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Preparation of a new 1,2,3-trithiolane, *trans*-9,10,11-trithiabicyclo[6.3.0]undecane, and its oxidation reactions

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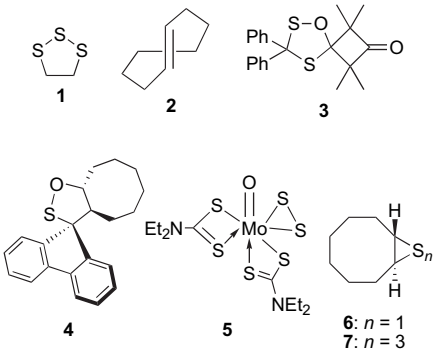
Abstract—The reaction of *trans*-cyclooctene with S_8O yielded a novel bicyclic 1,2,3-trithiolane and *trans*-9,10,11-trithiabicyclo[6.3.0]-undecane (**7**). Oxidation of the trithiolane with dimethyldioxirane yielded three monoxides, which are assigned to two isomeric 9-oxides, *rel*-(1*R*,8*R*,9*S*)-9-oxide (**15**) and *rel*-(1*R*,8*R*,9*R*)-9-oxide (**16**), and 10-oxide (**17**). Further oxidation of *rel*-(1*R*,8*R*,9*S*)-9-oxide (**15**) provided *rel*-(1*R*,8*R*,9*S*,11*S*)-9,11-dioxide (**18**) and *rel*-(1*R*,8*R*,9*R*,11*S*)-9,11-dioxide (**19**), while that of *rel*-(1*R*,8*R*,9*R*)-9-oxide (**16**) gave *rel*-(1*R*,8*R*,9*R*,11*S*)-9,11-dioxide (**19**) and *rel*-(1*R*,8*R*,9*R*,11*R*)-9,11-dioxide (**20**). The structures of **18** and **19** were determined by X-ray crystallography. The structures of other oxides were elucidated by the spectroscopic data and results of further chemical transformations. Two isomers, **15** and **16**, isomerized to one another. A 9,11-dioxide **20** isomerized to **19**, which is in equilibrium with **18**, where **18** is thermodynamically the most stable isomer.

1. Introduction

1,2,3-Trithiolane **1** is the trithio analog of molozonide, and several derivatives, including their oxides, have been reported so far.[1,2] Most of the derivatives were prepared by reaction of alkenes with sulfur allotropes under vigorous[3–12] or mild[13–15] conditions, and a few were obtained by dimerization of a thioketone *S*-oxide,[16] by reaction of 1,2-dithiols and their equivalents with sulfurating reagents,[17–19] or by reduction of a pentathiane followed by air oxidation.[20] On the other hand, oxidations of acyclic and cyclic di-,[21] tri-,[22] tetra-,[23] and higher polysulfanes[24,25] have attracted considerable attention from the viewpoints of regiochemistry, stereochemistry, stability, and reactivities of the oxides formed. We have been studying the synthesis and oxidation of cyclic di-, tetra-, and pentasulfanes.[24,25] *trans*-Cyclooctene (**2**) has high reactivity toward sulfurating reagents. Adam and his co-workers have reported that the reactions of **2** with **3**–**5** gave the corresponding *trans*-episulfide **6** in high yields.[26–30] In relation to our study on S_8O as an S_2O equivalent,[31] we examined the reaction of **2** with S_8O,[32] and found the formation of a novel 1,2,3-trithiolane derivative **7** together with **6**.



Concerning oxides of 1,2,3-trithiolanes, a limited number of 1- and 2-oxides[17,19,33,34] and 1,1-dioxides[16,34] have been reported. Ghosh and Bartlett reported on oxidation of trithiolane **8** with MCPBA giving *endo*- and *exo*-1-oxides and *endo*-2-oxide, and with ozone giving *endo*- and *exo*-2-oxides.[17] Oxidation of **9** with MCPBA yielded *endo*- and *exo*-3-oxides.[17] Satoh and Sato reported that oxidation of **10** with MCPBA gave 1-oxide **11**, while that with NCS or NBS provided 1,1-dioxide **12** through **11**.[34] Further oxidation of **11** with MCPBA gave disulfinic acid **13**, where intervention of 1,3-dioxide **14** was proposed.[34] In this paper we report on the preparation of a novel 1,2,3-trithiolane **7** and its oxidation giving three monoxides and three 1,3-dioxides together with isomerization between them.

Keywords: Trithiolane; Cyclooctene; Octasulfur monoxide; Oxidation; Isomerization.
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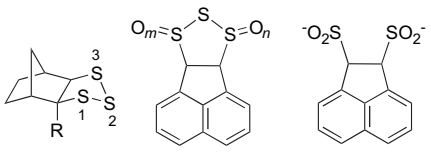
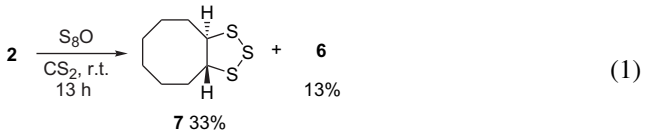


2. Results and discussion

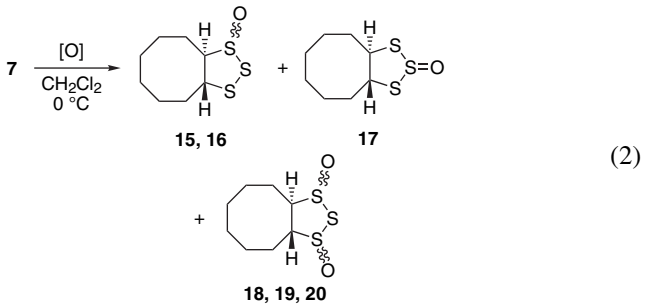
trans-Cyclooctene (**2**)[35] was treated with S_8O[32] in CS_2 at room temperature. After chromatographic purification, we isolated *trans*-9,10,11-trithiabicyclo[6.3.0]undecane **7**, a 1,2,3-trithiolane, as a yellow oil in 33% yield together with *trans*-episulfide **6** in 13% yield (Eq. 1).



(1)

The ^{13}C NMR spectrum of **7** showed four signals due to sp^3 carbons at δ 24.6 (CH_2), 26.5 (CH_2), 34.8 (CH_2), and 63.5 (CH), and the ^1H NMR spectrum exhibited two methine protons at δ 3.78–3.84 as a multiplet. As we could not determine the stereochemistry of **7**, whether cis or trans, with these NMR data, we examined derivation of **7** into its oxides to make the structure unsymmetrical for observing the vicinal coupling constant between the methine protons.

Trithiolane **7** was treated with an acetone solution of dimethyldioxirane (DMD)[37,38] (1 equiv) in dichloromethane at 0 °C to give two 9-oxides **15** (16%) and **16** (33%), 10-oxide **17** (15%), and two 9,10-dioxides **18** (8%) with recovery of **7** (9%) (Eq. 2; Table 1, entry 1). When 2 equiv of DMD were used, 9,10-dioxides **18**, **19**, and **20** were formed in the ratio of 21:64:10 with the recovery of **7** (based on ^1H NMR integral ratio) (entry 2). Oxidation of **7** with MCPBA (1 equiv) provided a similar set of products. Except **20**, all the oxides were isolated.



(2)

2.1. Structure determination of the oxides of 7

While monoxides **15**–**17** were oily materials, we could obtain single crystals of dioxides **18** and **19** suitable for X-ray crystallography. The ORTEP drawings of **18** and **19** are depicted in Figures 1 and 2, respectively. The

Table 1. Yields of products in oxidation of trithiolane **7**

Entry	Oxidant (equiv)	Yields (%)						
		15	**16**	**17**	**18**	**19**	**20**	**7**
1	DMD[a] (1)	16	33	15	8	0	0	9
2	DMD[a] (2)	0	0	0	21[b]	64[b]	10[b]	5[b]
3	MCPBA (1)	20	53	7	4	[c]	0	0

[a] Dimethyldioxirane.
[b] ^1H NMR integral ratio.
[c] A small amount of **19** was detected by ^1H NMR.

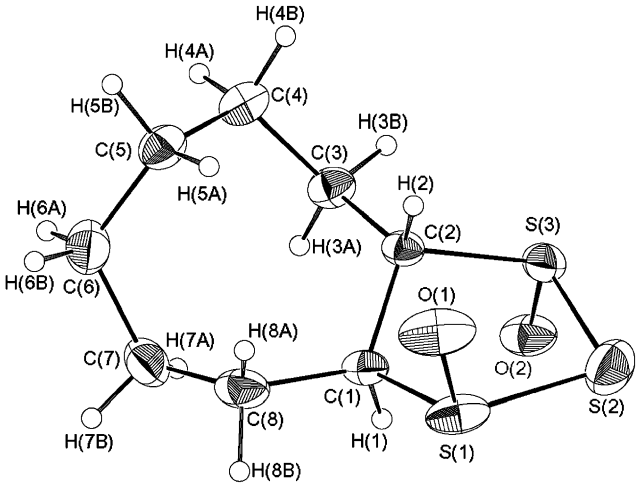


Figure 1. ORTEP drawing of *rel*-(1*R*,8*R*,9*S*,11*S*)-9,10,11-trithiabicyclo[6.3.0]undecane 9,11-dioxide (**18**) (30% ellipsoidal probability). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1–O1 1.482(2); S1–C1 1.833(3); S1–S2 2.1249(16); S2–S3 2.1259(14); S3–O2 1.473(2); S3–C2 1.832(3); C1–C2 1.524(4); C1–S1–S2 93.58(10); S1–S2–S3 101.13(5); C2–S3–S2 94.09(10); C2–C1–S1 108.0(2); C1–C2–S3 107.29(18); H1–C1–C2–H2 −157(3); S3–C2–C1–S1 68.3(2); S1–S2–S3–C2 14.07(9); C1–S1–S2–S3 14.74(10); O1–S1–C1–C2 62.7(2); O2–S3–C2–C1 62.8(2).

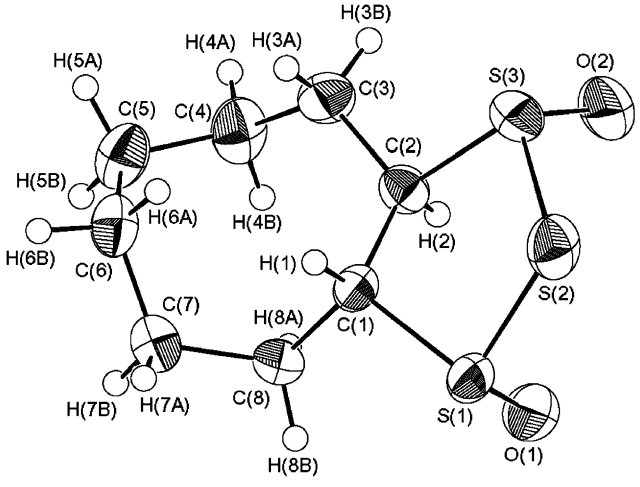
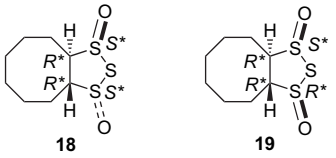


Figure 2. ORTEP drawing of *rel*-(1*R*,8*R*,9*R*,11*S*)-9,10,11-trithiabicyclo[6.3.0]undecane 9,11-dioxide (**19**) (30% ellipsoidal probability). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S1–O1 1.487(5); S1–C1 1.837(5); S1–S2 2.110(2); S2–S3 2.118(2); S3–O2 1.487(5); S3–C2 1.846(6); C1–C2 1.520(7); C1–S1–S2 92.49(19); S1–S2–S3 99.57(8); C2–S3–S2 96.12(18); C2–C1–S1 108.3(4); C1–C2–S3 114.8(4); H1–C1–C2–H2 −172.9(7); S3–C2–C1–S1 −51.0(3); S1–S2–S3–C2 15.4(2); C1–S1–S2–S3 −37.1(2); O1–S1–C1–C2 −58.8(4); O2–S3–C2–C1 129.9(4).

conjunction of the two rings in **18** and **19** was trans, and their relative stereochemistries including the configuration of the S═O groups were determined to be *rel*-(1*R*,8*R*,9*S*,11*S*)-9,11-dioxide and *rel*-(1*R*,8*R*,9*R*,11*S*)-9,11-dioxide, respectively. Of necessity, the stereochemistry of **7** was determined to be trans, showing that the stereochemistry of the starting *trans*-alkene was retained.

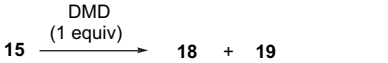


In the crystal, the trithiolane ring of **18** took a half-chair conformation, and the eight-membered ring took a boat–chair conformation, which is one of the most stable family of conformations of cyclooctane.[39] Each of the two oxygen atoms in **18** possessed the axial position and was trans to the vicinal hydrogen atom [O(1)–S(1)–C(1)–H(1) 178(2)°, O(2)–S(3)–C(2)–H(2) 177(2)°]. The ^{13}C NMR spectrum, measured at room temperature, showed only four signals due to sp^3 carbons, indicating that **18** has a symmetric structure in the NMR time scale in solution. In the ^{1}H NMR spectrum, H(1) and H(2) appeared at δ 4.23–4.25 as a multiplet.

In the case of dioxide **19**, the trithiolane and the cyclooctane rings took conformations similar to those of **18**. One of the two oxygen atoms [O(1)] possessed the axial position and the other [O(2)] possessed the equatorial one in the crystal, where the former is trans to the vicinal hydrogen [O(1)–S(1)–C(1)–H(1) 179.0(5)°] and the latter was cis to the vicinal hydrogen [O(2)–S(3)–C(2)–H(2) 9.9(4)°]. In the ^{1}H NMR spectrum, two methine protons resonated at δ 3.57 and 4.82 with the vicinal coupling constant of 12.0 Hz, indicating that the hydrogen atoms take a trans conformation also in solution.

The structure of 10-oxide **17** was elucidated as follows. In the ^{13}C NMR spectrum, all carbons were nonequivalent with each other and in the ^{1}H NMR spectrum the vicinal coupling constant between the methine protons (δ 4.19 and 4.60) was 11.3 Hz. Unlike the cases of **15** and **16** as discussed below, oxidation of **17** with DMD gave a mixture of unidentified compounds and not dioxides **18** or **19**, which indicates that **17** is not a 9-oxide but a 10-oxide of **7**.

^{1}H and ^{13}C NMR spectroscopies of **15** and **16** showed that all of their protons and carbons were nonequivalent. Oxidation reactions of **15** and **16** were investigated to obtain further information on regio- and stereochemistries of their S═O groups. When **15** was oxidized with DMD at 0 °C, dioxides **18** (43%) and **19** (47%) were formed (Eq. 3). On the other hand, oxidation of **16** yielded another dioxide **20** (54%) and **19** (35%) together with a small amount of **18** (2%) (Eq. 4). The formation of a small amount of **18** seems to be due to isomerization of **19** as described later. The ^{13}C NMR spectrum of the mixture of **19** and **20** (with a small amount of **18**), measured at −20 °C, showed only four sp^3 carbon signals due to **20** at δ 23.3, 25.5, 27.9, and 75.8. The methine protons of **20** were observed at δ 3.72–3.80 as a multiplet. Thus, dioxide **20** has a symmetric structure in the NMR time scale, and the structure was assigned to be *rel*-(1*R*,8*R*,9*R*,11*R*)-9,11-dioxide **20**.



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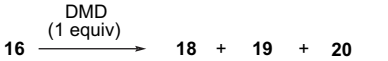

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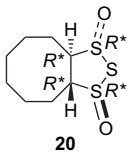
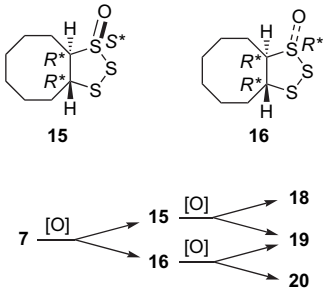


Three possible stereoisomers of 9,11-dioxides (**18**–**20**) were thus obtained and their structures were clearly determined. Based on the results of Eqs. 3 and 4, the structures of monoxides **15** and **16** are assigned to be *rel*-(1*R*,8*R*,9*S*)-9-oxide and *rel*-(1*R*,8*R*,9*R*)-9-oxide, respectively. As summarized in Scheme 1, oxidation of trithiolane **7** and 9-oxides **15** and **16** proceeded without stereoselectivity to give two possible stereoisomers, **15** and **16**, **18** and **19**, and **19** and **20**, respectively. Table 2 summarizes NMR data of the methine protons and carbons of **7** and its oxides, **15**–**20**.



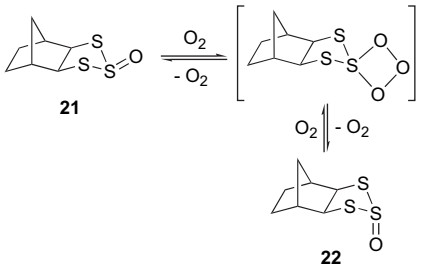
Scheme 1.

Table 2. NMR data of methine protons and methine carbons of **7** and **15**–**20**

	Methine protons (δ)	Methine carbons (δ)
7	3.78–3.84 (m)	63.5
15	3.39–3.44 (m), 3.92–3.98 (m)	57.2, 79.9
16	3.48–3.54 (m), 3.64–3.69 (m)	60.2, 86.6
17	4.19 (ddd), 4.60 (ddd) (J_{vic}=11.3 Hz)	60.8, 70.2
18	4.23–4.25 (m)	73.4
19	3.57 (ddd), 4.82 (ddd) (J_{vic}=12.0 Hz)	73.9, 81.2
20	3.72–3.80 (m)	75.8

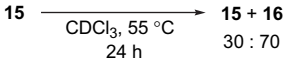
2.2. Isomerization

We observed mutual isomerization between monoxides **15** and **16**. When a solution of **15** in $CDCl_3$ was warmed at 55 °C, **16** appeared gradually and the ratio of **15** and **16** reached 30:70 after 24 h (Eq. 5). Similarly, a solution of pure **16** became a 29:71 mixture of **15** and **16** under same conditions (Eq. 6). Ghosh and Bartlett reported that mutual

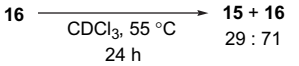


Scheme 2.

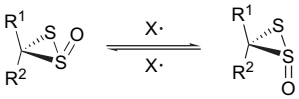
isomerization between **21** and **22** (2-oxides of **8**) took place not under argon but under O_2, and they proposed the adduct of **21** with $^3O_2$ as the intermediate (Scheme 2).[17] In contrast, the isomerization between **15** and **16** was not influenced by the presence or the absence of air. When 1,1-diphenyl-2-picryl hydrazyl (DPPH) was added to a solution of **15** or **16**, the isomerization was accelerated and the equilibrium was attained in 19 h. This acceleration by a radical scavenger was in quite contrast to our previous observations of remarkable retardation by DPPH in the epimerization of dithiirane 1-oxides (Eq. 7), where we proposed that a radical contaminant (X•) caused the epimerization.[40,41] In the present case, DPPH itself might act as a radical catalyst.



(5)

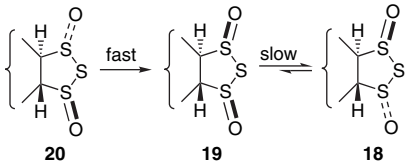


(6)



(7)

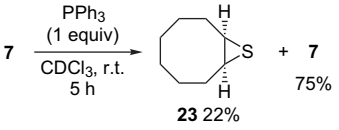
9,11-Dioxides **19** and **20** isomerized to **18**. When a solution of a mixture of **18** (2%), **19** (35%), and **20** (54%) in $CDCl_3$, obtained in Eq. 4, was stood at room temperature for one day, **20** disappeared completely and the amounts of **18** (24%) and **19** (59%) increased. After four days, **18** became the major component (69%) and **19** became the minor one (16%). These observations indicate that the isomerization of **20** to **18** takes place stepwise through **19** and that isomerization of **20** to **19** is faster than that of **19** to **18** (Scheme 3). The thermodynamic instability of **19** and **20** compared with **18** would be due to the repulsion between the oxygen atom(s) with the vicinal hydrogen atom.



Scheme 3. Isomerization of **20** to **18** through **19**.

2.3. Desulfuration of 7

Desulfuration of **7** was examined in expectation of the formation of the corresponding 1,2-dithietane.[42,43] Trithiolane **7** was treated with triphenylphosphine (1 equiv) in $CDCl_3$ at room temperature to give *cis*-episulfide **23**[26] (22%) with recovery of **7** (75%) (Eq. 7). Compound **23** would be formed by an intramolecular S_N2 reaction as shown in Scheme 4.



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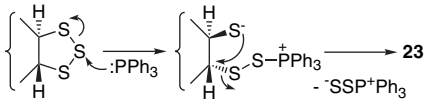

Scheme 4.

3. Conclusion

The reaction of *trans*-cyclooctene with S_8O at room temperature yielded *trans*-9,10,11-trithiabicyclo[6.3.0]undecane (**7**), a new 1,2,3-trithiolane, stereospecifically, together with the corresponding *trans*-episulfide. In this reaction S_8O behaved like elemental sulfur activated under vigorous conditions and worked towards *trans*-cyclooctene as an S_n-transfer reagent under mild conditions, which should be contrasted with S_8O acting as an S_2O-transfer reagent towards diazomethanes,[31] 1,3-butadienes,[31] and cycloheptatriene.[44] Oxidation of **7** with DMD provided two 9-oxides (**15** and **16**), one 10-oxide (**17**), and three 9,11-dioxides (**18**, **19**, and **20**). The 9,11-dioxides are the first example of stable 1,2,3-trithiolane 1,3-dioxides. Configuration of the sulfinyl groups in **15**, **16**, **19**, and **20** was relatively unstable and we observed mutual isomerization between **15** and **16** and stepwise isomerization of **20** to **18** through **19**.

4. Experimental

4.1. General

The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H 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 performed with silica gel (70–230 mesh), and high-pressure liquid chromatography (HPLC) with a packed SiO_2 column (INERTSIL PREP-SIL: 10 or 20 mm i.d., GL Science Inc.); the eluent is shown in parentheses. *trans*-Cyclooctene was prepared by photoisomerization of commercially available *cis*-cyclooctene.[35,36] S_8O was prepared

by oxidation of S_8 with trifluoroperacetic acid.[32] An acetone solution of dimethyldioxirane (DMD) was prepared by oxidation of acetone with Oxone® (Sigma–Aldrich).[37,38]

4.2. Reaction of *trans*-cyclooctene with S_8O

trans-Cyclooctene (305 mg, 2.77 mmol) was added to a solution of S_8O (4.10 g, 15 mmol) in CS_2 (70 mL) under argon. The mixture was stirred for 13 h at room temperature. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography (hexane/dichloromethane 4/1) to remove elemental sulfur and then subjected to HPLC (hexane/dichloromethane 4/1) to give *trans*-9,10,11-trithiabicyclo[6.3.0]undecane (**7**) (188 mg, 33%) and *trans*-episulfide **6** (52 mg, 13%) in this order. Trithiolane **7** was purified by bulb-to-bulb distillation (1.2 mmHg, 115 °C).

4.2.1. *trans*-9,10,11-Trithiabicyclo[6.3.0]undecane (7). Yellow oil. ^{1}H NMR δ 1.54–1.84 (m, 10H), 2.14–2.22 (m, 2H), 3.78–3.84 (m, 2H); ^{13}C NMR δ 24.6 (CH_2), 26.5 (CH_2), 34.8 (CH_2), 63.5 (CH); MS *m*/*z* 206 (M^+). HRMS: calcd for $C_8H_{14}S_3$: M, 206.0258. Found: M^+, 206.0258. Anal. Calcd for $C_8H_{14}S_3$: C, 46.55; H, 6.84. Found: C, 46.70; H, 6.86.

4.3. Oxidation of trithiolane 7

4.3.1. DMD (1 equiv). DMD (0.0753 M, 2.70 mL, 0.20 mmol) was added dropwise to a solution of **7** (42 mg, 0.20 mmol) in dichloromethane (2 mL) under argon at 0 °C. The mixture was stirred for 2 h at 0 °C. The mixture was transferred to a round-bottom flask and the solvent was removed under reduced pressure with the flask being dipped in an ice-water bath. The residue was subjected to column chromatography (dichloromethane) to give trithiolane **7** (4.0 mg, 9%), 10-oxide **17** (6.4 mg, 15%), a mixture of 9-oxides **15** and **16**, and 9,11-dioxide **18** (3.7 mg, 8%) in this order. The mixture of **15** and **16** was separated with HPLC (hexane/ether 2/1) to give 9-oxide **15** (6.8 mg, 16%) and 9-oxide **16** (14.5 mg, 33%).

4.3.2. DMD (2 equiv). DMD (0.0753 M, 2.63 mL, 0.20 mmol) was added dropwise to a solution of **7** (20.4 mg, 0.10 mmol) in dichloromethane (1 mL) under argon at −35 °C. The mixture was stirred for 2 h at −35 °C. At this temperature the solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the mixture showed that the mixture consisted of **18**, **19**, **20**, and **7** in the ratio of 21:64:10:5. Compound **20** could not be isolated because of its instability.

4.3.3. MCPBA (1 equiv). A solution of MCPBA (88.6%, 40.4 mg, 0.21 mmol) in dichloromethane (3 mL) was added dropwise to a solution of **7** (43.8 mg, 0.21 mmol) in dichloromethane (2 mL) under argon at 0 °C. The mixture was stirred for 2 h at 0 °C. To the mixture were added aqueous Na_2SO_3 and then aqueous $NaHCO_3$. The mixture was extracted with dichloromethane, and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was subjected to column chromatography (dichloromethane) to give 10-oxide **17** (3.3 mg, 7%), a mixture of **15** and **16**, and 9,10-dioxide **18** (2.1 mg, 4%) in this order. The mixture of **15** and **16** was separated with HPLC (hexane/ether 2/1) to give 9-oxide **15** (9.4 mg, 20%) and 7-oxide **16** (24.9 mg, 53%).

4.3.4. *rel*-(1*R*,8*R*,9*S*)-9,10,11-Trithiabicyclo[6.3.0]undecane 9-oxide (15). Colorless oil. ^{1}H NMR δ 1.55–1.88 (m, 9H), 1.91–2.00 (m, 1H), 2.16–2.26 (m, 2H), 3.39–3.44 (m, 1H), 3.92–3.98 (m, 1H); ^{13}C NMR δ 23.9 (CH_2), 24.7 (CH_2), 26.2 (CH_2), 26.4 (CH_2), 27.5 (CH_2), 34.9 (CH_2), 57.2 (CH), 79.9 (CH); IR (neat) 1094 cm^{-1} (S=O); MS *m*/*z* 222 (M^+). HRMS: calcd for $C_8H_{14}OS_3$: M, 222.0207. Found: M^+, 222.0201.

4.3.5. *rel*-(1*R*,8*R*,9*R*)-9,10,11-Trithiabicyclo[6.3.0]undecane 9-oxide (16). Colorless oil. ^{1}H NMR δ 1.38–1.47 (m, 1H), 1.50–1.88 (m, 9H), 2.22–2.37 (m, 2H), 3.48–3.54 (m, 1H), 3.64–3.69 (m, 1H); ^{13}C NMR δ 22.6 (CH_2), 24.7 (CH_2), 25.9 (CH_2), 26.5 (CH_2), 29.4 (CH_2), 33.5 (CH_2), 60.2 (CH), 86.6 (CH); IR (neat) 1088 cm^{-1} (S=O); MS *m*/*z* 222 (M^+). HRMS: calcd for $C_8H_{14}OS_3$: M, 222.0207. Found: M^+, 222.0209.

4.3.6. 9,10,11-Trithiabicyclo[6.3.0]undecane 10-oxide (17). Colorless oil. ^{1}H NMR δ 1.53–1.74 (m, 5H), 1.79–1.90 (m, 3H), 1.98–2.15 (m, 2H), 2.22–2.37 (m, 2H), 4.19 (ddd, *J*=11.3, 8.1, 3.5 Hz, 1H), 4.60 (ddd, *J*=11.3, 8.6, 3.0 Hz, 1H); ^{13}C NMR δ 24.3 (CH_2), 25.2 (CH_2), 25.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 27.6 (CH_2), 60.8 (CH), 70.2 (CH); IR (neat) 1107 cm^{-1} (S=O); MS *m*/*z* 222 (M^+). HRMS: calcd for $C_8H_{14}OS_3$: M, 222.0201. Found: M^+, 222.0200.

4.3.7. *rel*-(1*R*,8*R*,9*S*,11*S*)-9,10,11-Trithiabicyclo[6.3.0]undecane 9,11-dioxide (18). Colorless plates, mp 114–116 °C (dichloromethane/ethanol). ^{1}H NMR δ 1.50–1.60 (m, 2H), 1.65–1.82 (m, 4H), 2.03–2.08 (m, 2H), 2.26–2.35 (m, 2H), 2.57–2.65 (m, 2H), 4.23–4.25 (m, 2H); ^{13}C NMR δ 24.6 (CH_2), 25.2 (CH_2), 26.1 (CH_2), 73.4 (CH); IR (KBr) 1066 cm^{-1} (S=O); MS *m*/*z* 238 (M^+). HRMS: calcd for $C_8H_{14}O_2S_3$: M, 238.0156. Found: M^+, 238.0140.

4.3.7.1. Crystallographic data for 18. $C_8H_{14}O_2S_3$, M_w=238.39, colorless plate, 0.34×0.24×0.08 mm^3, monoclinic, $P2_1/c$, a=7.3540(3), b=16.4810(8), c=9.5776(7) Å, β=115.430(2)°, V=1048.34(10) $Å^3$, ρ_{calcd}=1.510 g cm^{-3}, Z=4, μ (Mo Kα)=0.672 cm^{-1}. Mac Science DIP3000 diffractometer with a graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The data reduction was made by the maXus program system. Intensity data of 2045 unique reflections were collected in the range of $-9\leq h\leq 9$, $-20\leq k\leq 20$, and $-11\leq l\leq 12$. Absorption corrections were done by a multi-scan method (SORTAV[45]). The structure was solved with a direct method (SIR97[46]) and refined with full-matrix least-squares (SHELXL-97[47]) using all independent reflections, where nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. $R1$=0.0524 ($I\geq 2\sigma I$, 1858 reflections), $wR2$=0.1394 (for all), and GOF=1.038, 175 parameters; max/min residual electron density=0.771/−0.604 e$Å^{-3}$.

4.3.8. *rel*-(1*R*,8*R*,9*R*,11*S*)-9,10,11-Trithiabicyclo[6.3.0]undecane 9,11-dioxide (19). Colorless plates, mp 109–111 °C (dichloromethane/ethanol). ^{1}H NMR δ 1.51–1.80 (m, 5H), 1.81–1.87 (m, 2H), 1.93–2.02 (m, 1H), 2.09–2.19

(m, 1H), 2.30–2.39 (m, 1H), 2.41–2.48 (m, 1H), 2.49–2.58 (m, 1H), 3.57 (ddd, J=12.1, 9.4, 2.5 Hz, 1H), 4.82 (ddd, J=12.0, 7.7, 3.9 Hz, 1H); ^{13}C NMR δ 23.9, 24.2, 24.9, 26.3, 26.5, 28.5, 73.9, 81.2; IR (KBr) 1083, 1059 cm^{-1} (S=O); MS m/z 238 (M^+). HRMS: calcd for $C_8H_{14}O_2S_3$: M, 238.0156. Found: M^+, 238.0146.

4.3.8.1. Crystallographic data for 19. $C_8H_{14}O_2S_3$, M_w=238.39, colorless plate, 0.34×0.22×0.08 mm^3, orthorhombic, *Pbca*, a=13.285(3), b=16.608(3), c=9.411(2) Å, V=2067.4(7) Å^3, ρ_{calcd}=1.525 g cm^{-3}, Z=8, μ(Cu Kα)=6.259 cm^{-1}. Mac Science MXC3KHF diffractometer with graphite-monochromated Cu Kα radiation (λ=1.54178 Å), $\theta/2\theta$ scans method in the range $3°<2\theta<140°$ ($0<h<16, 0<k<20, 0<l<11$), 1938 independent reflections. Absorption correction was done by the psi-scan method.[48] The structure was solved with a direct method (SIR97[46]) and refined with full-matrix least-squares (SHELXL-97[47]) using all independent reflections, where nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed by calculation. $R1$=0.0862 ($I>2\sigma I$, 1907 reflections), $wR2$=0.2264 (for all), GOF=1.146, 119 parameters; max/min residual electron density=1.947/−0.709 eÅ^{-3}.

CCDC-299893 (**18**) and CCDC-299892 (**19**) contain the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

4.3.9. *rel*-(1*R*,8*R*,9*R*,11*R*)-9,10,11-Trithiabicyclo[6.3.0]-undecane 9,11-dioxide (20). ^{1}H NMR (−20 °C) δ 3.72–3.80 [m, 2H, C(1)–H and C(8)–H]; ^{13}C NMR (−20 °C) δ 23.3, 25.5, 27.9, 75.8.

4.4. Oxidation of 9-oxide 15

DMD (0.0803 M, 0.50 mL, 0.040 mmol) was added to a solution of 9-oxide **15** (9.1 mg, 0.041 mmol) in $CDCl_3$ (1 mL) under argon at 0 °C. The mixture was stirred for 2 h at 0 °C. To 0.5 mL of the mixture, was added 6.5 mg (0.018 mmol) of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene as the internal standard. The ^{1}H NMR spectrum of the mixture showed the formation of 0.018 mmol (43%) of 9,11-dioxide **18** and 0.019 mmol (47%) of 9,11-dioxide **19**.

4.5. Oxidation of 9-oxide 16

DMD (0.0803 M, 0.85 mL, 0.068 mmol) was added to a solution of 9-oxide **16** (14.6 mg, 0.0656 mmol) in $CDCl_3$ (1 mL) under argon at 0 °C. The mixture was stirred for 2 h at 0 °C. To 0.5 mL of the mixture, was added 7.2 mg (0.019 mmol) of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene as the internal standard. The ^{1}H NMR spectrum of the mixture showed the formation of 0.0041 mmol (2%) of 9,11-dioxide **18**, 0.023 mmol (35%) of 9,11-dioxide **19**, and 0.035 mmol (54%) of 9,11-dioxide **20**.

4.6. Isomerization

4.6.1. Isomerization of 9-oxide 15. In an NMR tube, a solution of 9-oxide **15** (2.1 mg, 0.094 mmol) in $CDCl_3$ (0.4 mL) was warmed at 55 °C for 24 h (during heating, indoor light was not shaded in particular). The mixture consisted of 30% of 9-oxide **15** and 70% of 9-oxide **16** based on the ^{1}H NMR integral ratio.

4.6.2. Isomerization of 9-oxide 16. In an NMR tube, a solution of 9-oxide **16** (2.3 mg, 0.010 mmol) in $CDCl_3$ (0.4 mL) was warmed at 55 °C for 24 h (during heating, indoor light was not shaded in particular). The mixture consisted of 29% of 9-oxide **15** and 71% of 9-oxide **16** based on the ^{1}H NMR integral ratio.

4.7. Reaction of trithiolane 7 with triphenylphosphine

A solution of triphenylphosphine (26.2 mg, 0.10 mmol) in $CDCl_3$ (1.5 mL) was added dropwise to a solution of trithiolane **7** (21.6 mg, 0.10 mmol) in $CDCl_3$ (1 mL) under argon at room temperature. The mixture was stirred for 5 h at room temperature. To 0.5 mL of the mixture, was added 10.6 mg (0.029 mmol) of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene as the internal standard. The ^{1}H NMR spectrum of the mixture showed the formation of 0.022 mmol (22%) of *cis*-episulfide **23**[27] together with 0.075 mmol (75%) of **7**.

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