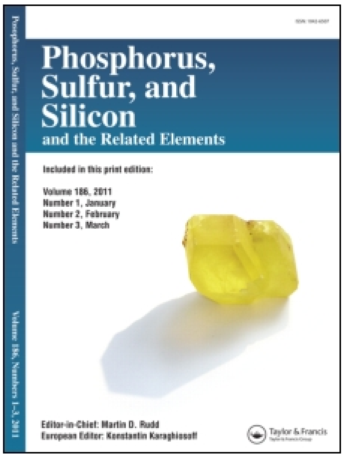

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Oxidation and Reduction Reactions of *cis*-9,10,11-Trithiabicyclo[6.3.0]undecane Synthesized by Reaction of *cis*-Cyclooctene with S_8O

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Oxidation and Reduction Reactions of *cis*-9,10,11-Trithiabicyclo[6.3.0]undecane Synthesized by Reaction of *cis*-Cyclooctene with S_8O

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Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Saitama, Japan

cis-Cyclooctene reacted with S_8O in refluxing carbon disulfide to give cis-9,10,11-trithiabicyclo[6.3.0]undecane (1,2,3-trithiolane). Oxidation of the 1,2,3-trithiolane with m-chloroperbenzoic acid (MCPBA) or dimethyldioxirane (DMD) yielded the corresponding 1-exo-oxide, 1-endo-oxide, 2-endo-oxide, 2-exo-oxide, 1-endo,3-exo-dioxide, 1-exo,3-exo-dioxide, 1,1,3-exo-trioxide, and 1,1,3,3-tetraoxide, depending on the amount of the oxidants. Formation of another 1,3-dioxide assignable to the 1-endo,3-endo-dioxide was observed in the oxidation of the 1-endo-oxide with MCPBA. Oxidation of the 2-exo-oxide with DMD gave the 1,1,3,3-tetraoxide in low yield. Reduction of the 1,2,3-trithiolane and its trans isomer with $LiAlH_4$ gave cis- and trans-cyclooctane-1,2-dithiol, respectively, in high yields. Oxidation of the sodium salt of the cis-1,2-dithiol with MCPBA provided the corresponding 1,2,5,6-tetrathiocane in low yield as the only identifiable product.

Keywords Cyclooctene; 1,2-dithiol; oxidation; reduction; sulfuration; 1,2,3-trithiolane

INTRODUCTION

Direct sulfuration of alkenes has been attracting considerable attention for a long time, and most alkenes are sulfurated by heating with elemental sulfur under vigorous[1] or mild conditions.[2,3] Recently we reported the reaction of *trans*-cyclooctene (*trans*-**1**) with S_8O[4,5] in carbon disulfide to yield the corresponding 1,2,3-trithiolane **2** (Eq. 1).[6,7] The high reactivity of *trans*-**1**, in addition to elemental sulfur activated by oxidation, would permit this reaction to proceed at room temperature.

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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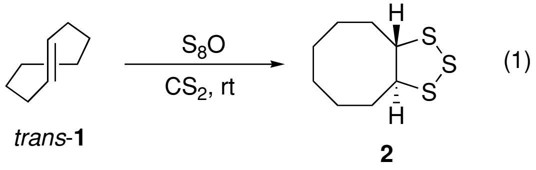
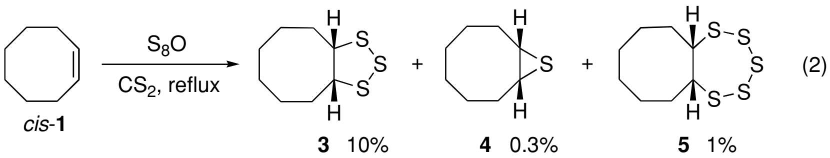
We report here the reaction of *cis*-cyclooctene (*cis*-**1**), which is less reactive than *trans*-**1**, with S_8O to provide the corresponding 1,2,3-trithiolane, and its oxidation and reduction reactions.



EQ 1

RESULTS AND DISCUSSION

The reaction of *cis*-cyclooctene (*cis*-**1**) with S_8O proceeded in refluxing carbon disulfide to yield *cis*-9,10,11-trithiabicyclo[6.3.0]dodecane (1,2,3-trithiolane **3**) as a yellow oil in 10% isolated yield together with episulfide $\mathbf{4}^{3a}$ (0.3%) and 1,2,3,4,5-pentathiepane **5** (1%) (Eq. 2). Under similar conditions, the reaction of *cis*-**1** with S_8 did not take place at all.



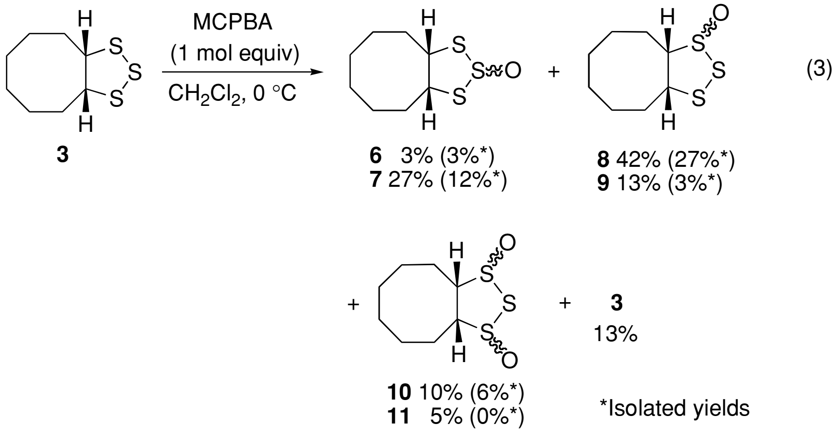
EQ 2

In the ^{13}C NMR spectrum of **3**, only four signals were observed, and the methine carbons resonated at $\delta = 62.6$. In the ^{1}H NMR spectrum, the methine protons were observed at $\delta = 3.65$–3.70 as a multiplet. The corresponding methine carbons and protons of pentathiepane **5** appeared in slightly lower-field regions ($\delta_C = 63.6$ and $\delta_H = 3.95$–3.99, respectively).

Oxidation

Oxidation of 1,2,3-trithiolane **3** with *m*-chloroperbenzoic acid (MCPBA) or dimethyldioxirane (DMD) was investigated. When **3** was treated with an equimolar amount of MCPBA in dichloromethane at 0°C, four monoxides (**6**–**9**) and two 1,3-dioxides (**10** and **11**) were formed in the ratio of 3:27:42:13:10:5 (^{1}H NMR integral ratio) with recovery of **3**

(13%) (Eq. 3). These products, except **11**, which decomposed on silica gel, were isolated by means of silica-gel column chromatography and HPLC. The isolated yields are given in the parentheses in Eq. 3. The oxidation employing two molar equivalents of MCPBA provided a 67:33 mixture of **10** and **11**, from which **10** was isolated in 18% yield by column chromatography. Dioxide **11** was obtained in the pure form by recrystallization of a mixture prepared by oxidation of 1-*exo*-oxide **8** with DMD in dichloromethane at 0°C.

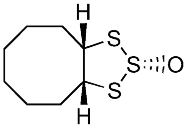


EQ 3

The structures of these oxides were determined by their spectroscopic data, X-ray crystallography, and some related reactions. Two (**6** and **7**) of the four monoxides were assigned to be 2-oxides because they presented only four signals in the ^{13}C NMR spectra. In their ^{1}H NMR spectra, the methine protons appeared at $\delta = 4.48$–4.55 for **6** and $\delta = 4.80$–4.85 for **7**. The low-field shift of **7** is due to the anisotropic effect of the *syn*-S=O group, and the structure of **7** was verified by X-ray crystallography (Figure 1) to be the 2-*exo*-oxide. The other 2-oxide **6** was essentially assigned to be the 2-*endo*-oxide. The assignment of 1-oxides **8** and **9** is described after that of 1,3-dioxides **10** and **11**.

The structures of dioxides **10** and **11** were determined unambiguously by X-ray crystallography to be the 1-*endo*,3-*exo*-dioxide (Figure 2) and the 1-*exo*-3-*exo*-dioxide (Figure 3), respectively.

In the ^{1}H NMR spectrum of **10**, the nonequivalent methine protons appeared at $\delta = 4.35$–4.40 and $\delta = 4.63$–4.67 as multiplets. The corresponding protons in **11** are equivalent ($\delta = 4.68$–4.72) due to the existence of a symmetric plane, and the chemical shift is very similar to that of one of the methine protons of **10** resonating at a lower field. The



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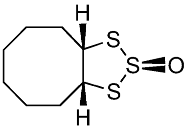
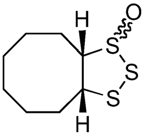


7



8 and **9**

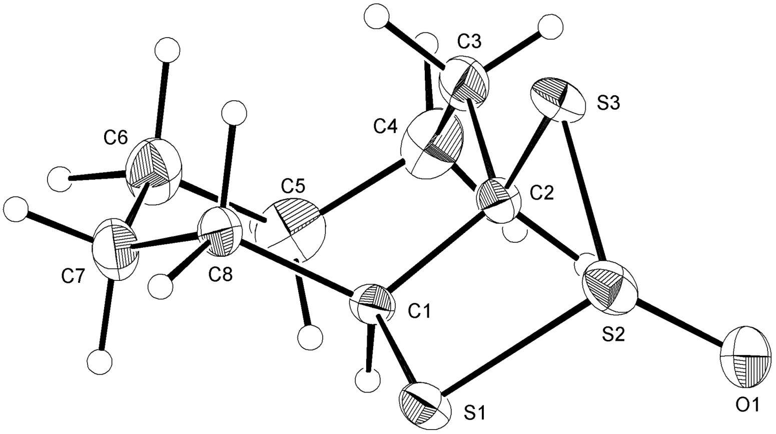
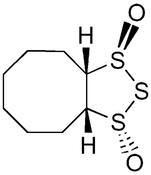


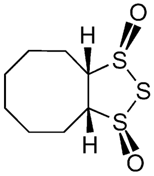
FIGURE 1 ORTEP drawing of 2-*exo*-oxide **7** with thermal ellipsoids drawn at 20% probability level. Relevant bond lengths (Å): C1-C2 1.526(2), C1-S1 1.8393(16), S1-S2 2.1018(6), S2-S3 2.0788(8), S3-C2 1.8285(19), S2-O1 1.4749(18).

low-field shift is due to the anisotropic effect of *syn*-S=O groups. To support the assignment, NMR shielding constants (σ) were calculated for **10** and **11** by the GIAO method at the B3LYP/6–311+G(2d,p)//B3LYP/6–31+G(d) level.[8,9] In the calculations, their initial coordinates were taken from the structures obtained by X-ray crystallography, and no remarkable conformational change was found in the optimized structures in comparison with the starting structures. The calculated chemical shifts of C(1)-*H* and C(2)-*H* in **10** were $\delta = 4.38$ and 4.53, respectively, and those of C(1)-*H* and C(2)-*H* in **11** were $\delta = 3.79$ and 5.51, respectively. The averaged value for **11** is $\delta = 4.65$, and the calculations reproduced the present observations very well. The C(2)-H bonds in **10** and **11** are in the 1,3-diaxial relationship with the S(1)=O(1) bonds so that the protons undergo the strong anisotropic effect of the S=O group.

Stereochemistries of 1-oxides **8** and **9** were elucidated on the basis of the NMR data and verified by further oxidation reactions giving 1,3-dioxides. In ^{1}H NMR spectroscopy, two methine protons of **8** resonated



10



11

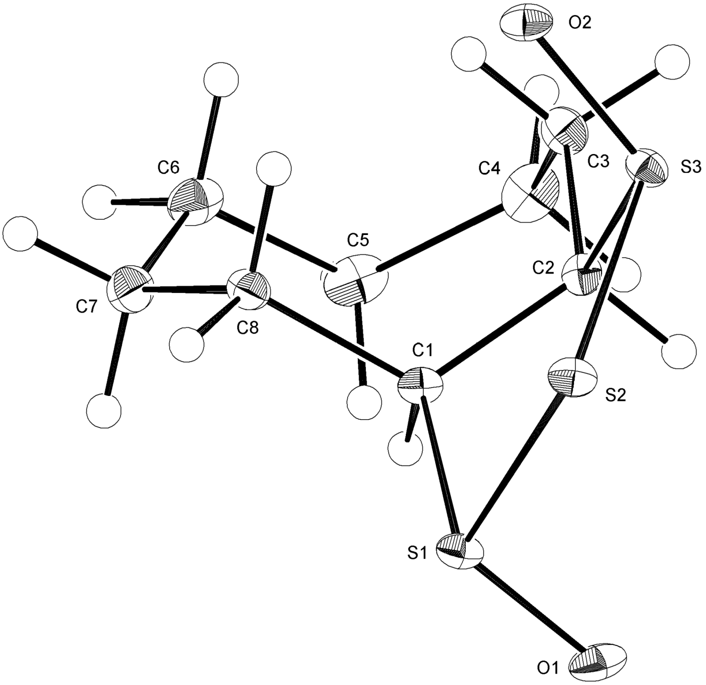


FIGURE 2 ORTEP drawing of 1-*endo*,3-*exo*-dioxide **10** with thermal ellipsoids drawn at 30% probability level. Relevant bond lengths (Å): C1-C2 1.515(4), C1-S1 1.839(3), S1-S2 2.1225(15), S2-S3 2.1250(16), S3-C2 1.818(3), S1-O1 1.470(3), S3-O2 1.466(3).

at $\delta = 3.99$–4.02 and $\delta = 4.67$–4.72 as multiplets, and those of **9** appeared at $\delta = 3.54$–3.59 and $\delta = 3.93$–3.98 as multiplets. The substantial low-field shift of one ($\delta = 4.67$–4.72) of two methine protons in **8** is indicative of the anisotropic effect of the *syn*-S=O group. Thus, **8** is assigned to be the *exo*-1-oxide and the other **9** to be the *endo*-1-oxide (Figure 4).

To verify the assignment, 1-oxides **8** and **9** were subjected to further oxidation. Oxidation of 1-*exo*-oxide **8** with DMD (0.9 molar equiv)

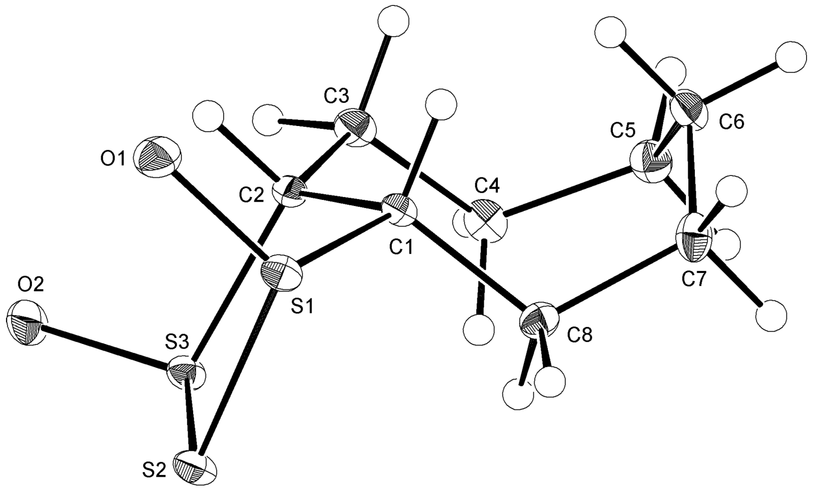
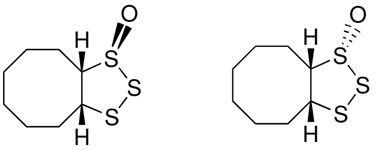


FIGURE 3 ORTEP drawing of 1-*exo*,3-*exo*-dioxide **11** with thermal ellipsoids drawn at 30% probability level. Relevant bond lengths (Å): C1-C2 1.518(4), C1-S1 1.840(3), S1-S2 2.1339(10), S2-S3 2.1184(10), S3-C2 1.850(3), S1-O1 1.477(2), S3-O2 1.480(2).

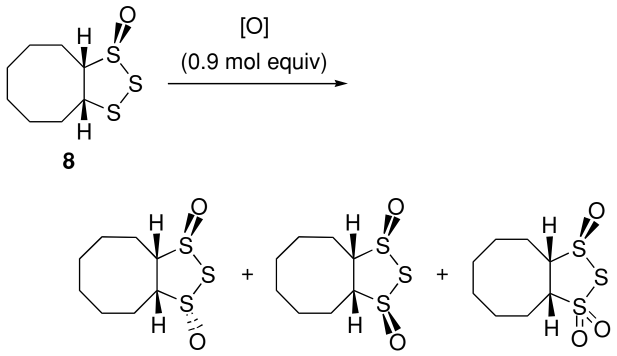
yielded 1-*endo*,3-*exo*-dioxide **10**, 1-*exo*,3-*exo*-dioxide**11**, and trioxide **12** (vide supra) in the ratio of 10:85:5 (Eq. 4). The oxidation with MCPBA (0.9 molar equiv) gave **10** and **11** in the ratio of 30:70. The formation of 1-*exo*,3-*exo*-dioxide **11** proves **8** to be the 1-*exo*-oxide, because **11** is never formed from 1-*endo*-oxide **9** directly.

On the other hand, oxidation of **9** with DMD (0.9 molar equiv.) provided 1-*endo*,3-*exo*-dioxide**10** as the main product together with 1,1,3-trioxide **12**. Interestingly, the oxidation with MCPBA (0.9 molar equiv.) gave a small amount of the third 1,3-dioxide, assignable to 1-*endo*,3-*endo*-dioxide **13** (Eq. 5), together with **10**. The two methine protons of dioxide **13** appeared equivalently at $\delta = 4.02$–4.08 in the ^{1}H NMR spectrum. Though we have not succeeded in the isolation of **13**, the



8 **9**

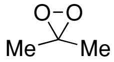
FIGURE 4 Structures of 1-oxides **8** and **9**.



(4)

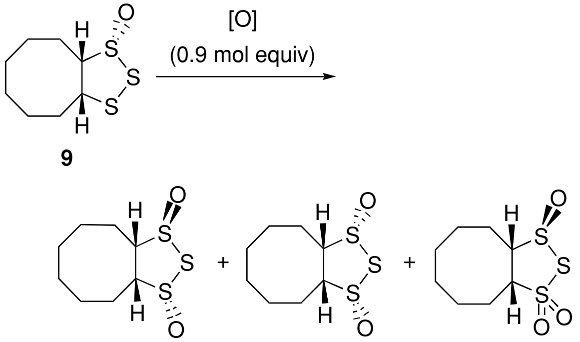
[O]	**10**	**11**	**12**
DMD	10%	85%	5%
MCPBA	30%	70%	0%

(^{1}H NMR integral ratios)

DMD =


EQ 4

formation of 1-*endo*,3-*endo*-dioxide**13** indicates that 1-oxide **9** is the 1-*endo*-oxide. In the oxidations of 1-oxides **8** and **9**, DMD and MCPBA attacked from the *exo* side of the eight-membered ring more preferentially than the *endo* side, probably because of the steric hindrance of the carbocyclic part.



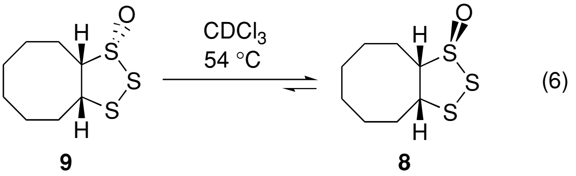
(5)

[O]	**10**	**13**	**12**
DMD	84%	0%	16%
MCPBA	90%	10%	0%

(^{1}H NMR integral ratios)

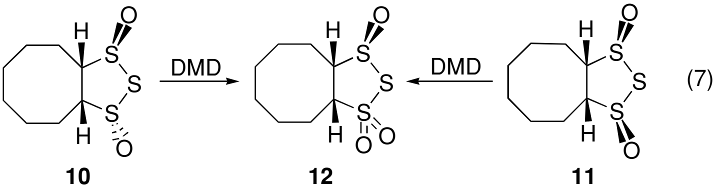
EQ 5

1-*exo*-Oxide **8** is thermodynamically more stable than 1-*endo*-oxide **9**. Heating a solution of **9** in $CDCl_3$ at 54°C for 25 h led to the isomerization to **8** by 88%, while heating **8** under the same conditions gave an 86:14 mixture of **8** and **9** (Eq. 6). Similar isomerization was observed in the 1-oxides of trithiolane **2**.[6]



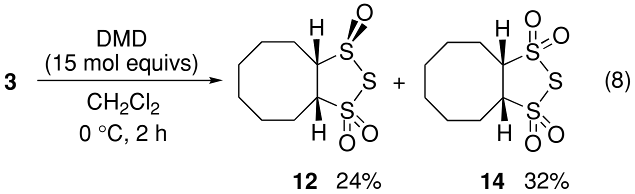
EQ 6

Trioxide **12** was also obtained in high yields by oxidations of 1,3-dioxides **10** and **11** (Eq. 7). The structure of **12** was verified by X-ray crystallography (Figure 5).



EQ 7

Oxidation of trithiolane **3** with a large excess amount of DMD (15 molar equiv.) in dichloromethane at 0°C for 2 h gave trioxide **12** and tetraoxide **14** in 24% and 32% isolated yields, respectively (Eq. 8). The structure of **14** was finally determined by X-ray crystallography (Figure 6). Compounds **12** and **14** are the first examples of tri- and tetraoxides of 1,2,3-trithiolanes.



EQ 8

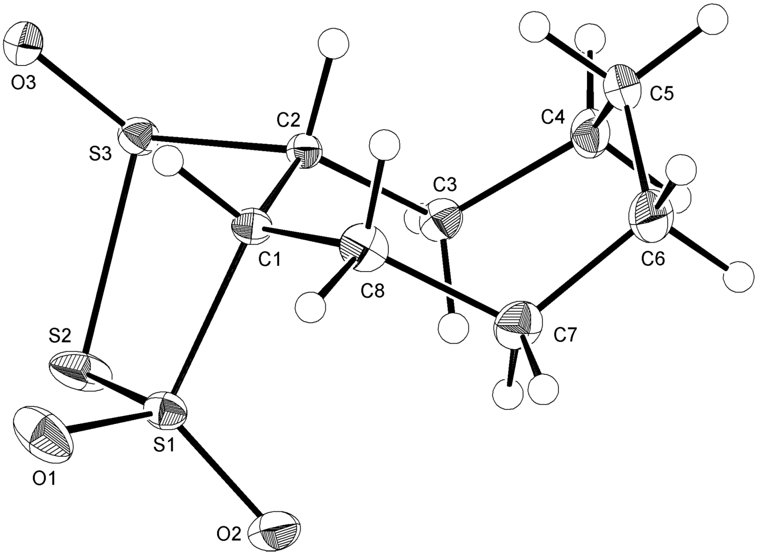
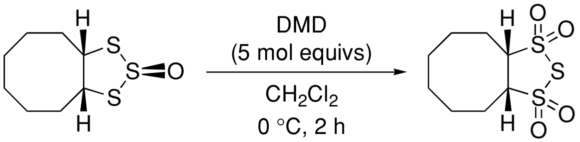


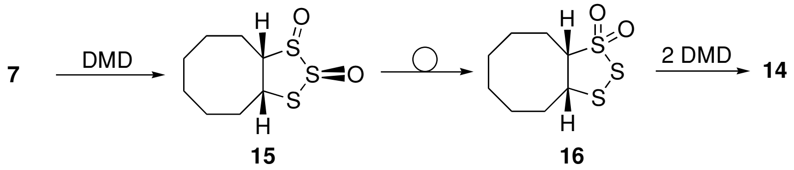
FIGURE 5 ORTEP drawing of trioxide **12** with thermal ellipsoids drawn at 30% probability level. Relevant bond lengths (Å): C1-C2 1.521(3), C1-S1 1.8197(19), S1-S2 2.0867(7), S2-S3 2.1157(7), S3-C2 1.8506(19), S1-O1 1.4315(17), S1-O2 1.4287(16), S3-O3 1.4719(15).

Finally, oxidation of 2-*exo*-oxide **7** was examined. 2-Oxide **7** was treated with DMD (5 molar equiv.) at 0°C to provide tetraoxide **14** in 7% yield as the only assignable compound (Eq. 9). The formation of **14** from **7** should include a migration of the oxygen atom from the 2-position to the 1-position. In a similar way as the well-documented rearrangement of *vic*-disulfoxides (RS(=O)S(=O)R) to thiosulfonates ($RS(O_2)SR$),[10,11] the initially formed 1,2-dioxide **15** would isomerize to 1,1-dioxide **16**, which undergoes further oxidation to give **14** (Scheme 1).



7 **14** 7% (9)

EQ 9



SCHEME 1 A plausible formation mechanism of tetraoxide **14** from 2-*exo*-oxide **7**.

Reduction

Treatment of trithiolane **3** with $LiAlH_4$ in ether gave *cis*-cyclooctane-1,2-dithiol (**17**) in 76% yield (Eq. 10). We also prepared the *trans* isomer **18** by reduction of *trans*-9,10,11-trithiabicyclo[6.3.0]dodecane (**2**)[6] with $LiAlH_4$ (Eq. 11). In the IR spectra, S–H stretching vibrations were observed at 2552 cm^{-1} for **17** and 2557 cm^{-1} for **18**.

Oxidation of *cis*-dithiol **17** was examined in the expectation of obtaining sulfenic acid **19** or bis(sulfenic acid) **20** or their respective

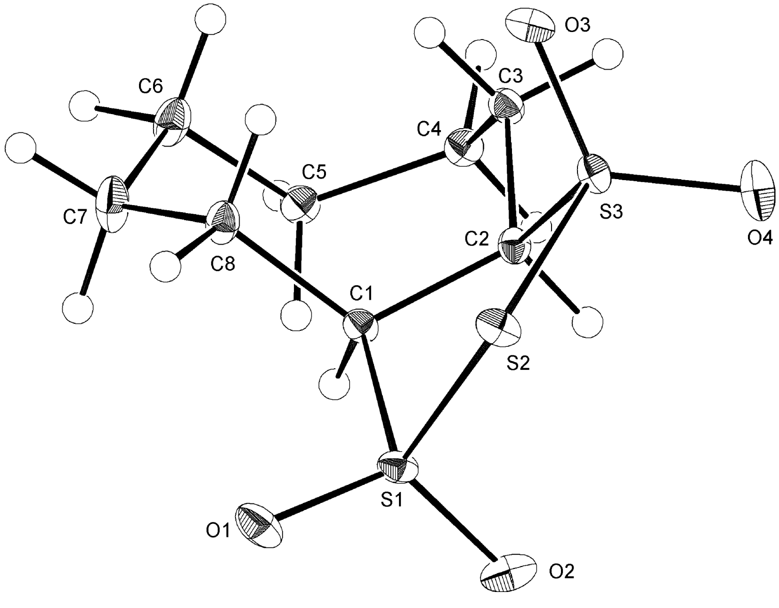
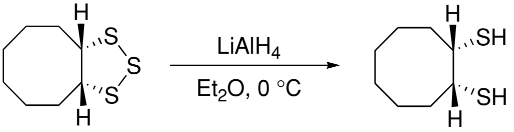


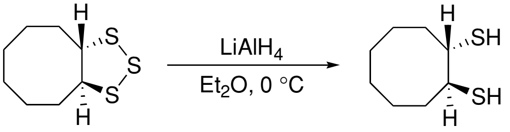
FIGURE 6 ORTEP drawing of tetraoxide **14** with thermal ellipsoids drawn at 30% probability level. Relevant bond lengths (Å): C1-C2 1.527(4), C1-S1 1.804(3), S1-S2 2.0969(2), S2-S3 2.1459(12), S3-C2 1.836(3), S1-O1 1.429(2), S1-O2 1.429(2), S3-O3 1.417(3), S3-O4 1.435(2).



3 **17** 76%

(10)

EQ 10

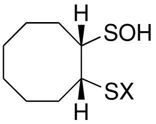


2 **18** 77%

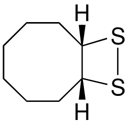
(11)

EQ 11

dehydration products **21** or **22**. However, the oxidation of the sodium salt of **17**, prepared by treatment with NaH, with MCPBA[12] gave tricyclic 1,2,5,6-tetrathiocane **23** in 5% yield as the only identifiable product (Eq. 12). The formation mechanism of **23** is not clear; at present it is not known whether the two sulfur–sulfur bonds were formed by a stepwise mechanism or by dimerization of **21**. The structure of **23** was determined by X-ray crystallography (Figure 7).



19 : X = H
20 : X = OH



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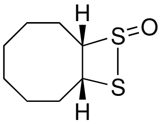
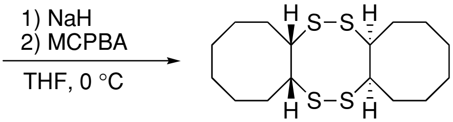


22

17



23 5%

(12)

EQ 12

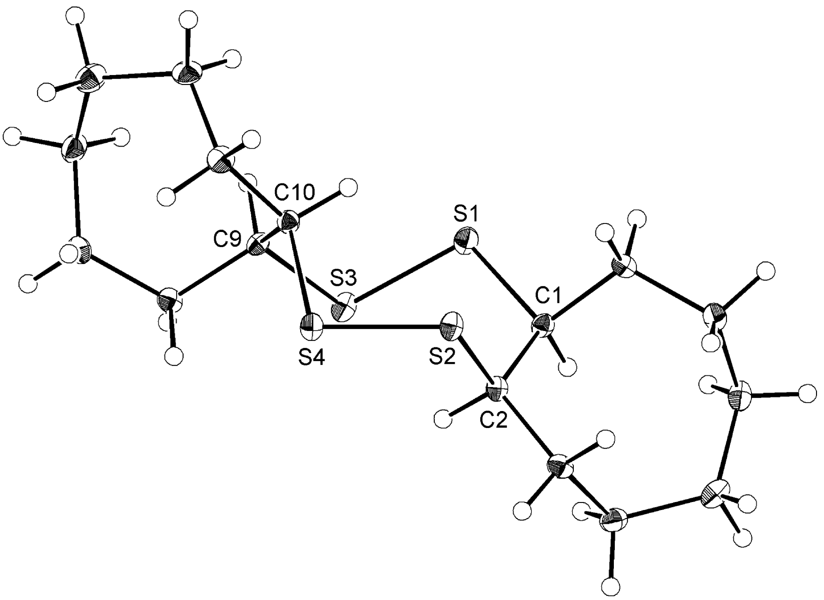


FIGURE 7 ORTEP drawing of **23** (one of two independent structures) with thermal ellipsoids drawn at 30% probability level. Relevant bond lengths (Å): C1-C2 1.526(5), C1-S1 1.849(3), S1-S3 2.0320(13), S3-C9 1.841(3), C9-C10 1.525(5), S4-C10 1.833(4), S2-S4 2.0356(12), S2-C2 1.836(4).

Conformations of Compounds 7, 10, 11, 12, 14, and 23 in the Crystal

Eight-membered rings in **7**,**10**,**11**,**12**, and **14** take a boat-chair conformation, which is one of most stable families of conformations of cyclooctane.[13] They can be classified into two groups, the group of **7**, **10**, and **14** and the group of **11** and **12**, based on the similarity of the conformation including the 1,2,3-trithiolane ring.

In the boat-chair conformation of 2-*exo*-oxide **7** (Figure 1), C(3) possesses the beak position and C(6)-C(7)-C(8) form the leg of the chair. The five-membered ring attaches to the base of the boat part [C(1)-C(2)] and takes a slightly distorted envelope conformation [C(2)-C(1)-S(1)-S(2) 14.0°]. Similarly, in 1-*endo*,3-*exo*-dioxide **10** (Figure 2) and tetraoxide **14** (Figure 6), the beak is C(3) and the leg of the chair is C(6)-C(7)-C(8). The five-membered rings in **10** and **14** attach to the base of the boat [C(1)-C(2)] and take an envelope conformation [S(1)-S(2)-S(3)-C(2) 4.6° for **10** and 5.5° for **14**].

On the other hand, 1-*exo*,3-*exo*-dioxide **11** (Figure 3) takes a boat-chair conformation with C(6) as the beak position and C(1)-C(2)-C(3) as the leg of the chair. The five-membered ring attaches to the leg of the chair [C(1)-C(2)] and adopts an envelope conformation [S(1)-S(2)-S(3)-C(2) 8.8°]. 1,1,3-*exo*-Trioxide **12** (Figure 5) takes a conformation similar to that of **11** [the beak position C(5); the leg of the chair C(2)-C(1)-C(8); C(1)-S(1)-S(2)-S(3) 4.4°].

In dimer **23** (Figure 7), the two cyclooctane and the 1,2,5,6-tetrathiocane rings take boat-chair and twist-boat-chair conformations, respectively. The 1,2,5,6-tetrathiocane ring attaches to the bow of the cyclooctene rings.

CONCLUSION

We synthesized *cis*-9,10,11-trithiabicyclo[6.3.0]undecane (1,2,3-trithiolane **3**) by the reaction of *cis*-cyclooctene (*cis*-**1**) with S_8O in refluxing carbon disulfide. Oxidation reactions of 1,2,3-trithiolane **3** with MCPBA or DMD were investigated in detail, and 1-oxides **8** and **9**, 2-oxides **6** and **7**, 1,3-dioxides **10** and **11**, 1,1,3-trioxide **12**, and 1,1,3,3-tetraoxide **14** were isolated and fully characterized. The other 1,3-dioxide assignable to 1-*endo*,3-*endo*-dioxide **13** was observed in the oxidation of **9** with MCPBA. The oxidation of 2-*exo*-oxide **7** with DMD gave tetraoxide **14** in low yield. Compounds **12** and **14** are the first examples as tri- and tetraoxides, respectively, of 1,2,3-trithiolanes. The bicyclic system involving a cyclooctane ring would contribute to the stability of the oxides.

Reduction of **3** and its *trans* isomer **2** with $LiAlH_4$ gave *cis*- (**17**) and *trans*-cyclooctane-1,2-dithiol (**18**), respectively. Oxidation of the sodium salt of **17** with MCPBA provided tetrathiocane **23** in a low yield. Two new 1,2-dithiols **17** and **18** have a potential to serve as bidentate ligands for transition metals, and we are developing the potential.

EXPERIMENTAL

General

The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on Bruker AM400 or DRX400 (400 and 100.7 MHz, respectively) spectrometers using $CDCl_3$ as the solvent at 25°C, unless otherwise noted. IR spectra were taken on a Perkin Elmer System 2000 FT-IR spectrometer. Mass spectra were determined on a JEOL JMS-700AM spectrometer operating at 70 eV in the EI mode. Elemental analysis was performed by the Chemical Analysis Center of Saitama University. Column chromatography was carried out with silica gel (70–230 mesh), and high-pressure liquid chromatography (HPLC) with a packed SiO_2 column (INERTSIL PREP-SIL: 10 mm i.d. or 20 mm i.d., GL Science Inc.); the eluent is shown in parentheses. Gel permeation chromatography (GPC) was done on a Japan Analytical Industry LC-908. S_8O was prepared by oxidation of S_8 with trifluoroperacetic acid in dichloromethane.[5] An acetone solution of dimethyldioxirane (DMD) was prepared by oxidation of acetone with Oxone® (Sigma-Aldrich).[14] X-ray crystallographic analyses were performed with a Mac Science DIP3000 diffractometer (for **7**) or a Bruker AXS SMART diffractometer (for others) with a graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å).

Reaction of *cis*-Cyclooctene (*cis*-1) with S_8O

A mixture of *cis*-cyclooctene (411 mg, 3.73 mmol) and S_8O (501 mg, 1.84 mmol) in carbon disulfide (7 mL) was heated under reflux for 1 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (hexane:dichloromethane 5:1) and then HPLC (hexane:dichloromethane 85:15) to give pentathiepane **5** (7.2 mg, 1%), trithiolane **3** (37.6 mg, 10%), and episulfide **4**[3a] (0.7 mg, 0.3%) in this order.

cis-9,10,11-Trithiabicyclo[6.3.0]undecane (Trithiolane 3)

Yellow oil. ^{1}H NMR: δ = 1.48–1.62 (m, 6H), 1.73–1.80 (m, 2H), 1.86–2.01 (m, 4H), 3.64–3.70 (m, 2H); ^{13}C NMR: δ = 25.4, 28.0, 29.8, 62.6; MS *m/z* 206 (M^+). HRMS: Calcd for $C_8H_{14}S_3$: *M* 206.0258; Found: *m/z* 206.0258.

cis-9,10,11,12,13-Pentathiabicyclo[6.5.0]tridecane (Pentathiepane 5)

Yellow oil. ^{1}H NMR: δ = 1.53–1.62 (m, 6H), 1.75–1.80 (m, 2H), 1.92–1.97 (m, 4H), 3.94–4.00 (m, 2H); ^{13}C NMR: δ 26.0, 26.4, 31.6, 63.6; MS m/*z*270 (M^+). HRMS: Calcd for $C_8H_{14}S_5$: *M* 269.9669; Found: *m/z* 269.9704.

Oxidation of Trithiolane 3

MCPBA (1 molar equiv): To a solution of trithiolane **3** (41.5 mg, 0.20 mmol) in dichloromethane (1 mL) cooled at 0°C, a solution of MCPBA (88.6%, 39.2 mg, 0.20 mmol) in dichloromethane (2.5 mL) was added dropwise. The mixture was stirred for 2 h at 0°C, and then quenched by the addition of aq. Na_2SO_3 and then aq. $NaHCO_3$. The mixture was extracted with dichloromethane, and the extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The mixture was subjected to column chromatography (dichloromethane) to give **3** (5.2 mg, 13%), a mixture of 2-oxides (**6** and **7**), a mixture of 1-oxides (**8** and **9**), and 1-*endo*,3-*exo*-dioxide **10** (2.8 mg, 6%) in this order. The mixture of 2-oxides **6** and **7** was separated with HPLC (hexane:diethyl ether 3:1) to give 2-*endo*-oxide **6** (1.4 mg, 3%) and 2-*exo*-oxide **7** (5.1 mg, 12%). The mixture of 1-oxides **8** and **9** was separated with HPLC (hexane:diethyl ether 2:1) to give 1-*exo*-oxide **8** (11.7 mg, 27%) and 1-*endo*-oxide **9** (1.2 mg, 3%) as yellow solids.

MCPBA (2 molar equivs): To a solution of trithiolane **3** (54.6 mg, 0.26 mmol) in dichloromethane (4 mL) at 0°C under argon, MCPBA (89%, 106.5 mg, 0.55 mmol) was added, and the mixture was stirred for 3 h at 0°C. The reaction was quenched by the addition of aqueous Na_2SO_3 and then $NaHCO_3$. The mixture was extracted with dichloromethane, and the extract was washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the residue exhibited the formation of **10** and **11** in a ratio of 67:33. The residue was subjected to column chromatography (dichloromethane:diethyl ether 20:1) to give 11.4 mg (18%) of **10**. 1-*exo*,3-*exo*-Dioxide **11** decomposed on silica gel.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 10-*endo*-oxide (2-*endo*-Oxide 6)*

Colorless oil. ^{1}H NMR: δ = 1.54–1.70 (m, 6H), 1.84–1.92 (m, 2H), 2.17–2.25 (m, 2H), 2.46–2.56 (m, 2H), 4.48–4.54 (m, 2H); ^{13}C NMR: δ = 25.5, 27.9, 29.1, 69.6. IR (neat) 1105 (SO) cm^{-1}; MS *m/z* 222 (M^+). HRMS: Calcd for $C_8H_{14}OS_3$: *M* 222.0207. Found: *m/z* 222.0205.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 10-*exo*-oxide (2-*exo*-Oxide 7)*

Colorless prisms, mp 62–64°C dec. (hexane-dichloromethane). ^{1}H NMR: δ = 1.64 (br s, 6H), 1.81–1.88 (m, 2H), 1.98–2.04 (m, 2H), 2.14–2.24 (m, 2H), 4.80–4.85 (m, 2H); ^{13}C NMR: δ = 25.6 (CH_2), 28.0 (CH_2), 28.2 (CH_2), 64.8 (CH); IR (KBr) 1104 (SO) cm^{-1}; MS *m/z* 222 (M^+). Anal. Calcd for $C_3H_{14}OS_3$: C, 43.20; H, 6.35. Found: C, 43.44; H, 6.32%. *Crystallographic data*: $C_8H_{14}OS_3$, $M_r = 222.39$, colorless prism, 0.30 × 0.26 × 0.20 mm^3, monoclinic, $P2_1/c$, $a = 12.5710(6)$, $b = 7.1230(3)$, $c = 12.7620(7)$ Å, $\beta = 113.048(3)^\circ$, $V = 1051.53(9)$ Å^3, $p_{\text{calcd}} = 1.405$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K\alpha) = 0.658$ cm^{-1}. Intensity data of 2216 unique reflections were collected in the range of $-16 \leq h \leq 16$, $-9 \leq k \leq 8$, $-16 \leq l \leq 16$ at 298 K. $R_1 = 0.0351$ ($I \geq 2\sigma I$, 1942 reflections), w$R_2 = 0.0982$ (for all), and GOF = 1.050, 110 parameters; max/min residual electron density = 0.185/−0.271 e Å^{-3}.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 9*-exo-*oxide (1*-exo-*Oxide 8)*

Yellow needles, mp 63–64°C dec.(hexane-dichloromethane); ^{1}H NMR: δ = 1.40–1.91 (m, 10H), 2.12–2.30 (m, 2H), 4.00 (ddd, J = 8.0, 4.6, 1.3 Hz, 1H), 4.70 (td, J = 10.0, 4.5 Hz, 1H); ^{13}C NMR: δ = 22.6, 24.0, 25.2, 25.8, 26.1, 28.4, 59.4, 80.6; IR (KBr) 1094 (SO) cm^{-1}. Anal. Calcd for $C_8H_{14}OS_3$: C, 43.20; H, 6.35. Found: C, 43.21; H, 6.29%.

cis-*9,10,11-Trithiabicyclo[6.3.0]dodecane 9*-endo-*oxide (1*-endo-*Oxide 9)*

^{1}H NMR: δ = 1.40–1.64 (m, 6H), 1.71–1.99 (m, 3H), 2.03–2.10 (m, 1H), 2.18–2.29 (m, 1H), 2.42–2.48 (m, 1H), 3.54–3.59 (m, 1H), 3.93–3.98 (m, 1H); ^{13}C NMR: δ = 20.4 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 60.9 (CH), 79.3 (CH); IR (KBr) 1087 (SO) cm^{-1}; MS *m/z* 222 (M^+). HRMS: Calcd for $C_8H_{14}OS_3$: *M*, 222.0206. Found: *m/z* 222.0212.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 9*-endo,*11*-exo-*Dioxide (1*-endo,*3*-exo-*Dioxide 10)*

Colorless prisms, mp 104–106°C dec. (hexane-dichloromethane). ^{1}H NMR: δ = 1.61–1.89 (m, 8H), 2.11–2.28 (m, 2H), 2.50–2.57 (m, 2H), 4.35–4.40 (m, 1H), 4.65 (ddd, J = 9.9, 3.6, 2.6 Hz, 1H); ^{13}C NMR: δ= 22.9, 23.5, 24.6, 25.5, 27.4, 28.1, 75.4, 83.3; IR (KBr) 1078 (SO) cm^{-1}. Anal. Calcd for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92. Found: C, 40.18; H, 5.85%. *Crystallographic data*: $C_8H_{14}O_2S_3$, M = 238.37, colorless prism, 0.50 × 0.20 × 0.08 mm^3, monoclinic, $P2_1/c$, a = 12.4672(17), b = 7.5385(10), c = 11.4848(16) Å, β = 100.962(3)°, V = 1059.7(2) Å^3, p_{calcd} = 1.494 g cm^{-3}, Z = 4, μ(Mo-$K\alpha$) = 0.665 cm^{-1}. Intensity data of 1908 unique reflections were collected in the range of $-14 \leq h \leq 9$, $-9 \leq k \leq 7$, $-13 \leq l \leq 13$ at 103 K. $R_1 = 0.0408$ ($I \geq 2\sigma I$, 1705 reflections), wR_2 = 0.0979 (for all), and GOOF = 1.071, 118 parameters; max/min residual electron density = 0.562/−0.252 e Å^{-3}.

Oxidation of *exo*-1-Oxide 8

Isolation of 1-*exo*,3-*exo*-dioxide 11: To a solution of 1-*exo*-oxide **8** (21.6 mg, 0.097 mmol) in dichloromethane (1 mL) at 0°C under argon, DMD (0.100 M, 0.87 mL, 0.087 mmol) was added, and the mixture was stirred for 2 h at 0°C. The solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the residue indicated the formation of dioxide **10** and **11**, and the ratio of **8**:**10**:**11** was 10:9:81. The residue was recrystallized from a mixed solvent of hexane and dichloromethane to give 16.2 mg (70%) of pure **11**.

Determination of the yields: To a solution of **8** (16.0 mg, 0.072 mmol) in dichloromethane (1 mL) at 0°C under argon, DMD (0.077 M, 0.83 mL, 0.064 mmol) was added. The mixture was stirred for 2 h at 0°C, and the solvent was removed under reduced pressure. A ^{1}H NMR spectrum of the residue was obtained in the presence of 11.3 mg (0.062 mmol) of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene as the internal standard. Based on the integral ratio, the amounts of 1-*endo*-3-*exo*-dioxide **10**, 1-*exo*-3-*exo*-dioxide **11**, and 1,1,3-trioxide **12** were determined to be 0.0063 mmol (9%), 0.0056 mmol (78%), and 0.0035 mmol (5%), respectively.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 9*-exo*,11*-exo*-dioxide (1*-exo*,3*-exo*-Dioxide 11)*

Colorless crystals, mp 118–121°C dec. (hexane-dichloromethane). ^{1}H NMR: δ = 1.66–1.72 (m, 6H), 1.86–1.98 (m, 4H), 2.08–2.15 (m, 2H), 4.68–4.72 (m, 2H); ^{13}C NMR: δ = 24.1 (CH_2), 24.6 (CH_2), 26.5 (CH_2), 82.0 (CH); IR (KBr) 1067, 1098 (SO) cm^{-1}. Anal. Calcd for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92. Found: C, 40.38; H, 5.88%. *Crystallographic data*: $C_8H_{14}O_2S_3$, $M = 238.37$, colorless prism, 0.30 ×0.15 ×0.15 mm^3, monoclinic, $P2_1/n$, $a = 6.7419(13)$, $b = 9.4034(19)$, $c = 15.951(3)$ Å, $\beta = 92.118(4)^\circ$, $V = 1010.6(3)$ Å^3, $\rho_{\text{calcd}} = 1.567$ g cm^{-3}, $Z = 4$, μ(Mo-$K\alpha$) = 0.697 cm^{-1}. Intensity data of 2088 unique reflections were collected in the range of $-7 \leq h \leq 8$, $-11 \leq k \leq 11$, $-20 \leq l \leq 19$ at 123 K. $R_1 = 0.0531$ ($I \geq 2\sigma I$, 1853 reflections), w$R_2 = 0.1499$ (for all), and GOF = 1.033, 118 parameters; max/min residual electron density = 0.746/−0.514 e Å^{-3}.

Oxidation of 1-*endo*-3-*exo*-Dioxide 10

To a solution of **10** (16.9 mg, 0.071 mmol) in dichloromethane (1 mL) at 0°C under argon, DMD (0.0728 M, 0.78 mL, 0.057 mmol) was added. The mixture was stirred for 2 h at 0°C, and the solvent was removed under reduced pressure to give spectroscopically pure trioxide **12** (17.6 mg, 97%).

Oxidation of 1-*exo*-3-*exo*-dioxide 11

To a solution of **11** (16.2 mg, 0.068 mmol) in dichloromethane (1 mL) at 0°C under argon, DMD (0.100 M, 0.68 mL, 0.068 mmol) was added. The mixture was stirred for 2 h at 0°C, and the solvent was removed under reduced pressure to give a 10:90 mixture of **11** and trioxide **12**.

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 9,9,11*-exo-*trioxide (Trioxide 12)*

Colorless crystals, mp 93.5–94°C dec. (hexane-dichloromethane). ^{1}H NMR: $\delta = 1.47$–2.07 (m, 10H), 2.12–2.22 (m, 1H), 2.38–2.44 (m, 1H), 4.03–4.07 (m, 1H), 4.42 (td, $J = 11.5, 4.5$ Hz, 1H); ^{13}C NMR: $\delta = 22.5$, 23.2, 24.0, 25.0, 26.0, 28.4, 69.2, 70.7; IR (KBr) 1306, 1129 (SO_2), 1011 (SO) cm^{-1}. Anal. Calcd for $C_8H_{14}O_3S_3$: C, 37.77; H, 5.55. Found: C, 37.79; H, 5.47%. *Crystallographic data:* $C_8H_{14}O_3S_3$, $M_r = 254.37$, colorless prism, 0.38 ×0.20 ×0.05 mm^3, monoclinic, *C2/c*, $a = 22.3219(13)$ Å, $b = 6.8675(3)$ Å, $c = 14.0637(8)$ Å, $\beta = 94.9930(10)^\circ$, $V = 2147.7(2)$ Å^3, $p_{\text{calcd}} = 1.573$ g cm^{-3}, $Z = 8$, $\mu(\text{Mo-}K\alpha) = 0.668$ cm^{-1}. Intensity data of 1993 unique reflections were collected in the range of $-26 \le h \le 23$, $-8 \le k \le 8$, $-17 \le l \le 14$ at 153 K. $R_1 = 0.0335$ ($I \ge 2\sigma I$, 1812 reflections), w$R_2 = 0.0882$ (for all), and GOF = 1.033, 127 parameters; max/min residual electron density = 0.387/−0.245 e Å^{-3}.

Oxidation of Trithiolane 3 with DMD (15 Molar Equiv.)

DMD (0.085 M, 12.6 mL, 1.1 mmol, 15 molar equiv.) was added to a solution of trithiolane **3** (14.9 mg, 0.072 mmol) in dichloromethane (1 mL) at 0°C under argon. The mixture was stirred for 2 h at 0°C, and the solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the reaction mixture indicated the formation of trioxide **12** and tetraoxide **14** in the ratio of 52:48. The mixture was separated with GPC to give 4.3 mg of trioxide **12** (24%) and 6.2 mg of tetraoxide **14** (32%).

cis-*9,10,11-Trithiabicyclo[6.3.0]undecane 9,9,11,11-tetraoxide (Tetraoxide 14)*

Pale yellow crystals, mp 125–130°C dec. (hexane-dichloromethane). ^{1}H NMR: $\delta = 1.52$–1.76 (m, 6H), 1.98–2.07 (m, 2H), 2.12–2.22 (m, 2H), 2.53–2.59 (m, 2H), 4.38–4.43 (m, 2H); ^{13}C NMR: $\delta = 22.3$, 24.9, 26.8, 76.9; IR (KBr) 1328, 1127 cm^{-1} (SO_2). Anal. Calcd for $C_8H_{14}O_3S_3$: C, 35.54; H, 5.22. Found: C, 35.26; H, 5.11%. *Crystallographic data*: $C_8H_{14}O_4S_3$, $M_r = 270.37$, colorless prism, 0.28 × 0.25 × 0.20 mm^3, monoclinic, $P2_1/n$, $a = 8.7443(5)$, $b = 10.8760(6)$, $c = 12.1024(7)$ Å, $\beta =$

103.7030(10)°, $V = 1118.21(11)$ Å^3, $p_{\text{calcd}} = 1.606$ g cm^{-3}, $Z = 4$, μ(Mo-$K\alpha$) = 0.653 cm^{-1}. Intensity data of 2191 unique reflections were collected in the range of $-10 \leq h \leq 8$, $-13 \leq k \leq 12$, $-14 \leq l \leq 14$ at 103 K. $R_1 = 0.0314$ ($I \geq 2\sigma I$, 2030 reflections), w$R_2 = 0.0824$ (for all), and GOF = 1.031, 136 parameters; max/min residual electron density = 0.631/−0.228 e Å^{-3}.

Oxidation of 2-*exo*-Oxide 7 with DMD (5 Molar Equiv.)

DMD (0.083 M, 5.4 mL, 0.45 mmol, 5 molar equiv.) was added to a solution of 2-*exo*-oxide **7** (20.1 mg, 0.090 mmol) in dichloromethane (1 mL) at 0°C. The mixture was stirred for 2 h at 0°C, and the solvent was removed under reduced pressure. The residue was subjected to GPC to give tetraoxide**14** (1.9 mg, 7%).

Reduction of 1,2,3-Trithiolane 3

$LiAlH_4$ (15.2 mg, 0.40 mmol) was added to a solution of trithiolane **3** (27.6 mg, 0.13 mmol) in ether (5 mL) at 0°C under argon, and the mixture was stirred for 1 h at 0°C. The reaction was quenched with 6M HCl, and the mixture was extracted with ether. The extract was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (hexane:dichloromethane 5:1) to give dithiol **17** (17.4 mg, 76%) as a colorless oil, which was purified by bulb-to-bulb distillation (95°C/8 mm Hg).

cis-*Cyclooctane-1,2-dithiol (17)*

Colorless oil. ^{1}H NMR: δ = 1.50–1.71 (m, 6H), 1.86 (d, J = 7.3 Hz, 2H), 1.92–1.98 (m, 4H), 3.40–3.46 (m, 2H); ^{13}C NMR: δ = 25.5, 27.5, 35.2, 45.0; IR (neat) 2552 (SH) cm^{-1}. Anal. Calcd for $C_8H_{16}S_2$: C, 54.49; H, 9.15. Found: C, 54.67; H, 9.15%.

Reduction of *trans*-9,10,11-Trithiabicyclo[6.3.0]undecane (2)

A suspension of lithium aluminum hydride (40.1 mg, 1.06 mmol) in ether (12 mL) was added dropwise to a solution of **2**[6] (109 mg, 0.53 mmol) in ether (8 mL) at 0°C under argon. The mixture was stirred for 30 min, and the reaction was quenched with 6 M HCl. The mixture was extracted with ether, and the extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to GPC to give the dithiol **18** (71.5 mg, 77%), which was purified by bulb-to-bulb distillation (110°C/7 mmHg).

trans-*Cyclooctane-1,2-dithiol (18)*

Colorless oil. ^{1}H NMR: δ = 1.38–1.57 (m, 4H), 1.66–1.77 (m, 2H), 1.81–1.88 (m, 4H), 2.11–2.20 (m, 4H), 3.09–3.11 (m, 2H); ^{13}C NMR: δ = 26.4 (CH_2), 26.7 (CH_2), 34.2 (CH_2), 50.5 (CH); IR (neat) 2557 (SH) cm^{-1}. Anal. Calcd for $C_8H_{16}S_2$: C, 54.49; H, 9.15. Found: C, 54.45; H, 9.15%.

Oxidation of Sodium Salt of *cis*-Cyclooctane-1,2-dithiol (17)

THF (4 mL) was added to a mixture of **17** (29.3 mg, 0.17 mmol) and sodium hydride (60%, 35 mg, 0.88 mmol) under argon and the mixture was stirred for 1 h at room temperature. A solution of MCPBA (95%, 74.1 mg, 0.41 mmol) in THF (5 mL) was added dropwise, and the mixture was stirred for 2 h at room temperature. Aqueous ammonium chloride was added, and the mixture was extracted with ether. The extract was washed with water, dried, and concentrated under reduced pressure. The residue was subjected to column chromatography (hexane:dichloromethane 4:1) to give 1,2,5,6-tetrathiocane **23** (2.8 mg, 5%).

2,3,12,13-Tetrathia-cis-transoid-cis-*tricyclo[12.6.0.0^{4,11}]icosane (1,2,5,6-Tetrathiocane 23)*

Colorless prisms, mp 135–138°C dec. (hexane-dichloromethane). ^{1}H NMR: δ = 1.50–1.70 (m, 16H), 1.79–1.91 (m, 8H), 3.62–3.66 (m, 4H); ^{13}C NMR: δ = 25.6, 26.7, 31.4, 54.1. MS *m/z* 348 (M^+). HRMS: Calcd for $C_{16}H_{28}S_4$: M_r 348.1074; Found: *m/z* 348.1065.*Crystallographic data:* $C_{16}H_{28}S_4$, $M_r = 348.62$, colorless prism, $0.25 \times 0.20 \times 0.20$ mm^3, monoclinic, $P2_1/c$, $a = 14.3525(11)$ Å, $b = 8.3081(6)$ Å, $c = 29.255(2)$ Å, $\beta = 97.545(2)^\circ$, $V = 3458.3(5)$ Å^3, $p_{\text{calcd}} = 1.339$ g cm^{-3}, $Z = 8$, μ(Mo-$K\alpha$) = 0.539 cm^{-1}. Intensity data of 6068 unique reflections were collected in the range of $-13 \leq h \leq 17$, $-9 \leq k \leq 9$, $-29 \leq l \leq 34$ at 123 K. $R_1 = 0.0556$ ($I \geq 2\sigma I$, 4969 reflections), w$R_2 = 0.1316$ (for all), and GOF = 1.084, 361 parameters; max/min residual electron density = 1.144/−0.289 e Å^{-3}.

CCDC-671572 (**7**), 671573 (**10**), 671574 (**11**), 671575 (**12**), 671576 (**14**), and 671577 (**23**) contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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