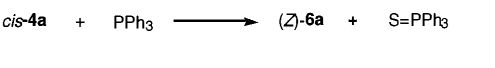
(1)

The dithiirane 1-oxides **4a** decomposed at each melting point to give the corresponding thioketone *S*-oxides (sulfines) **6a**, thioketone **7a**, and ketone **8**. In solution, thermal isomerization between *cis*-**4a** and *trans*-**4a** took place in addition to decomposition. Thus, heating pure *cis*-**4a** in $CDCl_3$ at 60°C for 20 h yielded a mixture of *cis*-**4a** (36%), *trans*-**4a** (21%), (*E*)-**6a** (10%), (*Z*)-**6a** (11%), **7a** (2%), and **8** (20%) (Eq. (2)). A similar result was obtained by heating *trans*-**4a** in $CDCl_3$.

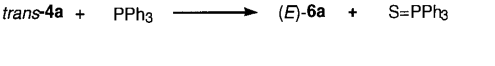


(2)

The desulfurization of *cis*-**4a** and *trans*-**4a** by Ph_3P gave (*Z*)-**6a** and (*E*)-**6a**, respectively, in quantitative yields with complete retention of configuration [12] (Eqs. (3) and (4)).



(3)



(4)

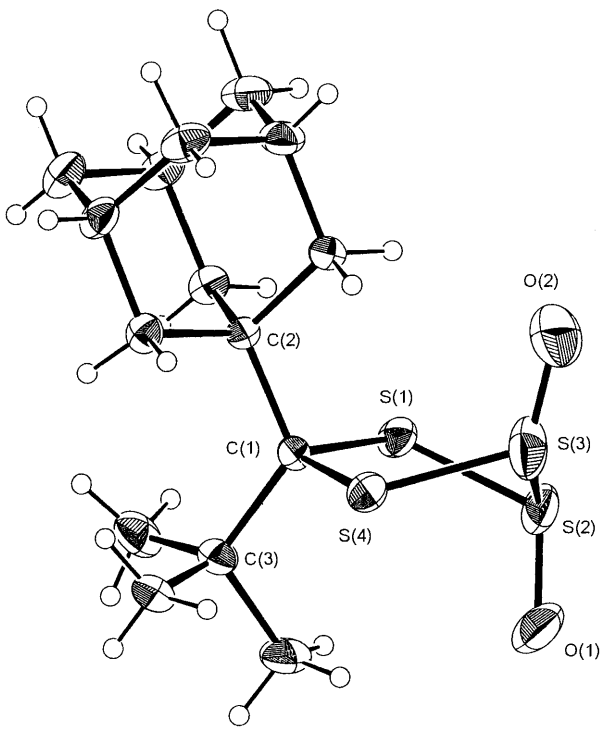
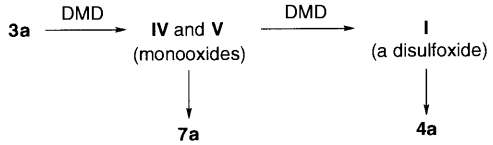


Fig. 1. ORTEP drawing of (2*R**,3*R**)-5-(1-adamantyl)-5-*tert*-butyltetrathiolane 2,3-dioxide (**5**) (ellipsoids at 50% probability). Relevant bond lengths (Å) and bond angles (°): C1–S1, 1.868(2); S1–S2, 2.054; S2–S3, 2.301(1); S3–S4, 2.052(1); S4–C1, 1.861(2); C1–C2, 1.606(3); C1–C3, 1.599(3); S2–O1, 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).

2.2. Determination of the precursor of dithiirane 1-oxides *4*

2.2.1. NMR study

After the treatment of tetrathiolane **3a** with DMD (four molar equivalents) at −20°C, the solvent and



Scheme 1.

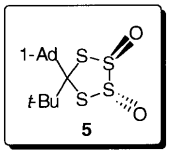
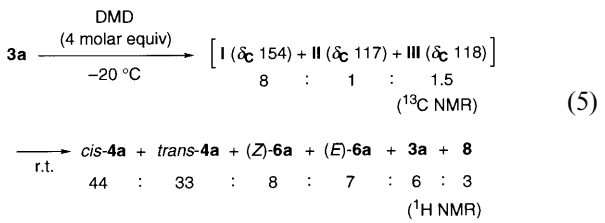


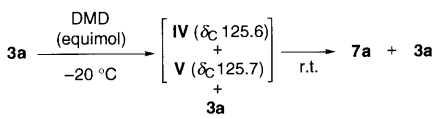
Fig. 2.

excess DMD were removed *in vacuo* below −20°C, and ^{13}C-NMR spectra of the residue were measured in a temperature range from −10°C to room temperature. At −10°C, three quaternary carbon peaks assignable to the tetrathiolane carbon were observed at δ 154 (**I**), 118 (**II**), and 117 (**III**) in the peak–height ratio of ca. 8:1:1.5. Raising of the temperature to room temperature led to the gradual disappearance of these peaks and, instead, the signals due to dithiirane 1-oxides **4a** appeared as the main ones along with those of sulfines **6a**, tetrathiolane **3a**, and ketone **8** (Eq. (5)). This observation strongly suggested that the compound **I** is the main precursor of the dithiirane oxides **4a**. The tetrathiolane **3a** was not observed in the ^{13}C-NMR spectrum at −10°C, indicating that **3a** was formed by a secondary reaction (vide infra).



(5)

The oxidation of **3a** with an equimolecular amount of DMD provided interesting results. The ^{13}C-NMR spectrum of the reaction mixture at −20°C showed the presence of alternative intermediates **IV** (δ_C 125.6) and **V** (δ_C 125.7) with equal peak heights along with unreacted tetrathiolane **3a**. The intermediates **IV** and **V** decomposed on warming the mixture to room temperature, and the thioketone **7a** appeared instead (Eq. (6)), indicating that **IV** and **V** were precursors of **7a**.



(6)

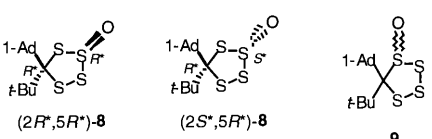
The compound **I** (δ_C 154), the precursor of dithiirane 1-oxides **4a**, was isolated as pale yellow crystals by recrystallization at low temperature. The compound **I** was stable in the solid state even at room temperature for several hours. The IR spectrum of **I** showed two strong absorptions due to S=O stretching vibrations (1109 and 1135 cm^{-1}), and a result of the elemental analysis indicated that the compound **I** is a dioxide of **3a**. Thus, the compound **I** was determined to be a disulfoxide of **3a**. Meanwhile, based on the amount of DMD used, the precursors (**IV** and **V**) of the thioketone **7a** are presumed to be two epimers of a monooxide of **3a**. The relationship among oxides of **3a** and the final products is thus summarized as shown in Scheme 1.

2.2.2. Structure determination of tetrathiolane 2,3-dioxide *5* by X-ray crystallography

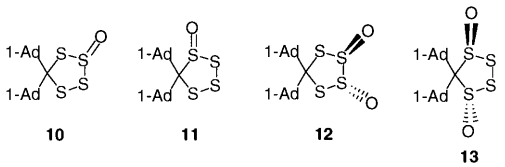
An X-ray analysis was performed on the disulfoxide **I** to determine the regio- and stereochemistry, which also provided important insight into the structure of the monooxides **IV** and **V**. Recrystallization of the dioxide **I** from a mixed solvent of dichloromethane and hexane at −20°C led to the two polymorphic crystals; pale-yellow plates (major, m.p. (dec) 74–76°C) and yellow prisms (minor, m.p. (dec) 67–68°C), which are separable mechanically and gave the same ^{1}H-NMR spectrum at −10°C. X-ray crystallographic analyses on the two crystals revealed that the disulfoxide **I** is the (2*R**,3*R**)-2,3-dioxide **5** [13]. Fig. 2 depicts an ORTEP drawing of **5** obtained from a yellow prism (minor) with the relevant bond lengths and bond angles. Both oxygen atoms in **5** occupy axial orientation 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 ca. 12% longer than that of the corresponding S–S bond of **3a** (2.052 Å) [2a] and the value is comparable to that of a calculated S–S bond length of *meso*-MeS(O)S(O)Me (2.303 Å) [14]. 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.

2.2.3. Structures of monooxides of *3*

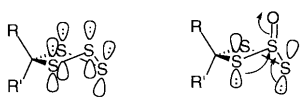
As a natural consequence, the structures of the monooxides **IV** and **V** are assigned to the two epimeric 2-oxides (2*R**,5*R**)-**8** and (2*S**,5*R**)-**8**. A possibility that one of the two is the 1-oxide **9** could be ruled out by the NMR study on the oxides of di-(1-adamantyl)tetrathiolane **3b**.



The mono- and dioxides of **3b** were prepared similarly, and the ^{13}C-NMR spectra were measured. In the case of the monooxide of **3b**, only one tetrathiolane carbon was observed at δ_C 127.85 at -20°C, indicating the formation of a single regioisomer as the monooxide (**10** or **11**). The tetrathiolane carbon of a dioxide of **3b** appeared at δ_C 156.9. In addition, the two 1-adamantyl groups of the dioxide are equivalent to each other spectroscopically, indicating a *C*2-symmetrical structure, **12** or **13**.



The oxidation reactions of **3a** and **3b** with DMD would proceed in similar regio- and stereoselectivities because the 1-adamantyl and *t*-butyl groups have a similar steric demand. Based on the confirmed structure of the 2,3-dioxide **5**, the dioxide of **3b** is assigned to **12** and the monooxide to **10**. Thus, monooxides **IV** and **V** derived from **3a** are also assigned to not regioisomers but epimers of the monooxide **8**. The sulfoxide group in the monooxides, **8** and **10**, would occupy axial orientation with respect to the tetrathiolane ring, because 3p lone pair electrons on the sulfur atoms in **3** extend to the axial direction of the tetrathiolane ring and, therefore, the axial attack of the less hindered 2-position by electrophilic DMD is more favorable kinetically than the equatorial one. In addition, the axial orientation of the sulfoxide group is probably more stable thermodynamically than the equatorial one owing to the stereoelectronic effects of the lone pair electrons of the adjacent sulfur atoms [15,16].



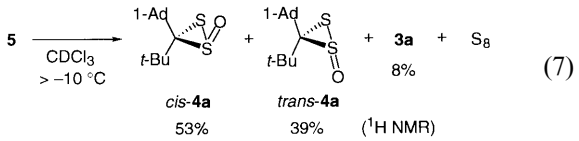
The above assignment on the regiochemistry of mono- and dioxides of **3** is based on an assumption that the regiochemistry of **5** in solution is the same as that in the solid state, which means that, for example, a 1,2-oxygen shift that leads to the rearrangement of **12** to **13** does not occur. As far as we know, such a 1,2-oxygen shift in cyclic oligosulfides is not observed [17,18] or is very slow [19] in solution at ambient temperature.

Table 1
Kinetics on the decomposition of **5**

Run	Additive	*c* (10^{-2} M)	Temperature (K)	*k* (10^{-4} s^{-1})
1	None	2.75	297.5 ± 0.3	6.83
2	None	0.40	297.3 ± 0.5	6.22
3	2,3-Dimethyl-1,3-butadiene	3.75	297.7 ± 0.1	6.40
4	Norbornene	2.63	297.5 ± 0.6	5.98

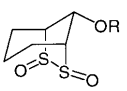
2.3. Decomposition of tetrathiolane 2,3-dioxide **5**

The pure 2,3-dioxide **5** decomposed cleanly in solution above -10°C to *cis*-**4a** (53%), *trans*-**4a** (39%), tetrathiolane **3a** (8%) (^{1}H-NMR), and elemental sulfur (detected by TLC) (Eq. (7)).

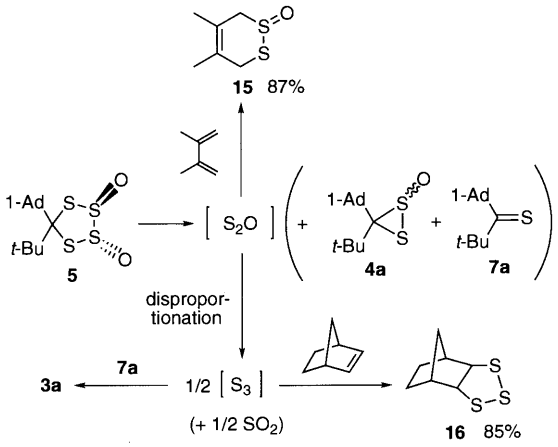


(7)

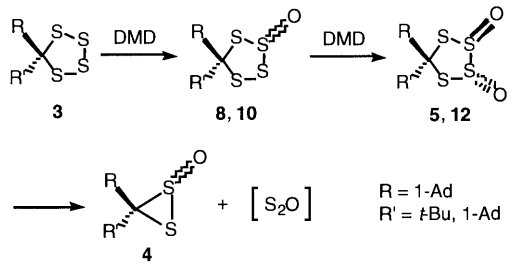
The decomposition of **5** obeyed the first-order kinetics with a half-life of approximately 15 min at 25°C in $CDCl_3$ and the rate was independent of the concentration (Table 1, runs 1 and 2). The thermal stability of **5** in solution is much higher than that of acyclic *vic*-disulfoxides, RS(O)S(O)R, studied by Freeman and Angeletakis [7a–c], which could be observed below -40°C, and is a little higher than or comparable to that of bridged bicyclic *vic*-disulfoxides **14** [7d]. The dioxide **5** showed no tendency to rearrange to the OS-sulfenyl sulfinate [R–S(O)OS–R] in contrast to the behavior of other *vic*-disulfoxides [5a,d,6a,7]. Ring expansion by rearrangement, from a five- to six-membered ring, would result in widening of the S(1)–C(1)–S(4) angle and narrowing of the C(2)–C(1)–C(3) angle at the same time; the former deformation increases the unfavorable steric interactions between the bulky substituents and the neighboring sulfur atoms, and the latter also increases the steric repulsion between the two bulky substituents.



The counterpart of **4a** that is formed by decomposition of **5** is most probably 'S_2O'. S_2O is known to disproportionate to SO_2 and 'S_3' [20]. S_2O and S_3 are sulfur analogues of O_3 and have been drawing much attention in inorganic chemistry [21], coordination chemistry [22], physical chemistry [23], computational chemistry [24], and space science [25] but not in organic chemistry [26,27]. Trapping experiments were done to verify the formation of such interesting, small sulfur species, S_2O and S_3. The results are summarized in Scheme 2. Thus, 2,3-dioxide **5** was allowed to decompose in the presence of 2,3-dimethyl-1,3-butadiene (eight equivalents) at room temperature to give the 3*H*,6*H*-1,2-dithiin 1-oxide **15** in 87% yield along with *cis*-**4a** (53%), *trans*-**4a** (33%), thioketone **7a** (11%), and



Scheme 2.



Scheme 3.

tetrathiolane **3a** (3%). In contrast, the presence of norbornene (ten equivalents) led to the formation of the trithiolane **16** [28] in 85% yield along with *cis*-**4a** (50%), *trans*-**4a** (38%), **7a** (10%), and **3a** (2%).

The formation of **15** and **16** can be explained as the result of the reaction of 2,3-dimethyl-1,3-butadiene with S_2O [26] and that of norbornene with S_3 [27], respectively. The decomposition rate of **5** and yields of **4a** were independent of the presence of the trapping reagents (Table 1, runs 3 and 4). The decomposition of **5** in the presence of both 2,3-dimethyl-1,3-butadiene and norbornene furnished **15** overwhelmingly (72%) as the trapping product. Therefore, we conclude that **5** splits into **4a** and S_2O (and **7a** as a by-product) initially, and the S_2O reacts quickly with 2,3-dimethyl-1,3-butadiene in a [4 + 2] manner [26] to give **15**, whereas the reaction of S_2O with norbornene does not take place or is sluggish, allowing S_2O to disproportionate to S_3 and SO_2; the S_3 thus formed reacts with norbornene effectively to give **16**. The reaction of S_3 with the thioketone **7a** also explains the formation of **3a** (see Eqs. (5) and (7)).

Formation of the trithiolane **16** at elevated temperatures [27–29] was reported previously in reactions of norbornene with a reactive sulfur species, which were unspecified or proposed to be S_3 or S_2. In the above trapping experiments no adducts [30] between S_2 and 2,3-dimethyl-1,3-butadiene were observed.

3. Conclusion

The oxidation of tetrathiolanes **3** with DMD provides the 2-oxides (**8** and **10**) initially and then the 2,3-dioxides (**5** and **12**). The structure of **5** was unambiguously determined by X-ray crystallography. The tetrathiolane 2,3-dioxide, the first isolable *vic*-disulfoxide, is stable in the solid state for several hours at room temperature but decomposes in solution to give the dithiirane 1-oxides **4** and S_2O, the latter of which disproportionates to S_3 and SO_2 almost stoichiometrically at ambient temperature (Scheme 3).

4. Experimental

Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H- (400 MHz) and ^{13}C-NMR (100.6 MHz) spectra were determined on Bruker AM 400 and ARX400 spectrometers using $CDCl_3$ as the solvent unless otherwise noted. IR spectra were taken on a Hitachi 270-50 spectrometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

An acetone solution of dimethyldioxirane (DMD) was prepared by the reported method and its concentration was determined prior to use by oxidizing thioanisole to its sulfoxide with this solution [8].

In worktop of the reactions, extracts were dried over anhydrous $MgSO_4$ after washing with water. Column chromatography was performed with silica gel and the eluent is given in parentheses. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908. High-pressure liquid chromatography (HPLC) was performed with a packed SiO_2 column, INERTSIL PREP-SIL (10 mm i.d. 250 mm, GL Science INC.).

4.1. Preparation of thioketones 7

Di-1-adamantyl thioketone (**7b**) was prepared by the reported method [31]. In a similar manner, 1-adamantyl *tert*-butyl thioketone (**7a**) was prepared in 71% yield by treatment of a solution of the corresponding ketone hydrazone (1.468 g, 6.274 mmol) and Et_3N (7.05 g, 69.7 mmol) in benzene (20 ml) with a solution of S_2Cl_2 (0.94 g, 6.963 mmol) in benzene (20 ml) at 0°C, followed by usual aqueous worktop and chromatographic purification.

Di-1-adamantyl thioketone (**7b**). ^{1}H-NMR: δ 1.69–1.72 (m, 12H), 2.06 (br s, 6H), 2.20 (pseudo d, $J = 2.9$ Hz, 12H). ^{13}C-NMR: δ 29.2, 36.5, 43.5, 57.2, 279.3.

1-Adamantyl *tert*-butyl thioketone (**7a**). Purple needles; m.p. 45–46°C (EtOH). ^{1}H-NMR: δ 1.45 (s,

9H), 1.69–1.72 (m, 6H), 2.07 (br s, 3H), 2.18 (pseudo d, $J = 2.9$ Hz, 6H). ^{13}C-NMR: δ 29.2, 32.7, 36.5, 43.7, 53.9, 56.7, 279.0. MS m/z 236 [M^+]. Anal. Calc. for $C_{15}H_{24}S$: C, 76.21; H, 10.23. Found: C, 76.46; H, 10.44%.

4.2. Preparation of 5-(1-adamantyl)-5-tert-butyltetrathiolane (**3a**)

Tetrathiolane **3a** was prepared by the method reported previously [2a] or by the reaction of the thioketone **7a** with S_2Cl_2: To a solution of 1-adamantyl *tert*-butyl thioketone (**7a**) (400 mg, 1.7 mmol) in hexane (80 ml) was added a solution of S_2Cl_2 (480 mg, 3.57 mmol) in hexane (20 ml) at 0°C. The mixture was stirred for 1 h at 0°C and then for 1 h at room temperature. The mixture was poured into ice–water and extracted with ether. The extract was dried and the filtrate was concentrated under reduced pressure. The evaporation was stopped when an oily material just appeared. The residue was passed through a short column of silica gel (hexane) to give thioketone **7a** and a mixture of tetrathiolane **3a** and elemental sulfur. The mixture was further separated with GPC and the crude product was recrystallized from dichloromethane–hexane to give the tetrathiolane **3a** (258 mg, 46%). Yellow prisms, m.p. (dec) 110°C (EtOH). ^{1}H-NMR: δ 1.40 (br s, 9H), 1.63 (br s, 6H), 2.00 (br s, 3H), 2.14 (br s, 6H). ^{13}C-NMR: δ 29.3, 32.7, 36.5, 43.7, 45.5, 47.7, 115.4 (S–C–S). MS m/z 332 [M^+]. Anal. Calc. for $C_{14}H_{24}S_4$: C, 54.17; H, 7.27. Found: C, 54.36; H, 7.33.

4.3. Preparation of 5,5-di(1-adamantyl)tetrathiolane (**3b**)

In a manner similar to that described above, 5,5-di(1-adamantyl)tetrathiolane (**3b**) (66 mg, 28%) was prepared by the reaction of the thioketone **7b** (180 mg, 0.57 mmol) and S_2Cl_2 (154 mg, 1.14 mmol). Yellow prisms: m.p. (dec) 136–137°C (EtOH). ^{1}H-NMR: δ 1.63 (br s, 12H), 1.00 (br s, 15H), 2.55 (br s, 3H). ^{13}C-NMR: δ 29.4, 36.5, 43.5, 48.5, 116.7 (S–C–S). MS m/z 410 [M^+]. Anal. Calc. for $C_{21}H_{30}S_4$: C, 61.41; H, 7.36. Found: C, 61.61; H, 7.34.

4.4. Oxidation of 5-(1-adamantyl)-5-tert-butyltetrathiolane (**3a**)

4.4.1. Four molar equivalents of DMD

To a solution of tetrathiolane **3a** (95 mg, 0.29 mmol) in dichloromethane (16 ml) cooled at −78°C was added DMD (0.098 M, 12 ml, 1.18 mmol). The mixture was stirred for 1 h at −78°C and then for 4 h at room temperature. The solvent was removed under reduced pressure and the residue was purified with GPC to give a mixture of the dithiirane 1-oxides, *cis*- and *trans*-**4a**, (51 mg, 62%). The mixture was further separated with HPLC to give *cis*-**4a** (22.5 mg, 28%) and *trans*-**4a** (19 mg, 24%).

4.4.2. One molar equivalent of DMD

To a solution of **3a** (25.2 mg, 0.076 mmol) in CH_2Cl_2 (5 ml) cooled at −78°C was added DMD in acetone (0.08 M, 1 ml, 0.08 mmol). After stirring at −78°C for 5 h, the mixture was warmed to room temperature. The solvent was removed under reduced pressure to give a red solid. The residue was purified with GPC to afford sulfines **6a** (0.7 mg, 4%, $Z:E = 1:1$), dithiirane 1-oxides **4a** (6.6 mg, 31%, *cis*:*trans* = 1.2:1), thioketone **7a** (9.3 mg, 52%), and tetrathiolane **3a** (1.8 mg, 7%).

4.4.3. (1R*,3S*)-3-(1-Adamantyl)-3-tert-butyldithiirane 1-oxide (*cis*-**4a**)

Colorless solid; m.p. (dec) 106–107°C (EtOH). ^{1}H-NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.69 (pseudo ABq, $J = 12$ Hz, 6H), 2.05 (br s, 3H), 2.20 (br s, 6H); (C_6D_6) δ 0.74 (s, 9H), 1.54 (pseudo d, $J = 11$ Hz, 3H), 1.64 (pseudo d, $J = 12$ Hz, 3H), 1.92 (br s, 3H), 2.16 (br s, 6H). ^{13}C-NMR: δ 29.4, 29.7, 36.6, 41.8, 44.0, 86.2 (S–C–S). IR (KBr): 1120 cm^{-1}. MS: m/z 284 [M^+]. Anal. Calc. for $C_{15}H_{24}OS_2$: C, 63.33; H, 8.50. Found: C, 63.63; H, 8.67%.

4.4.4. (1R*,3R*)-3-(1-Adamantyl)-3-tert-butyldithiirane 1-oxide (*trans*-**4a**)

Colorless solid; m.p. (dec) 99–100°C (EtOH). ^{1}H-NMR ($CDCl_3$): δ 1.44 (s, 9H), 1.61 (pseudo ABq, $J = 11$ Hz, 6H), 1.74 (pseudo d, $J = 12$ Hz, 3H), 1.84 (pseudo d, $J = 12$ Hz, 3H), 1.97 (br s, 3H); (C_6D_6): δ 1.38 (s, 9H), 1.35 (br s, 6H), 1.52 (br s, 6H), 1.65 (br s, 3H). ^{13}C-NMR: δ 28.7, 32.2 (br), 36.4, 39.5, 41.9, 43.5, 87.7 (S–C–S). IR (KBr) 1123 cm^{-1}. MS: m/z 284 [M^+]. Anal. Calc. for $C_{15}H_{24}OS_2$: C, 63.33; H, 8.50. Found: C, 63.72; H, 8.58%.

4.5. Reaction of (1R*,3S*)-3-(1-adamantyl)-3-tert-butyldithiirane 1-oxide (*cis*-**4a**) with Ph_3P

A solution of *cis*-**4a** (7.0 mg, 0.025 mmol) and Ph_3P (7.2 mg, 0.028 mmol) in benzene (5 ml) was stirred for 1 h at room temperature. The solvent was removed under reduced pressure. The ^{1}H-NMR spectrum of the residue showed the exclusive formation of the (*Z*)-sulfine **6a**. The residue was subjected to column chromatography (CH_2Cl_2) to give Ph_3P=S (6.9 mg, 85%) and the (*Z*)-**6a** (4.9 mg, 79%).

4.5.1. 1-Adamantyl tert-butyl thioketone (*Z*)-*S*-oxide [(*Z*)-**6a**]

Colorless crystals; m.p. 89–90°C (EtOH). ^{1}H-NMR ($CDCl_3$): δ 1.37 (s, 9H), 1.71 (pseudo d, $J = 12$ Hz, 3H), 1.82 (pseudo d, $J = 12$ Hz, 3H), 2.03 (br s, 3H), 2.40

(pseudo d, $J = 2.4$ Hz, 6H). ^{1}H-NMR (C_6D_6): δ 0.99 (s, 9H), 1.59 (pseudo d, $J = 12$ Hz, 3H), 1.75 (pseudo d, $J = 11$ Hz, 3H), 1.91 (br s, 3H), 2.39 (pseudo d, $J = 2.6$ Hz, 6H). ^{13}C-NMR: δ 28.9, 31.0, 36.5, 38.8, 40.6, 47.4, 216.0; IR (KBr) 1053, 1102 cm^{-1}. MS: m/z 252 [M$^+$]. Anal. Calc. for $C_{15}H_{24}OS$: C, 71.38; H, 9.58. Found: C, 70.86; H, 9.61%.

4.6. Reaction of (1R*,3R*)-3-(1-adamantyl)-3-tert-butyldithiirane 1-oxide (trans-**4a**) with Ph_3P

In a similar manner, *trans*-**4a** (9.1 mg, 0.032 mmol) was treated with Ph_3P (8.6 mg, 0.033 mmol) in benzene (5 ml) to give Ph_3P=S (8.3 mg, 86%) and the (*E*)-sulfine [(*E*)-**6a**] (7.5 mg, 93%).

4.6.1. 1-Adamantyl tert-butyl thioketone (E)-S-oxide [(E)-**6a**)]

Colorless crystals; m.p. 79–81°C (EtOH). ^{1}H-NMR ($CDCl_3$): δ 1.56 (s, 9H), 1.72 (pseudo ABq, $J = 12$ Hz, 6H), 2.02 (br s, 6H), 2.07 (br s, 3H). ^{1}H-NMR (C_6D_6): δ 1.39 (pseudo d, $J = 11$ Hz, 3H), 1.49 (pseudo d, $J = 13$ Hz, 3H), 1.50 (s, 9H), 1.64 (pseudo d, $J = 2.6$ Hz, 6H), 1.73 (br s, 3H). ^{13}C-NMR: δ 28.2, 29.8, 36.2, 39.5, 40.8, 44.1, 216.9. IR (KBr) 1056, 1125 cm^{-1}. MS: m/z 252 [M$^+$]. Anal. Calc. for $C_{15}H_{24}OS$: C, 71.38; H, 9.58. Found: C, 71.28; H, 9.60%.

4.7. Oxidation of 5,5-di(1-adamantyl)tetrathiolane (**3b**)

To a solution of **3b** (41.5 mg, 0.10 mmol) in dichloromethane (8 ml) cooled at −78°C was added DMD in acetone (0.07 M, 1.7 ml, 0.12 mmol). After stirring at −78°C for 5 h, the solvent was removed under reduced pressure to give a green–yellow oily residue. The residue was purified by HPLC to afford sulfine **6b** (4.1 mg, 12%), dithiirane 1-oxide **4b** (14.0 mg, 38%), thioketone **7b** (7.9 mg, 25%), and tetrathiolane **3b** (5.7 mg, 14%).

4.7.1. 3,3-Di-(1-adamantyl)dithiirane 1-oxide (**4b**)

Colorless plates; m.p. (dec) 143–144°C (EtOH). ^{1}H-NMR: δ 1.56–1.86 (m, 18H), 1.96 (br s, 3H), 2.04 (br s, 3H), 2.21 (br s, 6H). ^{13}C-NMR: δ 28.7 (CH), 29.7 (CH), 36.4 (CH_2), 36.6 (CH_2), 39.5 (CH_2), 44.1 (C), 44.7 (C), 87.4 (S–C–S) (one CH_2 carbon was not observed under the conditions); IR (KBr) 1118 cm^{-1}; MS m/z 362 [M$^+$]. Anal. Calc. for $C_{21}H_{30}OS_2$: C, 69.56; H, 8.34. Found: C, 69.74; H, 8.51.

4.7.2. Di-1-adamantyl thioketone S-oxide (**6b**)

Colorless crystals; m.p. 159–160°C (EtOH). ^{1}H-NMR: δ 1.65–1.85 (m, 12H), 2.03 (br s, 12H), 2.44 (pseudo d, $J = 2.4$ Hz, 6H). ^{13}C-NMR: δ 28.3, 29.0, 36.2, 36.6, 39.0, 41.0, 44.7, 47.9, 216.6; IR (KBr) 1018, 1086 cm^{-1}; MS m/z 330 [M$^+$]. Anal. Calc. for $C_{21}H_{30}OS$: C, 76.31; H, 9.15. Found: C, 76.20; H, 9.26%.

4.8. Isolation of (2R*,3R*)-5-(1-adamantyl)-5-tert-butyltetrathiolane 2,3-dioxide (**5**)

To a solution of tetrathiolane **3a** (48.3 mg, 0.15 mmol) in dichloromethane (8 ml) cooled at −20°C was added DMD (0.080 M, 7.5 ml, 0.60 mmol), and the mixture was stirred for 1.3 h. The volatile materials were removed in vacuo below −20°C and the residue was recrystallized below −20°C from a mixed solvent of dichloromethane and ethanol. The recrystallization was repeated three times to give analytically pure 2,3-dioxide **5** (15.3 mg, 28%) as pale-yellow, fine plates. M.p. (dec) 65–66° (CH_2Cl_2–EtOH). ^{1}H-NMR (263 K): δ 1.45 (br s, 9H), 1.65 (br s, 6H), 2.09 (br s, 9H). ^{13}C-NMR (263 K): δ 29.2 (CH), 33.4 (br s, CH_3), 35.9 (CH_2), 42.2 (CH_2), 44.5 (C), 46.9 (C), 153.9 (C); IR (KBr, 298 K) 1134, 1104 cm^{-1}. Anal. Calc. for $C_{15}H_{24}O_2S_4$: C, 49.42; H, 6.63. Found: C, 48.84; H, 6.57.

4.9. X-ray crystallography of 2,3-dioxide **5**

Single crystals of **5** for X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of dichloromethane and hexane; the two polymorphic crystals, pale-yellow plates (major, m.p. (dec) 74–76°C) and yellow prisms (minor, m.p. (dec) 67–68°C), were mechanically separated under a microscope.

Yellow prisms: $C_{15}H_{24}O_2S_4$, M_w 364.59. Monoclinic, space group $P2_1/n$, $a = 6.4150(3)$, $b = 18.878(1)$, $c = 13.7410(9)$ Å, $\beta = 97.349(4)$, $V = 1650.4(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.467$ g cm^{-3}, μ(Mo–K$_\alpha$) = 5.54 mm^{-1}. A yellow prism with dimensions $0.30 \times 0.12 \times 0.10$ mm was mounted on a Mac Science DIP3000 diffractometer with a graphite-monochromater. Oscillation and non-screen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K and the data reduction was made by the MAC DENZO program system. Intensity data of 4111 independent reflections were collected in the range of $0 \leq h \leq 7$, $0 \leq k \leq 26$, $-19 \leq l \leq 19$. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR [32] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares to minimize the functions, $\Sigma(|F_o| - |F_c|)^2$, for 3683 reflections [$I \_ 2\sigma(I)$] (286 parameters). The final R (R_w) = 0.077 (0.086) and GOF = 3.761; max/min residual electron density = 2.06/−1.97 e Å^{-3}.

Pale-yellow plates: intensity data of 2565 independent reflections were collected in the range of $0 \leq h \leq 9$, $0 \leq k \leq 19$, $0 \leq l \leq 25$. Orthorhombic, space group $P2nn$, $a = 6.5200(6)$, $b = 13.970(1)$, $c = 18.386(2)$ Å, $V = 1665.6(3)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.454$ g cm^{-3}, $\mu(\text{Mo}-\text{K}_\alpha) = 5.49$ mm^{-1}. Refinement was performed for 1992 reflections [$I \leq 2\sigma(I)$] (210 parameters). The structure was solved as a mixture consisted of 86% of one enantiomer (2*R*,3*R* or 2*S*,3*S*) and 14% of the other. The final R (R_w) = 0.090 (0.094) and GOF = 3.422; max/min residual electron density = 2.37/−0.83 e Å^{-3}.

4.10. Decomposition of tetrathiolane 2,3-dioxide **5** in the presence of 2,3-dimethyl-1,3-butadiene

Decomposition of 2,3-dioxide **5** in the presence of 2,3-dimethyl-1,3-butadiene was carried out in $CDCl_3$ and monitored by ^{1}H-NMR, where yields of the products were determined by comparing their integral ratios with that of the internal standard dibenzyl.

To 2,3-dioxide **5** (5.5 mg, 0.015 mmol) placed in an NMR sample tube was added a 0.021 M $CDCl_3$ solution (0.4 ml) of dibenzyl containing 1,3-dimethyl-1,3-butadiene (10.2 mg, 0.124 mmol) at room temperature. Decomposition of **5** was monitored by ^{1}H-NMR at 297.7 ± 0.1 K. Final yields of products were obtained from the integral ratio in the ^{1}H-NMR spectrum after 4 h: the dithiin 1-oxide **15**, 87; *cis*-dithiirane 1-oxide **4a**, 53; *trans*-**4a**, 33; thioketone **7a**, 11; tetrathiolane **3a**, 3%. The yield of **15** was calculated based on the assumption that 1 mol of **5** generates 1 mol of S_2O which provides 1 mol of **15**. Signals for **15** was specified by comparison with those of the authentic sample (see section 4.13).

4.11. Decomposition of tetrathiolane 2,3-dioxide **5** in the presence of norbornene

In a similar manner, decomposition of 2,3-dioxide **5** (3.8 mg, 0.0105 mmol) in the presence of norbornene (9.5 mg, 0.101 mmol) in $CDCl_3$ (0.4 ml) at 297.5 ± 0.6 K was monitored by ^{1}H-NMR. In this case, triptycene was employed as the internal standard. The signals due to 2,3-dioxide **5** disappeared mostly after 90 min. The solvent and unreacted norbornene was removed under reduced pressure: trithiolane **16** [28], 85; *cis*-dithiirane 1-oxide **4a**, 50; *trans*-**4a**, 38; thioketone **7a**, 10; tetrathiolane **3a**, 2%. The yield of **16** was calculated based on the assumption that 1 mol of **5**, after disproportionation of S_2O, gives 0.5 mol of S_3, which yields 0.5 mol of **16**.

4.12. Decomposition of tetrathiolane 2,3-dioxide **5** in the presence of 2,3-dimethyl-1,3-butadiene and norbornene

In a similar manner, decomposition of 2,3-dioxide **5** (4.7 mg, 0.013 mmol) in the presence of 2,3-dimethyl-1,3-butadiene (8.5 mg, 0.103 mmol) and norbornene (9.9 mg, 0.105 mmol) in $CDCl_3$ (0.4 ml) at 294 K was monitored by ^{1}H-NMR. Triptycene was used as the internal standard. The yields of the products were obtained from the integral ratios in the ^{1}H-NMR spectra measured before and after evaporation of the solvent and unreacted trapping reagents: dithiin 1-oxide **15**, 72; trithiolane **16**, 3; *cis*-dithiirane 1-oxide **4a**, 53; *trans*-**4a**, 34; thioketone **7a**, 10; tetrathiolane **3a**, 3%.

4.13. Preparation of 4,5-dimethyl-3*H*,6*H*-1,2-dithiin 1-oxide (**15**)

To a solution of 4,5-dimethyl-3*H*,6*H*-1,2-dithiin [33] (40 mg, 0.27 mmol) in dichloromethane (5 ml) was added DMD (0.07 M, 4 ml, 0.28 mmol) at −78°C. The mixture was stirred for 1.5 h at −78°C and allowed to warm to 0°C. The solvent was removed under reduced pressure at 0°C to give spectroscopically pure 4,5-dimethyl-3*H*,6*H*-1,2-dithiin 1-oxide (**15**) as a pale-yellow oil. ^{1}H-NMR: δ 1.96 (s, 3H), 2.02 (s, 3H), 3.18 (d, 1H, $J = 13.9$ Hz), 3.23 (d, 1H, $J = 13.6$ Hz), 3.76 (d, 1H, 13.8 Hz), 3.92 (d, 1H, $J = 13.4$ Hz). ^{13}C-NMR: δ 19.7, 21.9, 34.0, 60.2, 123.7, 131.2; IR (neat) 1074 cm^{-1}. Anal. Calc. for $C_6H_{10}OS_2$: C, 44.41; H, 6.21. Found: C, 43.99; H, 6.09% (for a sample purified by GPC).

5. Supplementary material

Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-141119). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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